THE CHEMICALLY-SPECIFIC STRUCTURE OF AN AMORPHOUS MOLYBDENUM GERMANIUM ALLOY BY ANOMALOUS X-RAY SCATTERING*

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THE CHEMICALLY-SPECIFIC STRUCTURE OF AN AMORPHOUS MOLYBDENUM GERMANIUM ALLOY BY ANOMALOUS X-RAY SCATTERING

A DISSERTATION

SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

> Hope Ishii May 2002

Abstract

Since its inception in the late 1970s, anomalous x-ray scattering (AXS) has been employed for chemically-specific structure determination in a wide variety of noncrystalline materials. These studies have successfully produced differential distribution functions (DDFs) which provide information about the compositionally-averaged environment of a specific atomic species in the sample. Despite the wide success in obtaining DDFs, there are very few examples of successful extraction of the *fully*chemically-specific partial pair distribution functions (PPDFs), the most detailed description of an amorphous sample possible by x-ray scattering. Extracting the PPDFs is notoriously difficult since the matrix equation involved is ill-conditioned and thus extremely sensitive to errors present in the experimental quantities that enter the equation. Instead of addressing this sensitivity by modifying the data through mathematical methods, sources of error have been removed experimentally: A focussing analyzer crystal was combined with a position-sensitive linear detector to experimentally eliminate unwanted inelastic scattering intensity over most of the reciprocal space range probed.

This instrumentation has been used in data collection for the extraction of PPDFs from amorphous (a)-MoGe₃. This composition arises as a phase separation endpoint in the Ge-rich region of the vapor-deposited Mo-Ge amorphous alloy system but is not present at equilibrium. Since the first Ge-rich compound in the Mo-Ge equilibrium system is MoGe₂, previous workers have speculated that perhaps a unique MoGe₃ compound exists in the amorphous system. Rather than indicating a distinct MoGe₃ compound with definitive local structure, however, the coordination results are more consistent with a densely-packed alloy having a wide range of solid solubility.

Significant improvement in the quality and reliability of experimental PPDFs from a-MoGe₃ by AXS has been achieved solely through the experimental modifications to eliminate inelastic scattering. The coordination uncertainties are estimated at 5% for the Mo-Ge and Ge-Ge coordinations and 15% for the Mo-Mo coordination. These PPDFs from data collected at a second generation synchrotron source demonstrate the promise of the technique for routine PPDF extraction from binary alloys when applied in the future on dedicated beamlines at third generation synchrotron sources.

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Contents

A	bstra	nct		ii
A	ckno	wledge	ements	iv
1	Intr	roduct	ion	1
	1.1	Motiv	ation and Goals	1
	1.2	Appro	oach	4
	1.3	The N	Ietal-Insulator Transition & Phase Separation	5
	1.4	Synch	rotron Radiation	7
	1.5	Overv	iew of Dissertation	10
2	And	omalou	as X-ray Scattering	12
	2.1	Scatte	ering from Amorphous Materials	12
		2.1.1	Real-Space Structure from Scattered Intensity	15
		2.1.2	Differential and Partial Distribution Functions	17
		2.1.3	Anomalous Dispersion	24
		2.1.4	Necessity of Experimental ASFs	31
	2.2	Poten	tial Error in the Elastic Scattered Intensity	32
		2.2.1	Resonant Raman Scattering	32

		2.2.2 Compton Scattering 34
	2.3	Energy Selection
		2.3.1 Contrast
		2.3.2 Accuracy
		2.3.3 Energy Resolution & Scattering Geometry 38
		2.3.4 k -Range
	2.4	Complementary Techniques to AXS
		2.4.1 EXAFS 41
		2.4.2 Isotopic Substitution Neutron Diffraction
	2.5	Predicting the Outcome of AXS for
		Extraction of Partials
		2.5.1 Weighting of Species
		2.5.2 SVD Analysis and Conditioning of the Matrix
	2.6	Conditioning, Regularization and Modelling
3	San	nple Preparation 52
	3.1	Sputtering
	3.2	Substrates
	3.3	Free-Standing Films
	3.4	Preliminary Characterization
4	Exp	perimental Procedures 59
	4.1	Synchrotron Beamline
	4.2	X-ray Scattering Setup
		4.2.1 Analyzer Scattering Geometry
		4.2.2 Analyzer

		4.2.3	Detector	68
	4.3	Incide	ant and Detected Energy Resolutions and Energy Dispersion $\ .$.	70
		4.3.1	Incident Energy Widths	70
		4.3.2	Factors Affecting Width of Detected Peaks	73
		4.3.3	Effect of Defocussing on Detected Energy Resolution	77
	4.4	Scatte	ering Data Collection	79
	4.5	X-ray	Absorption Data Collection	82
5	Dat	a Ana	lysis	85
	5.1	Sampl	le Constants	86
		5.1.1	Composition	86
		5.1.2	Thickness	90
		5.1.3	Anomalous Scattering Factors	91
		5.1.4	Absorption Coefficient	92
	5.2	Extra	ction of Elastic Scattering	94
	5.3	Correc	ctions	97
		5.3.1	Detector Non-Linearity	98
		5.3.2	Substrate Scattering	99
		5.3.3	Absorption	100
		5.3.4	Polarization	101
		5.3.5	Multiple Scattering	103
	5.4	Norma	alization	105
	5.5	Impac	et of Experimental Limits	108
	5.6	Soluti	on for Distribution Functions	111
		5.6.1	A Comparison of Damping Functions	112
		5.6.2	To Real Space	116

	5.7	Data Analysis Code	117
6	Res	ults	119
	6.1	SF and RDF	120
	6.2	DSFs and DDFs	124
	6.3	PSFs and PPDFs	128
	6.4	Comparison with Previous X-ray Scattering Results	132
7	Dis	cussion	135
	7.1	Internal Comparisons	136
		7.1.1 Sum of PSFs to Give SF	136
		7.1.2 Sum of PSFs to Give DSFs & Testing the DSF Approximation	139
	7.2	Comparison with Results from l -GeBr ₄	144
	7.3	Crystals of Neighboring Compositions	147
		7.3.1 Testing for Phase Separation	150
	7.4	Coordination Results	154
	7.5	Comparison of PPDF Results with Previous EXAFS Results $\ . \ . \ .$	162
	7.6	Stability of Coordination Results with Respect to Error	168
		7.6.1 Background Error	169
		7.6.2 Normalization Constant Error	172
		7.6.3 Conclusions about the Impact of Introduced Error	176
		7.6.4 A Conservative Estimate	177
	7.7	Role of $MoGe_3$	177
8	Cor	clusions and Future Work	179
	8.1	Experimental Removal of Inelastic Scattering	180
	8.2	Coordination Results and Their Reliability	182

xi

8.3	Relevance of the $MoGe_3$ Composition	184
8.4	New Questions	185
8.5	Future Work on a -MoGe ₃	186
8.6	Improvements for Future AXS	189
A Alg	gorithms	192
A.1	Fitting Experimental f''	192
	A.1.1 Input	193
	A.1.2 Fit	193
	A.1.3 Output	194
A.2	Kramers-Krönig Transform	195
	A.2.1 Input	195
	A.2.2 Calculation	196
	A.2.3 Output	199
B Dat	ta Analysis Code	200
Biblio	graphy	202

List of Tables

2.1	Effects of x_B and energy choice below the A element edge on the	
	usually-neglected BB term in the A edge DSF	21
2.2	Naturally-occurring isotopes of Mo and Ge	45
3.1	Sample deposition: gun parameters and deposition rates	53
3.2	Preliminary measurements of composition and thickness	58
5.1	Initial and final measurements of composition and thickness	89
5.2	Experimental anomalous scattering factors (ASFs) for the energies	
	probed	92
5.3	Sample 2 μt constants obtained by θ -scans compared with those obtained	
	by back-calculating μ from the edge jump	93
7.1	Results of fitting two Gaussians to the first peak of $4\pi r \rho_{GeGe}(r)$ for a	
	variety of r_{max} values.	153
7.2	Local coordination parameters for <i>a</i> -MoGe ₃	155
7.3	The coordination parameters from EXAFS from Kortright's 25% Mo	
	sample	165
7.4	Local coordination parameters for a -MoGe ₃ excerpted from Table 7.2.	166

List of Figures

1.1	The Ge-rich end of the Mo-Ge equilibrium phase diagram	2
1.2	The continuous spectrum of radiation emitted by a bending magnet	
	source at SSRL	9
1.3	Schematic of a wiggler insertion device	10
2.1	The Cromer-Liberman (CL) $f^{\prime\prime}$ and f^{\prime} values for the Mo K edge	30
2.2	Kissel's f'' values for the Mo K edge	30
2.3	The Cromer-Liberman (CL) f'' and Kissel (K) f'' values for the Mo K	
	edge	31
2.4	Radiative resonant Raman scattering	34
2.5	Position of the peak in Compton scattering as a function of the scat-	
	tering vector, $k,{\rm for}$ an incident energy 100 eV below the Ge K edge	35
2.6	The total scattering, elastic scattering and Compton scattering from	
	an independent atom with an average composition of $MoGe_3$	36
2.7	The relationship between the scattering vector magnitude, $k,$ and $\sin\theta$	
	for incident photon energies of 11 and 20 keV	40
2.8	The calculated Turing number as a function of k for several different	
	systems.	48

3.1	The target and substrate configuration for the magnetron sputtering	
	deposition system.	54
4.1	The x-ray optics of BL 10-2	60
4.2	The experimental optics	62
4.3	The transmission scattering geometry	62
4.4	Dispersive parafocussing by a mosaic crystal analyzer for a point source	
	of x-rays at the sample position	64
4.5	Dispersion of scattered radiation by the graphite analyzer crystal. $\ .$	65
4.6	Schematic of the bent graphite analyzer	67
4.7	One-dimensional backgammon design for position-sensitive detection	
	of photons	69
4.8	The acceptance of the analyzer crystal	71
4.9	The divergence of x-rays exiting the monochromator. \ldots	71
4.10	The x-ray optics determining the vertical divergence at the BL 10-2 $$	
	monochromator	73
4.11	An (exaggerated) extended source imaged by parafocus sing. $\ . \ . \ .$	76
4.12	The effects of positioning the linear detector at a defocussed position	
	and extended source size	78
4.13	Schematic of the equipment for absorption data collection	83
4.14	Schematic of f' for two different incident energy resolutions	84
5.1	Signal versus position on the PSD (corresponding to energy of the scat-	
	tered radiation) for three incident energies below the Ge K absorption	
	edge	96

5.2	Comparison of data before and after corrections have been applied for	
	Sample 2 (27 at% Mo)	98
5.3	Nonlinearity of the linear position-sensitive detector.	99
5.4	Normalized absorption correction factor for all samples at 11 keV	101
5.5	Polarization correction factor for incident energies of 11 and 20 keV as	
	a function of scattering vector magnitude.	102
5.6	Multiple scattering correction factors for Sample 2 and Sample 3 at	
	different energies	104
5.7	Normalized data and the coherent independent intensity for Sample 2	
	(27 at% Mo)	108
5.8	Possible distributions of incident photons near an absorption edge	109
5.9	Simple Gaussian damping functions $D_G(k)$ with various values of α	
	and the resulting RDFs	113
5.10	Delayed-onset Gaussian damping functions $D_2(k)$ with $\alpha = 0.02$ and	
	various k onset values and the resulting RDFs	114
5.11	Variable- α damping functions $D_3(k)$ with various k onset values and	
	the resulting RDFs	115
5.12	k times $D_3(k)$, the variable- α damping function, with several k onset	
	values	116
5.13	The broadening of a delta function at $r = 2.7$ Å by the Gaussian damp-	
	ing function $D_G(k)$ with $\alpha = 0.02$ and $\Delta k = 0.025 \text{ Å}^{-1}$.	117
6.1	The SF from data taken 100 eV below the Mo edge (19.900 keV). $$.	120
6.2	The radial distribution function from data taken 100 eV below the Mo $$	
	edge (19.900 keV). \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	121

6.3	The radial distribution function obtained 100 eV below the Ge edge	
	overlaid with the radial distribution function from 100 eV below the	
	Mo edge, both cut off at the same k_{max}	122
6.4	The differential structure factors, DSF_{Ge} and DSF_{Mo}	125
6.5	The Ge and Mo differential distribution functions (DDFs)	126
6.6	The $S(k)$ -like function resulting from a sine Fourier transform of the	
	low-r region from $r = 0 - 1.5$ Å of the Mo DDF	127
6.7	The partial structure factors, $S_{\alpha\beta}(k)$, obtained by solution of the Munro	
	matrix	129
6.8	The partial pair distribution functions, $4\pi r^2 \rho_{\alpha\beta}(r)$ from the partial	
	structure factors above	131
6.9	The total structure factor from the present sample overlaid on those	
	from Kortright's work.	133
6.10	The differential structure factors (DSFs) from the present sample over-	
	laid on plots of the Mo and Ge DSFs from Kortright's work	134
7.1	The total structure factors measured at 19.900 keV and constructed	
	from the weighted sum of partial structure factors	137
7.2	The RDFs from the measured and constructed SFs at 19.900 keV	138
7.3	The k -dependence of the weighting factors for the three PSFs compris-	
	ing the SF for a -MoGe ₃ at 19.900 keV	139
7.4	The measured DSF at the Ge edge and the constructed DSF from the	
	appropriate PSFs and weighting factors.	140
7.5	The measured DSF at the Mo edge and the constructed DSF from the	
	appropriate PSFs and weighting factors.	141

7.6	The weighting factors used to construct the DSF plotted for each ele-	
	ment edge, Mo and Ge	143
7.7	The PPDFs from a -MoGe ₃ compared with those from l -GeBr ₄	146
7.8	The crystal structure and crystal PPDFs for the α phase of <i>c</i> -MoGe ₂ .	148
7.9	The crystal structure and crystal PPDFs for the β phase of $c\text{-MoGe}_2.$	149
7.10	The crystal structure and crystal RDF for c -Ge	150
7.11	The two-Gaussian fit to the first peak of $4\pi r \rho_{GeGe}(r)$ over the range	
	r = 2.2 - 3.1 Å.	153
7.12	Representative single Gaussian fits to the first near neighbor peaks of	
	the experimental PPDFs and the residual	156
7.13	Schematics illustrating the possible transition from 10-fold coordina-	
	tion of Mo by Ge atoms in β -MoGe ₂ to the final structure with 8-fold	
	coordination.	160
7.14	The total structure factor 100 eV below the Mo K edge obtained for	
	positive, negative and no purposefully-introduced background error in	
	the intensity.	171
7.15	The PPDFs extracted from the Munro matrix containing the background	-
	error-contaminated intensity in the final row of the Munro matrix	171
7.16	The total structure factor 100 eV below the Mo K edge obtained for	
	positive, negative and no purposefully-introduced normalization con-	
	stant error in the final row of the Munro matrix	173
7.17	The PPDFs extracted from the Munro matrix containing the intensity	
	contaminated by a normalization constant error in the final row of the	
	Munro matrix	174

7.18	The PPDFs extracted from the Munro matrix containing the intensities	
	contaminated by a normalization constant error introduced into both	
	intensities comprising the difference below the Ge K edge. $\ . \ . \ .$.	175
8.1	The condition number for the Munro matrix for various schemes of	
	data collection at different sets of energies for $MoGe_3$	188
B.1	Flowchart for Matlab data analysis code to obtain radial, differential	
		001
	and partial pair distribution functions.	201

Chapter 1

Introduction

1.1 Motivation and Goals

The Mo-Ge amorphous alloy system undergoes a metal-to-insulator transition as metal concentration is decreased below 10 at% Mo. Contrary to early implicit assumptions, vapor-deposited amorphous metal-germanium and metal-silicon samples are not necessarily single phase. Indications of phase separation in the Mo_xGe_{1-x} system in the composition range $0 \le x \le \sim 23$ at% Mo were first observed by Kortright and Bienenstock [1, 2] in x-ray data that provided convincing evidence of the coexistence of amorphous Ge (*a*-Ge) with a very fine scale Mo-modified amorphous material. Further work by Rice and Regan [3, 4] verified the presence of two phases, and the composition of the Mo-modified phase was calculated to correspond approximately to $MoGe_3$ (23-27 at% Mo). It has been suggested that the insulator-metal transition in many of these intermetallic systems may be the result of percolation of conductive islands such as these Mo-rich regions [4, 5, 6].

When alloyed with Si or Ge, a tremendous array of metallic elements, M, across

the periodic table (including M=Mo, Fe) form crystalline disilicides and digermanides as the Si- or Ge-rich equilibrium phase. It is not surprising, therefore, that other amorphous metal-germanide and metal-silicide systems studied (for example, Fe-Ge and Fe-Si) phase separate into a-Ge/a-Si and a-MGe₂/a-MSi₂ at low metal concentrations. The chemical bond typically dominates, and it is presumed that this 1:2 M-to-Ge/Si stoichiometry provides the most stable phase in the amorphous state as in the crystalline state. (See Figure 1.1.) The 1:3 Mo-to-Ge composition discovered in the Mo-Ge system is therefore unexpected, and its structure has yet to be elucidated.



Figure 1.1: The Ge-rich end of the Mo-Ge equilibrium phase diagram. The stable Mo-Ge compound with the highest Ge concentration is MoGe₂.

It is our goal to determine the structure of the a-MoGe₃ phase by anomalous x-ray scattering with the hope of gaining a better understanding of why this composition arises in the amorphous Mo-Ge system and what role it may play in the metalinsulator transition.

X-ray scattering in an elemental amorphous material such as a-Ge yields radiallyaveraged information (the radial distribution function or RDF) about the atomic environment of an average Ge atom due to the inherent lack of long-range order in the system. The RDF gives the compositionally-weighted average of the number of atoms at a distance r from another atom. For amorphous alloy systems, anomalous xray scattering (AXS) allows us to extract chemically-specific structural information in the form of differential and partial distribution functions. The differential distribution functions (DDFs) provide the chemical environment about a particular species in the sample in the form of the compositionally-weighted average of the number of atoms a distance r from an atom of a specific element. The partial pair distribution functions (PPDFs)¹ give the average number of β atoms a distance r away from an α atom where α and β take on the identity of all atomic species in the sample. The PPDFs fully characterize the average pair chemical environments in a material: For the Mo-Ge system, there are three independent PPDFs to be determined containing information about the Ge-Ge, Mo-Ge, and Mo-Mo correlations respectively.

Our second goal is to improve the reliability of partial pair distribution functions obtained from x-ray scattering. Since its inception in the late 1970s [7], the AXS technique has demonstrated its utility for structure determination through DDFs in a wide variety of materials for which the related isotopic-substitution neutron scattering approach is inappropriate. Many technologically interesting systems consist of thin films or contain elements whose isotopes are extremely rare and costly or simply unavailable. Even where affordable isotopes are available, the neutron scattering cross-sections for the elements in question may not provide enough contrast. For these systems, the AXS technique is favored over neutron scattering. Despite the wide success of differential anomalous scattering in obtaining DDFs, there are very

¹Historically, the partial pair distribution functions from structural analysis of non-crystalline materials have been denoted the PDFs. Recently, the acronym PDF has been used more generally for pair distribution functions which include RDFs and DDFs. Consequently, we use the acronym PPDF to distinguish the *partial* pair distribution functions.

few examples of successful extraction of PPDFs. We seek to improve the reliability of PPDFs and the accuracy with which an amorphous material's structure can be determined. This, in turn, increases the applicability of AXS to other structural problems.

1.2 Approach

The technique of AXS for extraction of PPDFs has the potential to be a very powerful technique for structure determination. It suffers, however, from high susceptibility to errors in experimentally-measured quantities. This is because extraction of the PPDFs requires solution of an ill-conditioned equation containing these quantities.

There exist methods of dealing with this suspectibility to error. Mathematical regularization routines have been devised using a variety of algorithms to stabilize the matrix equation and provide an approximate, but well-behaved, solution. These methods can effectively address random noise present in the data, but they do not deal with systematic error and may actually distort data containing such errors.

We choose a more direct approach: By experimentally reducing the error present in the x-ray scattering data (elastic scattering and atomic scattering factors), we begin the analysis with fewer necessary corrections and cleaner data, and we need not rely on regularization methods. Using a new experimental setup involving a sagittally-focussing graphite analyzer crystal paired with a position-sensitive detector, we obtain energy-resolved spectra at each scattering angle allowing us to isolate the elastic scattering. Instead of using tabulated values, the anomalous scattering factors are measured experimentally using the sample in the same experimental run with the same incident energy resolution as the scattering measurements. These changes in experimental method yield significant improvements in the resulting PPDFs without resort to regularization routines.

1.3 The Metal-Insulator Transition & Phase Separation

A summary of earlier studies underlying the present work on the amorphous Mo-Ge alloy system is presented here. The characterizations of the metal-to-insulator (MI) transition and phase separation that occur at high Ge concentrations are presented followed by a brief discussion of the bonding between Mo and Ge.

Devenyi and coworkers [8] carried out electrical and x-ray measurements on coevaporated samples of amorphous Mo-Ge alloys. They placed the MI transition composition between 7.5 and 16% Mo (two of their sample compositions) and noted structural evolution with composition changes. Their results suggested dense local packings around Mo resulting from strong Mo-Ge interactions. Yoshizumi et al. [9, 10] studied many cosputtered samples with compositions ranging between 9 and 23% Mo. They established that the MI transition occurs at 10 at.% Mo and showed that it is due to a vanishing electron diffusion constant. Specific heat measurements by Mael et al. [11] demonstrated a continuous and finite density of states through the MI transition. The lack of a discontinuity despite the MI transition with changing composition is consistent with the gradual variation in the volume fractions of a metallic phase and an insulating phase expected with phase separation.

The first indication that two structural environments are present in the Ge-rich amorphous Mo-Ge alloys arose in Kortright's work [1, 2]. He applied the complementary techniques of EXAFS (described in the following chapter) and x-ray scattering through RDFs and DDFs to study a wide range of compositions from 0 to 70% Mo. The RDFs for overall compositions below ~ 25% Mo were well-represented by a superposition of tetrahedrally-coordinated *a*-Ge and *a*-MoGe₃. The DDFs also clearly indicated the presence of a Mo-modified structure with a distinct local order. EXAFS results showed that Mo was in the same local environment for all compositions studied. At high Ge concentrations, the presence of tetrahedral *a*-Ge was evident from the EXAFS. Above ~ 23% Mo, all signs of this tetrahedral *a*-Ge disappeared from the EXAFS, and Kortright concluded that the samples were homogeneous.

Rice and coworkers [12] followed this work with anomalous small angle x-ray scattering (ASAXS) studies that showed the presence of nanometer-scale fluctuations in Mo composition and an increase in the correlation length of the fluctuation with increasing Mo content. Additional studies by Regan et al. [3, 4] assumed that one of the phases present was a-Ge and used the mean-square fluctuation of effective electron density to show that the composition of the Mo-modified phase was near MoGe₃. The results also revealed an anisotropy in the shape of the second phase particles in the sputtering growth direction.

The proposal that the MI transition is due to a conductive phase percolating in an insulating phase is supported by a simplistic calculation: In three-dimensional percolation based on a variety of continuum models, the critical volume fraction is always near 0.15 [13]. Since Mo and Ge have similar atomic sizes, a rough, firstorder approximation is that they occupy identical atomic volumes in the alloys. This allows the calculation of the overall composition of a mixture of 15% MoGe₃, the percolating, conductive phase, and 85% Ge, the insulating phase. The result is 10.3 at.% Mo in agreement with Yoshizumi's electrical measurements described above. The actual percolation process is expected to be more complex than that assumed by the continuum models due to the effects of the anisotropic growth [4].

The metallic behavior of the MoGe₃ phase raises the interesting question of how the Mo and Ge atoms bond. A strong bonding interaction between Mo and Ge is evidenced by the numerous intermetallic compounds present in the equilibrium system. In their theory of bonding of transition metals to non-transition metals, Gelatt et al. [14] have proposed a covalent-like hybridization between approximately degenerate transition metal d states and the non-transition metal s and p states. Mo $(5s^1 4d^5)$ and Ge $(4s^1 4p^3)$ both have half-filled valence shells and nearly-equal Pauling electronegativities of 2.16 and 2.01 respectively, so a low-energy configuration with filled bonding orbitals and empty antibonding orbitals is conceivable. Such covalent-like hybridization does not, of course, exclude metallic behavior, and the Fermi level can lie at non-zero density of states. Khyzhun and coworkers [15] later studied the electronic structure of *crystalline* MoGe₂ by x-ray emission and absorption spectroscopies and found a small amount of charge transfer from the Ge atoms to Mo atoms as expected from their electronegativities. In addition, the Mo d- and p-like valence states were found to be strongly hybridized with the Ge 4p-like states. The 4p-like states of Mo and Ge are highly delocalized in the crystalline molybdenum germanides, and the Fermi level lies at non-zero density of states. This attractive hybridization interaction between Mo and Ge is expected to produce evidence of short range chemical ordering in the PPDFs for the amorphous $MoGe_3$ phase.

1.4 Synchrotron Radiation

The x-rays used in this work are known as synchrotron radiation. Synchrotron radiation is produced when a charged particle travelling at relativistic speeds interacts with a magnetic field. The magnetic fields in a synchrotron storage ring force the electron (or positron) to accelerate in a direction perpendicular to its velocity. Any charged particle undergoing an acceleration emits electromagnetic radiation, and for an electron travelling with such high kinetic energy, photons in the ultraviolet to x-ray wavelength regimes are emitted at high brightnesses (photons/sec/mm²/mrad²/0.1% bandwidth).

Synchrotron radiation is uniquely suited to the application of anomalous x-ray scattering techniques on amorphous structures: In order to extract high-quality DDFs and PPDFs describing a material's structure, a high intensity source that can be tuned about the absorption edges of the elements in the sample is necessary. Laboratory x-ray tube and rotating anode sources do not provide tunability or enough flux.

High brightness and intensity are necessary for studies of amorphous materials by AXS. The x-ray beam must undergo monochromatization and scattering by an amorphous sample and, often, Bragg scattering by an analyzer crystal as well – all prior to detection. Monochromatization cuts out most of the photons travelling to the sample, and slits define the beam size and angular acceptance of the sample. In addition, amorphous samples yield scattering patterns with intensity broadly distributed across all scattering angles. Without high brightness and intensity, the extremely low intensity of photons reaching the detector would make AXS experiments impractical.

A continuous spectrum of radiation is also a necessity for AXS studies: The AXS techniques (described in detail in Chapter 2) *require* that the source of x-radiation be tunable. Through the acceleration of charge in the storage ring, a synchrotron source provides a continuous spectrum of radiation from which the desired energies can be chosen near an absorption edge of an atomic species in a sample.

Finally, synchrotron radiation has a well-defined **polarization**. In the plane of



Figure 1.2: The continuous spectrum of radiation emitted by a bending magnet source at SSRL. The beamline 10-2 wiggler source is about 2 orders of magnitude brighter. (After Figure 1.3 in Reference [16].)

orbit, the electric field vector of the emitted radiation is parallel to the instantaneous acceleration. Thus, the radiation is nearly linearly polarized in the plane of orbit. The degree of linear polarization can be measured experimentally, and most synchrotron AXS experiments have scattering planes perpendicular to the plane of orbit to take advantage of this known polarization. Since scattering occurs at the monochromator, at the sample and, in the present experiments, at the analyzer crystal, precise knowledge of the polarization is required in order to correct for it.

All synchrotron x-ray data for this work were obtained on beamline 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), a 2nd generation light source within the Stanford Linear Accelerator Center (SLAC) operated by Stanford University for the US Department of Energy (DOE). Beamline 10-2 is an end station for an insertion device. Insertion devices are based on the same principle that led to the first observation of synchrotron radiation: In passing through a periodic array of magnets



Figure 1.3: Schematic of a wiggler insertion device. Periodic arrays of magnets force the electrons to follow an oscillating path thereby emitting more radiation.

of alternating polarity, the electrons are forced into a tightly oscillating path and emit even more photons. The type of insertion device used in the present work is a *wiggler* which produces intense radiation over a wide spectrum via strong magnetic fields and a relatively large periodic spacing between individual magnets [16]. The increased photon flux density of the beamline 10-2 wiggler makes it just feasible to carry out these experiments at SSRL; AXS to extract reliable PPDFs pushes the limits of what is currently achievable at SSRL.

1.5 Overview of Dissertation

This dissertation is organized into chapters as follows: Chapter 2 describes the technique itself: anomalous x-ray scattering formalism and methodology for obtaining total, differential and partial distribution functions. The complimentary techniques of EXAFS and ISND are also described, and means of assessing the suitability of

AXS for extraction of the partial distribution functions for a given system are presented. Finally, methods for dealing with the difficulties associated with solution of the poorly-conditioned matrix problem and their drawbacks are discussed. Chapter 3 gives the specifics of sample preparation, and Chapter 4 details the experimental procedures used for data collection at SSRL as well as the analyzer instrumentation. Important considerations of incident and detected energy resolution are also discussed. Chapter 5 contains the description of the data analysis procedures from the extraction of the elastic scattering through corrections applied to the final solution for partial structure factors. The damping function applied in the Fourier transform to obtain the partial pair distribution functions is discussed in some detail. Chapter 6 describes the results for a-MoGe₃ in reciprocal and real space, and Chapter 7 verifies that the partial pair distribution functions are solutions to the matrix problem, compares their quality to earlier AXS work and presents the structural conclusions about this alloy in light of previous work on the Mo-Ge system. Chapter 8 presents conclusions about progress made with the AXS technique and conclusions about the a-MoGe₃ sputter-deposited alloy. Finally, suggestions are offered for future work to be carried out on the Mo-Ge system and other systems as well as further experimental improvements to make the AXS technique more widely and more routinely available for extraction of PPDFs from alloy systems.

Chapter 2

Anomalous X-ray Scattering

Anomalous x-ray scattering (AXS) provides a means of extracting chemically-specific structural information over intermediate length scales. Since no assumption is made of periodicity of the atomic arrangements in the sample, the technique can be used to study non-crystalline materials, such as the amorphous MoGe₃ alloy in this work, as well as short-range deviations from perfect (average) crystal order in crystalline materials. (See, for example, references [17] and [18].) The formalism and methodology for AXS are described in this chapter.

2.1 Scattering from Amorphous Materials

To see how the various structure factors and radial distribution functions are obtained for amorphous materials, we follow the development of Warren [19] beginning with the amplitude scattered by a single atom:

$$\epsilon_n = f_n e^{-i\bar{k}.\bar{r}_n} \tag{2.1}$$

where f_n is the atomic scattering factor of the n^{th} atom, \bar{r}_n is the vector position of that atom and \bar{k} is the scattering vector with length

$$k = \frac{4\pi}{\lambda}\sin\theta. \tag{2.2}$$

(Some authors use \bar{q} to denote the x-ray scattering vector reserving \bar{k} for EXAFS, a technique described later in this chapter.) The intensity (in electron units) of elastically scattered radiation from several independently scattering atoms can then be written as

$$I_{eu} = \sum_{m} \epsilon_m \sum_{n} \epsilon_n^* = \sum_{m} \sum_{n} f_m f_n^* e^{i\bar{k}.\bar{r}_{nm}}$$
(2.3)

where $\bar{r}_{nm} = \bar{r}_m - \bar{r}_n$. The coherent self-scattering (m=n) can be separated out as follows

$$I_{eu} = \sum_{n=m} |f_n|^2 + \sum_{m} \sum_{n \neq m} f_m f_n^* e^{i\vec{k}.\vec{r}_{nm}}$$
(2.4)

If we assume \bar{r}_{nm} in our amorphous sample takes all orientations in space with equal probability, then

$$\langle e^{i\bar{k}\cdot\bar{r}_{nm}}\rangle = \frac{1}{4\pi r_{nm}^2} \int_{\phi=0}^{\pi} e^{ikr_{nm}\cos\phi} 2\pi r_{nm}^2 \sin\phi \, d\phi = \frac{\sin(kr_{nm})}{kr_{nm}}$$
 (2.5)

where the distances r_{nm} are scalar quantities. This leads to the Debye scattering equation:

$$I_{eu} = \sum_{n=m} |f_n|^2 + \sum_m \sum_n f_m f_n^* \frac{\sin(kr_{nm})}{kr_{nm}}$$
(2.6)

Instead of summing over each atom in the sample, we now sum over each of the atomic species and introduce a continuous density functions $\rho_{\alpha\beta}(r)$. This density function describes the atomic number density of β atoms a radial distance r from an average α atom in the sample and is integrated over the volume of the sample. For a general sample containing N_Z different elements and having N total atoms, we can write

$$I_{eu} = N \sum_{\alpha}^{N_Z} \frac{N_{\alpha}}{N} |f_{\alpha}|^2 + N \sum_{\alpha}^{N_Z} \sum_{\beta}^{N_Z} \frac{N_{\alpha}}{N} f_{\alpha} f_{\beta}^* \int_S \rho_{\alpha\beta}(r) \frac{\sin kr}{kr} dV$$

This can be further simplified to

$$\frac{I_{eu}}{N} - \langle f^2 \rangle = \sum_{\alpha}^{N_Z} \sum_{\beta}^{N_Z} \mathbf{x}_{\alpha} f_{\alpha} f_{\beta}^* \int_S \rho_{\alpha\beta}(r) \frac{\sin kr}{kr} dV$$
(2.7)

where

$$\mathbf{x}_{\alpha} = \frac{N_{\alpha}}{N}$$
 and $\langle f^2 \rangle = \sum_{\alpha}^{N_Z} \mathbf{x}_{\alpha} |f_{\alpha}|^2.$

The compositionally-averaged square of the atomic scattering factor, $\langle f^2 \rangle$, represents the self-scattering contribution, and the indices α and β are summed over all the species in the sample. (For example, α takes on the identity of element 1 while β is summed over all N_Z species, and then α takes on the identity of element 2 while β is again summed over all N_Z species, etc.)

We now define $\rho_{\beta o}$ to be the average β atom density in the sample and add and subtract a term with this average density:

$$\frac{I_{eu}}{N} - \langle f^2 \rangle = \sum_{\alpha}^{N_Z} \sum_{\beta}^{N_Z} \mathbf{x}_{\alpha} f_{\alpha} f_{\beta}^* \left[\int_S \left[\rho_{\alpha\beta}(r) - \rho_{\beta o} \right] \frac{\sin kr}{kr} dV + \int_S \rho_{\beta o} \frac{\sin kr}{kr} dV \right]$$
(2.8)

The second term represents extremely small angle scattering that is generally not

measured in a wide-angle scattering experiment, and its contribution can be shown to be completely negligible [19] so that we finally obtain

$$I - \langle f^2 \rangle = \frac{I'_{eu}}{N} - \langle f^2 \rangle =$$

$$\sum_{\alpha}^{N_Z} \sum_{\beta}^{N_Z} \mathbf{x}_{\alpha} f_{\alpha} f_{\beta}^* \left[\int_0^\infty 4\pi r^2 \left[\rho_{\alpha\beta}(r) - \rho_{\beta o} \right] \frac{\sin kr}{kr} dr \right]$$
(2.9)

where $I = \frac{I'_{eu}}{N}$ represents the elastically scattered intensity per atom neglecting the second term in Equation 2.8.

2.1.1 Real-Space Structure from Scattered Intensity

Structural information is most commonly presented in the form of the radial distribution function (RDF). The RDF represents the average number of atoms separated by a distance r from another atom and is defined as $4\pi r^2 \rho(r)$ where $\rho(r)$ is the total number density of atoms as a function of r. For a polyatomic amorphous sample, the most complete structural description obtainable by x-ray scattering is the set of partial pair (radial) distribution functions (PPDFs). There are $N_Z(N_Z + 1)/2$ unique PPDFs for a system with N_Z atomic species (because A-to-B correlations are related to B-to-A correlations by $x_{\alpha}\rho_{\alpha\beta} = x_{\beta}\rho_{\beta\alpha}$). The PPDFs describe the average number of β -species atoms separated by a distance r from an average α -species atom where α and β take on the identities of all N_Z species in the sample.

We define the *partial structure factor* (PSF) as follows:

$$S_{\alpha\beta}(k) \equiv \int_0^\infty 4\pi r^2 \left[\rho_{\alpha\beta}(r) - \rho_{\beta o}\right] \frac{\sin kr}{kr} dr \qquad (2.10)$$

To see how the PSFs are related to measurable intensities, we can substitute the
above equation into Equation 2.9:

$$I - \langle f^2 \rangle = \sum_{\alpha}^{N_Z} \sum_{\beta}^{N_Z} \mathbf{x}_{\alpha} f_{\alpha} f_{\beta}^* S_{\alpha\beta}$$
(2.11)

Experimentally, the elastically scattered intensity is measured as a function of scattering vector magnitude k. The intensity is corrected for various effects discussed in Chapter 5 and normalized to a per-atom basis. Then, the self-scattering contribution is subtracted out to yield the quantity $I - \langle f^2 \rangle$ in the equation above. The *partial pair distribution function* (PPDF) which provides real space structure information is obtained by a Fourier transform of the partial structure factor:

PPDF =
$$4\pi r^2 \rho_{\alpha\beta}(r) = 4\pi r^2 \rho_{\beta o} + \frac{2r}{\pi} \int_0^\infty k S_{\alpha\beta}(k) \sin(kr) dk.$$
 (2.12)

Similarly, the total structure factor (SF) is defined as

$$S(k) \equiv \int_0^\infty 4\pi r^2 [\rho(r) - \rho_o] \frac{\sin kr}{kr} dr \qquad (2.13)$$

The total structure factor $S(k)^1$ is also referred to as the *interference function* and given the notation i(k) in the literature. It is obtained from the normalized experimental intensity per atom by removing the self-scattering and dividing by the scattering per compositionally-averaged atom, $\langle f \rangle^2$. Dividing by $\langle f \rangle^2$, sometimes referred to as a *sharpening function*, approximately removes the k-dependence of the scattering

¹This is the form defined by Zernicke and Prins in 1927 [20] and used by Debye and Menke to study l-Hg [21]. There are, in fact, several different definitions of structure factors as well as partial structure factors. The Faber-Ziman [22] and Ashcroft-Langreth [23] forms give essentially the same physical information as the form used here; both are related to the spatial pair correlations of number densities. The Bhatia-Thornton [24] form gives one pair correlation of number density, one pair correlation of concentration fluctuation and a cross term. The inter-relationships between some of the different forms have been given by Waseda [25]. Note, however, that Waseda incorrectly states that the Bienenstock group uses the Ashcroft-Langreth form.

factors effectively placing each atom's electrons at a point at the center of its distribution. In this way, the broadening of the atomic distribution by the size of the atoms is approximately removed:

$$S(k) = \frac{I - \langle f^2 \rangle}{\langle f \rangle^2} \tag{2.14}$$

Because the small-angle scattering contribution is neglected in Equation 2.9, $I(k) \to 0$ as $k \to 0$ and $I(k) \to \langle f^2 \rangle$ as $k \to \infty$. Thus, $S(k) \to -\frac{\langle f^2 \rangle}{\langle f \rangle^2} \approx -1$ as $k \to 0$ and $S(k) \to 0$ as $k \to \infty$. The radial distribution function is, again, a Fourier transform relative of the total structure factor:

RDF =
$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2r}{\pi} \int_0^\infty k S(k) \sin(kr) dk.$$
 (2.15)

where $\rho(r)$ is the atomic number density (including all species) as a function of distance from an average atom in the sample, and ρ_o is the average atomic number density in the sample.

2.1.2 Differential and Partial Distribution Functions

With the advent of synchrotron sources, it has become possible to obtain differential and partial structure factors and distribution functions. From the broadband radiation of a synchrotron source, a desired x-ray energy can be selected by a monochromator. By tuning the incident energy at which the scattered intensities are measured near the atomic absorption edges of the elements in the sample, the weighting factors $w_{\alpha\beta}$ can be varied for the individual partial structure factors $S_{\alpha\beta}$. For a sample with two atomic species, A and B, Equation 2.11 becomes

$$I - \langle f^2 \rangle = \mathbf{x}_A |f_A|^2 S_{AA} + 2\mathbf{x}_A \Re[f_A^* f_B] S_{AB} + \mathbf{x}_B |f_B|^2 S_{BB}$$

using the relationships $x_A S_{AB} = x_B S_{BA}$ and $f_A f_B^* + f_B f_A^* = 2\Re (f_A f_B^*)$. To simplify notation, we rewrite the above equation using weighting factors:

$$I - \langle f^2 \rangle = w_{AA} \ S_{AA} + w_{AB} \ S_{AB} + w_{BB} \ S_{BB} \tag{2.16}$$

$$w_{AA} = \mathbf{x}_A |f_A|^2$$
$$w_{AB} = 2\mathbf{x}_A \Re[f_A f_B^*]$$
$$w_{BB} = \mathbf{x}_B |f_B|^2$$

Since $\langle f^2 \rangle = w_{AA} + w_{BB}$, this equation can be written as

$$I = w_{AA} \left(S_{AA} + 1 \right) + w_{AB} \left(S_{AB} \right) + w_{BB} \left(S_{BB} + 1 \right)$$
(2.17)

The weighting factors are non-zero, and $I \to 0$ as $k \to 0$, so $S_{AA} \to -1$ and $S_{BB} \to -1$ as $k \to 0$ and $S_{AB} \to 0$ as $k \to 0$. All of the partial structure factors approach 0 as $k \to \infty$.

DSFs and **DDFs**

Differential anomalous scattering $(DAS)^2$ was the first form of anomalous scattering to be effectively implemented. DAS involves taking intensity measurements at two

²Energy-modulated x-ray scattering was first proposed by Shevchik in 1977 [7], and successful experiments were first carried out by Fuoss et al. in 1980 [26, 27].

energies below the absorption edge of one atomic species in the sample and subtracting one from the other. For a sample with two atomic species, the differential is

$$\frac{\delta(I - \langle f^2 \rangle)}{\delta E} \simeq (2.18)$$
$$2f_A\left(\frac{\delta f_A}{\delta E}\right) \mathbf{x}_A S_{AA} + 2\left(\frac{\delta \left[\Re\left(f_A f_B^*\right)\right]}{\delta E}\right) \mathbf{x}_A S_{AB} + 2f_B\left(\frac{\delta f_B}{\delta E}\right) \mathbf{x}_B S_{BB}$$

At energies near the A atomic absorption edge, only that species' atomic scattering factor is a strong function of energy. Thus, $\left(\frac{\delta f_B}{\delta E}\right) \simeq 0$, and the last term in the equation is negligible. In a physical experiment, intensities collected at two energies below the A absorption edge are subtracted:

$$\Delta_A \left[I - \langle f^2 \rangle \right] = x_A \Delta_A \left[|f_A|^2 \right] S_{AA} + 2 x_A \Delta_A \left[\Re \left(f_A f_B^* \right) \right] S_{AB}$$
$$= \Delta_A \left[w_{AA} \right] S_{AA} + \Delta_A \left[w_{AB} \right] S_{AB}$$
(2.19)

where $\Delta_A[]$ indicates the difference in the value of the quantity in brackets at the two energies. This difference is then divided by a weighting factor [27]³, a *sharpening* function which, as in the case of the total structure factor, approximately removes the k-dependence of the scattering factors:

$$W(k) = \mathbf{x}_A \Delta_A \left[f'_A \right] \left(\sum_{\beta} \Gamma_{\beta} \Re \left[f_{\beta}(k, E_1) + f_{\beta}(k, E_2) \right] \right)$$
(2.20)

where $\Delta_A[f'_A]$ is the change in f' between the two energies, E_1 and E_2 , and Γ_β are estimations of the fraction of β atoms in the first coordination shell. The *differential*

³Note reference [27] incorrectly contains a factor of 2.

structure factor (DSF) for a two-component alloy is thus given by

$$\Delta_A \left[S(k) \right] = \frac{\Delta_A \left[w_{AA} \right] S_{AA} + \Delta_A \left[w_{AB} \right] S_{AB}}{W(k)} \tag{2.21}$$

Like S(k), $\Delta_A[S(k)] \to -1$ as $k \to 0$ and $\Delta_A[S(k)] \to 0$ as $k \to \infty$.

Fourier transforming the DSF produces the *differential distribution function* or DDF. In this manner, all BB atom correlations have been removed, and the result is the average environment for the A atoms.

DDF =
$$4\pi r^2 \rho_A = 4\pi r^2 \rho_o + \frac{2r}{\pi} \int_0^\infty k \Delta_A[S(k)] \sin(kr) dk$$
 (2.22)

The DDF for the A atom is thus a weighted sum of the PPDFs involving the A atom where the weighting factors depend on the scattering factors of the elements involved. The technique of DAS has been applied widely with great success. One of the reasons for this success is that, with care, the difference of two intensity measurements taken under identical experimental conditions below an absorption edge causes systematic errors to largely cancel. (This necessitates that all data be taken during the same beamtime without altering the sample mounting.) Ludwig [28] found that the coordination numbers obtained from his DDFs were as accurate as those from the RDFs as a result of this error cancellation. However, subtracting two large-valued functions still requires good precision.

The definition of the DSF assumes that the $\Delta_A[w_{BB}]$ term is entirely negligible below each A edge. There are a few cases in which care must be taken to satisfy this condition: First, when elements present in the sample are neighbors or nearneighbors in a row of the periodic table, f_B may still be changing significantly with energy below the A edge (especially when $Z_B < Z_A$). Second, when the two energies

Table 2.1: Effects of x_B and energy choice below the A element edge on the usuallyneglected $\Delta_A[w_{BB}]$ term. Values are calculated from Cromer-Liberman values at k = 0 for a binary Mo-Ge alloy below the Ge K edge.

	$k = 0 \text{\AA}^{-1}$	11003 eV $\&$	$8088~{\rm eV}$ &
		$11088~{\rm eV}$	$11088~{\rm eV}$
$x_{Mo} = 0.269$	$\Delta_{Ge}[f_{Ge}^2]$	$105.8e^2$	$290.5e^{2}$
	$\Delta_{Mo}[f_{Mo}^2]$	$1.1e^{2}$	$42.3e^{2}$
$\mathbf{x}_{Mo} = 0.269$	$ \Delta_{Ge}[w_{MoMo}] $	0.15%	2.1%
$\mathbf{x}_{Mo} = 0.731$	$\overline{ \Delta_{Ge}[w_{GeGe}] + \Delta_{Ge}[w_{GeMo}] }$	1.1%	15.4%

below the A edge are chosen to be very far apart to give a large change in f_A , the $\Delta_A[w_{BB}]$ term may become non-negligible. Finally, when the mole fraction of B is large, the $\Delta_A[w_{BB}]$ term may also become non-negligible. The top half of Table 2.1 shows the potential tremendous gain in contrast below the Ge edge possible using a difference between measurements at 3000 eV and 15 eV below the Ge edge compared with a difference at 100 eV and 15 eV; however, the Mo contribution, assumed to be zero in the Ge edge DDF, increases as well. The bottom half of Table 2.1 illustrates the magnitude of $|\Delta_{Ge}[w_{MoMo}]|$ relative to $|\Delta_{Ge}[w_{GeGe}]| + |\Delta_{Ge}[w_{GeMo}]|$. The 15% contribution of the $\Delta_{Ge}[w_{MoMo}]$ term for a 73 at% Mo sample using measurements taken 3000 and 15 eV below the Ge edge is big enough that the DSF approximation breaks down. Typical DAS measurements are taken between 10 and 200 eV below the Ge edge.

PSFs and PPDFs

To extract the PPDFs in a two-element sample, elastic intensity measurements at a minimum of three x-ray energies are required. The Keating [29] method (or the three-wavelength method) was proposed in the early 60s:

$$\begin{pmatrix} I_1 - \langle f^2 \rangle_1 \\ I_2 - \langle f^2 \rangle_2 \\ I_3 - \langle f^2 \rangle_3 \end{pmatrix} = \begin{pmatrix} w_{AA_1} & w_{AB_1} & w_{BB_1} \\ w_{AA_2} & w_{AB_2} & w_{BB_2} \\ w_{AA_3} & w_{AB_3} & w_{BB_3} \end{pmatrix} \begin{pmatrix} S_{AA} \\ S_{AB} \\ S_{BB} \end{pmatrix}$$
(2.23)

where the numerical subscripts refer to different incident x-ray energies and the weighting factors $w_{\alpha\beta}$ are defined in Equation 2.16. By inverting the matrix, the PSFs can be calculated and Fourier transformed to obtain $\rho_{\alpha\beta}$ and the PPDFs, $4\pi r^2 \rho_{\alpha\beta}(r)$. The PPDFs extracted in this way were not very reliable (in fact, non-physically negative in places) [30, 28]. Due to the small variation in the weighting factors, the matrix problem is *ill-conditioned*, and small errors in the intensity data and atomic scattering factors result in large errors in the PPDFs. Obtaining reliable PPDFs requires elimination of sources of error and/or more complicated conditioning techniques.

A second approach to the PPDF problem was proposed by Munro [31]. Improvements in the PPDFs are possible by inserting two differences in the matrix. In this approach, intensity measurements are needed at five different incident x-ray energies. Assuming proper care is taken to assure that identical experimental conditions for measurements below each absorption edge, much of the systematic error cancels in subtraction. In addition, the differences are already more linearly independent than the original data sets because they are already species-specific so that the conditioning of the matrix improves [31]:

$$\begin{pmatrix} \Delta_{A} \left[I - \langle f^{2} \rangle \right] \\ \Delta_{B} \left[I - \langle f^{2} \rangle \right] \\ I - \langle f^{2} \rangle \end{pmatrix} = \begin{pmatrix} \Delta_{A} \left[w_{AA} \right] & \Delta_{A} \left[w_{AB} \right] & \Delta_{B} \left[w_{BB} \right] \approx 0 \\ \Delta_{A} \left[w_{AA} \right] \approx 0 & \Delta_{B} \left[w_{AB} \right] & \Delta_{B} \left[w_{BB} \right] \\ w_{AA} & w_{AB} & w_{BB} \end{pmatrix} \begin{pmatrix} S_{AA} \\ S_{AB} \\ S_{BB} \end{pmatrix}$$
(2.24)

To simplify future references to this much-used equation, it can be written as $\mathbf{e} = \mathbf{M}\mathbf{p}$ where \mathbf{e} are the measured elastic intensity functions, \mathbf{M} is the Munro matrix and \mathbf{p} are the PSFs we seek to extract.

Writing out the matrix elements explicitly⁴ gives

$$\begin{pmatrix} (I - \langle f^2 \rangle)_1 - (I - \langle f^2 \rangle)_2 \\ (I - \langle f^2 \rangle)_3 - (I - \langle f^2 \rangle)_4 \\ (I - \langle f^2 \rangle)_5 \end{pmatrix} = \\ \begin{pmatrix} x_A (|f_{A_1}|^2 - |f_{A_2}|^2) & 2x_A \Re \left(f_{B_1}^* [f_{A_1} - f_{A_2}] \right) & x_B (|f_{B_1}|^2 - |f_{B_2}|^2) \\ x_A (|f_{A_3}|^2 - |f_{A_4}|^2) & 2x_A \Re \left(f_{A_3}^* [f_{B_3} - f_{B_4}] \right) & x_B (|f_{B_3}|^2 - |f_{B_4}|^2) \\ x_A |f_{A_5}|^2 & 2x_A \Re (f_{A_5} f_{B_5}^*) & x_B |f_{B_5}|^2 \end{pmatrix} \begin{pmatrix} S_{AA} \\ S_{AB} \\ S_{BB} \end{pmatrix}$$

where the numerical subscripts refer to different incident x-ray energies.

In solving for the PSFs (and PPDFs via Fourier transform), there is no requirement that a difference below, for example, the A element edge results in a negligible coefficient for the S_{BB} term ($\Delta_A[w_{BB}] \approx 0$). Near-complete elimination of the

⁴Reference [30] p. 34 and reference [28] have incorrect matrix elements M(1,2), M(2,2) and M(2,3); however, the proper matrix elements were used in solving for the PSFs in that work [32].

 $\Delta_A[w_{BB}]$ term is unnecessary since the matrix can be solved with non-zero elements.

Even with the improvements of the Munro approach, non-physical regions of negative atomic density are still seen [30, 33]. The less strongly weighted PSFs and PPDFs tend to display *mirroring*, errors that are essentially equal in magnitude and opposite in sign. This effect is believed to be caused by systematic error [33, 34] and renders the PPDFs unreliable and difficult to interpret. In a study of l-GeBr₄, Ludwig and coworkers [28] found error levels of 5-10%, 30% and 100% in the Br-Br, Ge-Br and Ge-Ge PPDFs respectively. Thus even with the Munro approach, the extraction of PPDFs remains highly sensitive to error.

2.1.3 Anomalous Dispersion

The anomalous x-ray scattering techniques described above in Section 2.1.2 all rely on the variation in scattering factor, a measure of the "scattering power" of an element, near absorption edges in the sample to change the weighting factors $w_{\alpha\beta}$. These changes in weighting factors provide the contrast needed to extract chemically specific information. Obtaining the most accurate scattering factor possible is, therefore, a high priority.

Although calculations of Rayleigh scattering from first principles⁵ can now be carried out using the second-order S-matrix in quantum electrodynamics and selfconsistent relativistic wave functions [35], these calculations are computationally costly, and the calculated energies at which absorption edges occur do not agree with experiment [35]. As such, the use of form factors and anomalous scattering factor approximations are advantageous.⁶ Tabulated values are readily available, and

⁵In the independent particle approximation, all atomic electrons are assumed to move independently in a common central potential due to the nuclear charge and the average distribution of all electrons.

⁶The S-matrix calculations include the contribution of transitions to unoccupied bound states

absorption edges arise where expected experimentally.

Form Factor & Anomalous Scattering Factor Approximation

The atomic scattering factor, f, can be written as a form factor in combination with anomalous scattering factors:

$$f(k, E) = f_o(k) + f'(k, E) + if''(k, E)$$
(2.25)

For a given atom in the sample, the atomic scattering factor represents the amplitude of coherently scattered radiation from the atom relative to that of a single free electron. (f is sometimes referred to as the scattering amplitude.) The form factor, f_o , is the contribution of a free, unperturbed atom, and the anomalous scattering factors, f' and f'', correct for the effects of dispersion near the absorption edges.

In the time-dependent, non-relativistic formulation of scattering, the atomic scattering factor can be written as $[26]^7$

$$f(k, E) = \sum_{n} \left[< n | e^{i(\mathbf{S} - \mathbf{S}') \cdot \mathbf{r}} | n > \right]$$

$$-\frac{1}{\hbar m} \sum_{j} \left[< n | e^{i\mathbf{S}' \cdot \mathbf{r}} \epsilon \cdot \mathbf{P} | j > < j | e^{i\mathbf{S} \cdot \mathbf{r}} \epsilon \cdot \mathbf{P} | n > \right]$$

$$\times \left[\left(E_{jn} - \hbar \omega - \frac{i\hbar \gamma_{jn}}{2} \right)^{-1} + (E_{jn} + \hbar \omega)^{-1} \right]$$
(2.26)

where $\langle j |$ is a wavefunction of the atom, ϵ is the polarization vector of the photon, **P** is the momentum operator, γ_{jn} is the convolved width of the j and n states, n

⁽bound-bound transitions) which have been ignored in the past. These transitions are especially important for atoms or ions with less than 10 bound electrons. The form factor and anomalous scattering factor approximations are not sufficient for these low-Z elements.

⁷after Sakurai [36].

represents the occupied states in the atom and j, the unoccupied, and the scattering vector is $\mathbf{k} = \mathbf{S} - \mathbf{S}'$.

Atomic Form Factor

At energies far from the absorption edges, the first term in Equation 2.26 above, referred to as the atomic form factor, dominates. It can be written as follows:

$$f_o = \sum_n \langle n | e^{i(\mathbf{S} - \mathbf{S}') \cdot \mathbf{r}} | n \rangle = \int \rho(r) \ e^{i(\mathbf{S} - \mathbf{S}') \cdot \mathbf{r}} \ dr$$
(2.27)

Thus, f_o is simply the (3-dimensional) Fourier transform of the atomic electron probability density. It is a function of scattering vector k and independent of energy.⁸

Calculations of f_o are available for free atoms and many ions using a variety of wave functions: Cromer and Mann [37] parameterized form factors calculated from numerical non-relativistic Hartree-Fock (HF) wave functions for neutral atoms and most "chemically significant" ions for $2 \le Z \ge 103$. Waasmaier and Kirfel [38] later developed improved parameterizations for the form factors tabulated in the **International Tables for X-Ray Crystallography**, Section 2.2. For neutral atoms, these form factors are all calculated using relativistic Hartree-Fock (RHF) wave functions from two sources. (The form factors for both Ge and Mo are from Doyle and Turner (1968) [39] using wavefunctions of Coulthard (1967) which assume the nucleus is a point.)

⁸Fuoss [26] notes that f_o is, in general, a complex quantity and real only for centrosymmetric electron density distributions.

Anomalous Scattering Factors

The anomalous scattering factors, referred to in this work as the ASFs (not to be confused with the atomic scattering factor, f), provide a correction to the atomic form factor, f_o , to account for dispersion. Near the absorption edge of an atomic species in the sample, the incident radiation begins to interact resonantly with the electrons in that atom, and the second term in Equation 2.26 above becomes significant. (The third term is always small since $E_{jn} + \hbar \omega$ is large.) The atomic scattering factor, f, is no longer simply equal to the Fourier transform of the atomic electron density distribution, f_o ; a correction of f' + if'' must be added.

In the classical theory of dispersion, the atoms are assumed to scatter as damped electric dipole oscillators interacting with an electromagnetic wave. This dipole approximation is carried out by using only the leading term in the Maclaurin series expansion of e^{iSr} in the calculation of the matrix components. Near the absorption edge, the damping becomes significant.⁹ The effect of the imaginary part, if'', is to add an out-of-phase component to the scattered wave resulting in a decrease in the transmitted amplitude, i.e. an absorption. f'' can be related to the x-ray absorption cross-section by the optical theorem

$$f_{\alpha}''(\omega) = \frac{m_e c \,\omega}{4\pi e^2} \sigma_{\alpha}^{cs}(\omega) \tag{2.28}$$

or, in terms of the mass absorption coefficient,

$$f_{\alpha}''(\omega) = m_{\alpha} \, \frac{m_e c \, \omega}{4\pi e^2} \sigma_{\alpha}(\omega) \tag{2.29}$$

where ω is the incident photon frequency, σ_{α}^{cs} is the photoelectric cross-section of the

 $^{^{9}}$ James, Chap. 4 [40].

 α species in units of [area], σ_{α} is the mass absorption coefficient in units of [area / mass], m_{α} is the mass of the α atom, m_e and e are the mass and charge of an electron and c is the speed of light.

The real and imaginary ASFs can be related by the Kramers-Krönig dispersion relationship [41]:

$$f'(\omega_o) = \frac{2}{\pi} \oint_0^\infty \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega$$
(2.30)

where $\omega = 2\pi E/h$ and \oint represents the Cauchy principle value of the integral. It is important to note that the Kramers-Krönig transform is valid *only* in the dipole approximation. In addition, this relationship yields the imaginary part of the ASF in the forward-scattering direction $(2\theta = 0^{\circ})$ only.

For K absorption edges, f' and f'' have only small variations of magnitude with k(or θ) which are commonly taken to be negligible [42, 43]. (The dipole approximation yields k-independent ASFs, but including higher order terms in the calculations leads to a slight k-dependence.) The angular variation is clearly negligible for f'' and on the order of 0.15 electrons for f'. (For L edges, which are not examined in this work, the angular variation of f' is much stronger and can be up to 2 electrons for Sm [44].) Because the angular dependences of the ASF are typically small and experimental errors have been likely to overshadow this effect, they are ignored in this work:

$$f''(k, E) \approx f''(E)$$
 and $f'(k, E) \approx f'(E)$.

See Chapter 8 for further discussion.

Hönl (1933) [45] first calculated the anomalous scattering factors for only the K shell electrons using hydrogenic wavefunctions, and these data were used in diffraction

studies for several decades. Cromer and Liberman's tables of the anomalous scattering factors [46, 47, 48] are the present standards for calculations. These were carried out using relativistic Dirac-Slater-like wavefunctions computed using the Kohn-Sham potential rather than the Slater potential and using experimental energy levels rather than the computed Dirac-Slater eigenvalues. The resulting photoelectric crosssections calculated therefore demonstrate experimentally-observed edge positions, a tremendous advantage for use in experimental work. The cross-section is related by the optical theorem to f'' and f' is calculated by the Kramers-Krönig transform (with the dipole approximation).

In their work, Cromer and Liberman estimated a relativistic correction to the high energy limit of forward scattering within the framework of the dipole approximation - a constant of $\frac{5}{3}(E_{tot}/mc^2)$ where E_{tot} is the total energy of the atom [47]. It was first noted by Jensen (1979) [49] that higher multipoles become more relevant at higher energies and that the dipole approximation omits a significant term for large ω . Jensen proposed a correction (1980) [50] to Cromer and Liberman's original correction; however, Kissel and Pratt (1990) [51] pointed out that Jensen's suggestion also does not give the correct high-energy limit. They noted that the correct high energy limit was obtained in much earlier work by Franz in 1936, and they published tabulated corrections which have been generally accepted. Free atom f''s referred to in this work are the Cromer and Liberman (CL) f'' values with the Kissel and Pratt correction and the S-matrix-calculation-derived f''s of Kissel et al. (1995) [35]. Fitting of experimental f'' curves to calculated values is described in Chapter 5.

Figure 2.1 shows the CL f'' and f' values for Mo. Clearly, the closer to the absorption edge energy, the larger the magnitude of f' and the greater the contrast possible. However, the slope of f' as a function of energy also increases in magnitude giving



Figure 2.1: The Cromer-Liberman (CL) f'' and f' values for the Mo K edge. The variation in f' below the absorption edge provides the contrast necessary for anomalous x-ray scattering.



Figure 2.2: Kissel's f'' values for the Mo K edge, unedited. The bound-bound transitions present singularities that make calculations difficult, and the absorption edge does not appear at experimentally observed energies.

a greater potential error. Balancing these considerations is discussed in Section 2.3. In Figure 2.2, the Kissel f'' data for the Mo edge are shown. Sharp bound-bound transitions and edge energies not coincident with experiment make Kissel's values less convenient for the experimentalist. Figure 2.3 compares the CL and Kissel f'' and f' values for Mo. The use of Kissel versus Cromer-Liberman f'' values will be discussed in more detail in Chapter 5.



Figure 2.3: The Cromer-Liberman (CL) f'' and Kissel (K) f'' values for the Mo K edge. The Kissel f'' data has been shifted to match the CL edge energy, and bound-bound transitions have been removed.

2.1.4 Necessity of Experimental ASFs

Tabulated values of atomic form factors and anomalous scattering factors are available for free atoms; however, neighboring atoms in an actual sample affect the potential of the atom under investigation so that it does not behave exactly as a free atom. The effects of chemical binding within a given sample will have a large impact on the shape and position of the features in the absorption spectrum. In addition, socalled "white lines" caused by bound-bound transitions are highly sensitive to the chemical environment of the atom. Thus for the most accurate anomalous scattering factors, the linear absorption coefficient ($\mu_{\alpha} = \rho_{\alpha}\sigma_{\alpha}$) is directly measured through each K edge in the sample. From the optical theorem, experimentally measured f''values are obtained. Far from the absorption edge, theoretical values of f'' (on a shifted energy scale so that the absorption edge occurs at the experimental energy) are used to extend the energy range past the measured f''. Using the Kramers-Krönig transform, f'(E) is obtained. The energy resolution of the f' data is then the same as for the f'' data.

2.2 Potential Error

in the Elastic Scattered Intensity

Since the PPDFs are highly sensitive to error, we need to remove as much error as possible in the elastic scattered intensity. Inelastic scattering must be removed from the total intensities included in the data analysis. Resonant Raman and Compton scattering are two effects that frequently contribute to the total measured intensity.

2.2.1 Resonant Raman Scattering

Near the absorption edge of an element in the sample where the energy of incident photons is close to, but less than, an atomic inner-shell ionization energy, a type of inelastic scattering called radiative resonant Raman (RR) scattering occurs. The intensity of this RR scattering increases dramatically as the excitation energy $\hbar\omega_1$ approaches the absorption edge energy, and the energy difference between the RR peak and the elastically-scattered peak remains constant as the excitation energy is changed. This constant energy difference is reminiscent of the Stokes peak in optical Raman scattering - hence the name resonant "Raman" scattering. RR scattering differs, however, from ordinary vibronic Raman scattering in that there are not only discrete excitations but continuous energy losses as well, and there is negligible probability that the frequency of the scattered radiation is increased. Radiative RR scattering was first observed by Sparks [52] in 1974 using Cu K_{α} radiation from an x-ray tube on various metallic targets. The first synchrotron radiation experiments on RR scattering were carried out by Eisenberger and coworkers [53] in 1976 showing the evolution of K-L RR scattering into K_{α} fluorescence.

In radiative RR scattering, photoionization and radiationless de-excitation occur via a single quantum process [54]. (Even at threshold, ionization and decay cannot be treated properly as distinct processes.) Radiative RR scattering evolves into the true x-ray fluorescence as $\hbar\omega_1$ approaches and exceeds the absorption edge I_i .

Figure 2.4 illustrates the radiative resonant Raman scattering process. The process may be thought of in the following manner: Due to the very short core-hole lifetime, there is an energy broadening of the core state *i* leading to a finite probability of photoexcitation by an incident photon of an energy *less* than the absorption threshold energy. One may consider a (virtual) hole formed by the excitation of an electron sitting slightly above the core level *i* by a photon with energy $\hbar\omega_1$. An electron from a higher-lying state *f* fills this hole (see the dashed lines in Figure 2.4 a) so that the net result is an excitation of an electron from the state *f*. The excess energy is emitted as a photon of energy $\hbar\omega_2$. The excited electron can end up in either a bound state or be excited to or above the Fermi energy in Figure 2.4 such



Figure 2.4: Radiative resonant Raman scattering in the case where a) $\epsilon = 0$ and b) $\epsilon > 0$.

that

$$\hbar\omega_2 = \hbar\omega_1 - I_f - \epsilon$$

where $I_f < I_i$ and ϵ is the energy of the excited electron with respect to I_f . If the electron is excited into a bound state, $\epsilon < 0$, and if it is excited above the Fermi level, $\epsilon > 0$. The probability of $\hbar \omega_2 > \hbar \omega_1$ is negligible.

In AXS experiments, the K_{β} RR scattering often falls uncomfortably close to the elastic peak. For the case of incident radiation approaching the Ge K edge (from below), the K_{β} peak lies only 121 eV below the elastic peak. For the Mo edge, the spacing is 394 eV. Without sufficient detected energy resolution, the inelastic K_{β} RR scattering peak cannot be differentiated from the elastic peak.

2.2.2 Compton Scattering

A second source of inelastic scattering that must be removed in AXS experiments is the Compton scattering (sometimes called modified scattering) resulting from the inelastic collision of an incident x-ray with an electron in the atom. We can obtain an approximation for the position of the Compton peak in energy as a function of scattering angle by treating the incident x-ray as a particle in a billiard ball calculation:

$$\lambda_{Compton} - \lambda_{incident} = \frac{h}{mc} \left(1 - \cos 2\theta \right) \tag{2.31}$$

This is a simplification since it ignores binding effects, but it shows that the peak in Compton scattering shifts to lower energies as k is increased. This behavior is shown in Figure 2.5 for Ge.



Figure 2.5: Position of the peak in Compton scattering as a function of the scattering vector, k, for an incident energy 100 eV below the Ge K edge.

Because of the distribution of momenta of the electrons in an atom, the Compton scattering is not a narrow peak but rather a low, broad distribution of intensity as a function of energy. (This makes it all the more difficult to remove.) The integrated intensity of this Compton distribution is zero at k = 0 and increases as k increases.

For an atom, the Compton scattered intensity is

$$I_C(k) = Z - \sum_n f_n^e(k)^2$$
(2.32)

where Z is the atomic number of the atom, f^e is the scattering factor for each electron and n is the number of electrons in the atom. Comprehensive theoretically calculated Compton cross-sections are available; however, the free atom Compton scattering is modified when the scattering atom is in a solid. Figure 2.6 shows the contribution of the calculated, free atom Compton scattering to the total scattering for MoGe₃ as a function of k.¹⁰



Figure 2.6: The total scattering, elastic scattering and Compton scattering from an independent atom with an average composition of $MoGe_3$ are plotted on the left-hand axis as a function of the scattering vector, k. The Compton scattering as a percentage of the total scattering is plotted on the right-hand axis.

Since the Compton scattering is inelastic and occurs over a range of energies, the

¹⁰Elastic scattering calculated using the parameterized fits of Cromer and Mann [37]; Compton scattering calculated using the fits of Balyuzi [55]

detector energy resolution as well as the detector efficiency as a function of energy must be well-characterized in order to properly remove it. For high detected energy resolution, the intensity of Compton scattering included in the elastic peak can be negligible. For low energy resolution, the Compton scattering must be subtracted using calculated values, preferably modified by the detector bandpass function [56]. It is a common and often incorrect assumption that the detector response is identical at all energies, elastic and inelastic.

2.3 Energy Selection

There are several competing considerations in choosing energies for AXS data collection. One would like to take advantage of the greatest contrast available by taking data close to an absorption edge; however, the accuracy with which the anomalous scattering factors are known decreases on approach to the edge energy from lower energies. In addition, the energy resolution with which the sample is being probed must be taken into account. Finally, a large k-range is desirable for proper normalization of the elastic scattering and for good spatial resolution.

2.3.1 Contrast

From the simplest viewpoint, the greatest difference in the total scattering factor at two energies (near the absorption edge for the element of interest) will provide the greatest change in the weighting factors involved in Equations 2.21 and 2.24 and, therefore, the greatest contrast. From this viewpoint, energies both below and above the edge can be considered. From a more practical stance, however, taking data using incident energies above the absorption edge gives excessively high count rates due to fluorescent radiation. Although the fluorescent radiation is at a different energy than the elastically-scattered radiation from the sample, the logistics problem of collecting a small elastic signal in the vicinity of a large fluorescent signal is difficult to solve. From these considerations alone, it is common to choose widely-spaced energies *below* the absorption edge for AXS.

2.3.2 Accuracy

The accuracy of the nominal energy of the incident radiation depends on the calibration of the monochromator crystals as well as thermal stability. The ASFs are determined from experimental x-ray absorption spectroscopy data obtained by scanning the monochromator energy through the absorption edge. Since the real part of the dispersion correction f' varies rapidly with energy about the edge, a small error in the energy scale for the ASFs or in the incident energy for collecting scattering data can result in a very large error in the ASFs used in analyzing the scattering data. With this in mind, it is best not to work at energies too near the edge where the slope of f' with energy becomes large.

2.3.3 Energy Resolution & Scattering Geometry

Since it is not possible to achieve a truly monochromatic beam of x-rays, an important consideration is the incident energy resolution and the scattering geometry which dictate what is physically measured. The incident energy resolution indicates the range of energies that the sample is actually "seeing" about the nominal energy at the centroid of the distribution, assumed to be Gaussian for our purposes. At energies too near the absorption edge, part of the distribution of energies can fall above the absorption edge exciting fluorescent radiation. Narrow incident energy resolution permits a closer approach to the edge energy (assuming good thermal stability of the monochromator crystals), but generally reduces count rates slowing data collection.

The scattering geometry (see Chapter 4) used to analyze the emitted radiation in this work places a linear detector at a slightly defocussed position in a parafocussing geometry. This leads to a broadening of any given monochromatic beam of radiation on the linear detector. While fluorescent radiation can be, in theory, distinguished from the major elastic and inelastic scattering processes occuring in the sample by the energies of the emitted photons, this physical broadening of a single, monochromatic energy leads to a small degree of overlap between the elastic, resonant Raman and fluorescent peaks. The limitations on the present experiments are discussed further in Section 5.5.

2.3.4 *k*-Range

Finally, one must consider the maximum attainable scattering vector magnitude. k_{max} is determined by the incident energy which is near the absorption edge energy:

$$k_{max} = 4\pi E/hc \tag{2.33}$$

or
$$k_{max}[\text{\AA}^{-1}] \approx E \ [keV]$$

Thus, the higher the incident energy, the larger the k-range available. This is advantageous for several reasons: Higher k_{max} means better real space resolution and fewer termination oscillations that must be damped with additional loss of resolution. Also, the elastic scattering approaches the coherent scattering at high k so that normalization of the data to a per-atom basis is less ambiguous. A final consideration is that the absorption correction, the most significant of the corrections applied to the experimental intensity data (discussed in Chapter 5), has its greatest slope at high k for the transmission scattering geometry employed in this work. This creates a catch-22 in which the data are typically normalized by reference to the highest k region where the potential impact of error is greatest.

A drawback to a high incident energy is that it is more difficult to collect scattering data in the low-k range. Since $k = \left(\frac{4\pi}{hc}\right) E \sin \theta$, a plot of k versus $\sin \theta$ (Figure 2.7) illustrates that for higher incident energies, the low-k range occurs at lower scattering



Figure 2.7: The relationship between the scattering vector magnitude, k, and $\sin \theta$ for incident photon energies of 11 and 20 keV. It is experimentally more difficult to collect the low-k range of scattering data at 20 keV because it occurs at such small scattering angles.

angles. This presents experimental difficulties since, generally, care must be taken to prevent the direct, transmitted beam (at $2\theta = 0^{\circ}$) from entering the sensitive detector.

In solving for the PPDFs, the upper limit in k for calculations is set by the lowest Z element (Ge, in this case). For low Z elements, it is therefore advisable to take additional data at a high energy (but away from fluorescence peaks) in order to have

high- k_{max} data which can be well-normalized. This well-normalized data set is then a useful reference for normalizing scans taken at lower energies. In these experiments, the incident energies near the Mo K edge at 20 keV approach the limits of the energies presently available at SSRL with reasonable count rate, so the normalized Mo edge data were referenced in normalizing the Ge edge data.

2.4 Complementary Techniques to AXS

Methods other than AXS can be used to determine chemically-specific local structure in materials. The various advantages and disadvantages of two widely-used techniques, EXAFS and ISDN, are discussed below.

2.4.1 EXAFS

The extended x-ray absorption fine structure (EXAFS) is the oscillatory structure in the x-ray absorption coefficient well above an absorption edge. This structure is due to the interference of the outgoing and backscattered photoelectron waves and, thus, reflects the local structure about the absorbing species. (For a more detailed review of the technique, the reader is referred to references [57] and [58].) The information about local environment obtained from EXAFS is analogous to that from differential anomalous scattering (DAS): Both techniques give the structure about a single atomic species, but there are key differences as well. EXAFS is experimentally much simpler and quicker than AXS experiments. It is particularly useful in examining the first (and sometimes the second) nearest neighbor environment of dilute species in a multi-atom sample where x-ray diffraction fails. AXS techniques, which extend to larger radial distances, are better suited for more concentrated alloy systems such as *a*-MoGe₃ in several ways. One drawback of EXAFS is that it requires complex data analysis involving backscattered phases and amplitudes normally obtained via theoretical *ab initio* calculations. It also cannot provide the fully-chemically-specific atomic distribution information available in the PPDFs from AXS.

The fundamental differences between EXAFS and DAS arise from the different k-regions they access. Due to the pathlength 2r travelled by a backscattered photoelectron, there is a factor of 2 relating the k scales typically used in the two techniques:

$$2\,k_{EXAFS} = k$$

where k refers to the familiar x-ray scattering vector magnitude. The useful EXAFS are typically collected from $k_{EXAFS} = 2 - 15 \text{ Å}^{-1}$. This corresponds to $k = 4 - 30 \text{ Å}^{-1}$. Thus, EXAFS lacks the low k data and extends to much higher k than AXS experiments involving any element with Z < 50. It is therefore primarily sensitive to very near neighbors.

The lack of low k data is a major handicap of the EXAFS technique for the study of non-crystalline materials. (See [1] and references therein.) Since information about farther and more disordered density distributions (shells of atoms) is present at low k, EXAFS misses this information entirely. Even materials with a disordered first shell of neighbors produce difficulties in EXAFS analysis due to the decay of correlations. In fact, the low k limit puts an effective upper bound on the width of a distribution detectable by EXAFS. Asymmetric density distributions also are "seen" differently by the two techniques. AXS misses the high k components and smears out the distribution while EXAFS misses the low k components and shows only the sharpest edge of the distribution. These issues are of particular concern in the study of amorphous materials.

AXS and EXAFS are thus often complimentary techniques for providing chemicallyspecific information on the local atomic arrangements in non-crystalline materials. While AXS techniques give information in the intermediate regime with limited resolution, EXAFS accesses a higher-k region and can give accurate near neighbor distances and coordinations for the first shell of neighbors – provided the atomic near neighbor shells are distinct and reasonably sharp.

There have been a few studies combining AXS and EXAFS measurements ([59, 60]) to extract PSFs and PPDFs; however, the k-range available is then severely limited by the lower k-range of the EXAFS and the upper k-range of the scattering.

2.4.2 Isotopic Substitution Neutron Diffraction

An alternate, and sometimes complimentary, means of obtaining partial pair distribution functions is through isotopic substitution neutron diffraction, ISND. This technique requires the preparation of samples structurally identical and differing by the substitution of a constituent element by an isotope. The technique is founded on the assumption that the structure is not effected by isotopic substitution. The basic concept is similar to anomalous x-ray scattering: Rather than obtaining contrast through the change of the anomalous scattering factors with energy, the contrast mechanism is the change in the neutron scattering length as a function of the isotope.

The most fundamental difference between neutron and x-ray diffraction is the object that is physically probed: x-rays interact with the electron cloud about the nucleus whereas neutrons interact directly with the nucleus. X-ray diffraction patterns thus yield the distribution of electron density within a solid while neutron diffraction patterns yield the distribution of nuclei. For structural determinations, these techniques probe the same structure, but the sensitivity of each technique to different elements is very different due to the different physics of scattering. X-ray scattering is roughly proportional to the local electron density, and neutron scattering is nucleus-dependent and varies seemingly arbitrarily through the periodic table. As a result, structural information from metal-oxides is more readily obtained from neutron diffraction analysis while x-ray diffraction analysis will yield information primarily about the metal atoms [61].

ISND requires preparation of several samples of the same composition differing only in isotope. Depending on the element, isotopes may be extremely expensive, rare or simply unavailable. In addition, neutron reactors produce low brightness, and neutron cross-sections are much smaller than x-ray cross-sections leading to lengthy experiments limited to bulk samples. (Since the samples for this work are sputter deposited, preparation of sufficiently thick films is not feasible.) For isotopes available with oppositely-signed scattering lengths (specific to the isotopes), isotopic substitution can produce larger changes in neutron scattered intensity than can be achieved through the anomalous scattering effect in x-ray scattered intensity. Table 2.2¹¹ shows the natural abundance and neutron scattering lengths of Mo and Ge.

AXS, on the other hand, requires only one sample since the energy dependence of the scattering factor provides the means of contrast. Because the technique is not limited by the availability and cost of isotopes, more elements are readily accessible. However, AXS has the disadvantage for low atomic number elements. Since the maximum scattering vector magnitude is determined by the incident energy near the absorption edge energy in AXS, low Z elements typically yield anomalous scattering data that terminates before the structural oscillations have approached the coherent scattering making normalization difficult and giving strong termination oscillations

¹¹from Table 1, p. 21 of reference [62].

Table 2.2: Naturally-occurring isotopes of Mo and Ge. The abundance and neutron scattering lengths are listed. In general, heavy isotopes with natural abundances less than 1% are prohibitively expensive.

element	mass no.	ave. isotopic	b (fm)
		abundance $(\%)$	
	70	20.5	10.0
	72	27.4	8.51
Ge	73	7.8	5.02
	74	36.5	7.58
	76	7.8	8.2
	92	14.84	6.93
	94	9.25	6.82
	95	15.92	6.93
Mo	96	16.68	6.22
	97	9.55	7.26
	98	24.13	6.60
	100	9.63	6.75

that obscure the structure.

With AXS, synchrotron sources offer high brightness which translates into relatively quick experiments on small volume samples. Structure in technologically relevant thin film samples can be examined, and new generation synchrotrons provide even higher brightness. Although ISND has the clear advantage over AXS for the few sample systems in which isotopes of oppositely-signed neutron scattering lengths are readily available, AXS using the Munro matrix method generally yields comparable results to ISND [30].

There have been recent studies (see references [63, 64, 65, 66]) combining AXS and ISND to obtain differential and partial pair distribution functions with reasonable results. The advantage of this approach is that the weighting factors for each element are usually very different in the two techniques giving stronger contrast than may be available from a single technique. There are two potential issues in combining methods in such a manner. First, the different corrections and additional sources of systematic error involved will not cancel out as they will in a differential measurement using one method. Second, the methods do not probe the same things: neutron diffraction probes the nucleus while x-ray diffraction probes the electron distribution about the nucleus. Finally, neutron scattering techniques are generally inapplicable to thin films which are often of technological importance.

2.5 Predicting the Outcome of AXS for Extraction of Partials

For a given system, the potential success of the AXS technique for extracting partial structure factors can be predicted – even before any experiments are carried out – by considering a few measures discussed below.

2.5.1 Weighting of Species

The weighting of the different atomic species in the alloy affects the ability to extract all of the partial structure factors reliably. For the MoGe₃ system, a quick back-ofthe-envelope check on the weighting factors (see Equation 2.16) can be carried out by simply approximating the atomic scattering factors with the atomic numbers of the elements:

$$S = 42\% S_{GeGe} + 35\% S_{MoGe} + 23\% S_{MoMo}.$$

This indicates that the weighting factors of the three partials are of similar magnitude so that one correlation does not completely overshadow the others. As such, we can reasonably expect to extract all three.¹²

2.5.2 SVD Analysis and Conditioning of the Matrix

Singular value decomposition (SVD) is a well-known algorithm [67] that provides a more rigorous means of examining the extraction problem for MoGe₃. In this type of matrix factorization, an mxn matrix **M** is effectively rotated in domain and range to make it diagonal:

$$\mathbf{M} = \mathbf{U} \mathbf{\Sigma} \mathbf{V}^T$$

where **U** and **V** are mxm and nxn orthogonal matrices and Σ is an mxn diagonal matrix with elements $\sigma_{ij} = 0$ for $i \neq j$ and $\sigma_{ii} = \sigma_i \geq 0$. The σ_i are called the "singular values" of the matrix **M**.

A measure of the stability of the matrix problem is the *conditioning* of the matrix. This is defined as the ratio of the largest to the smallest singular value of the matrix

$$\operatorname{cond}(\mathbf{M}) = \frac{\sigma_{max}}{\sigma_{min}}.$$

The Turing number, T, is the condition number for the normalized matrix. The Turing number can be interpreted as a relative error magnification factor: A large Turing number indicates that the PSFs are highly susceptible to errors in the intensities and weighting factors.

As the atomic scattering factor varies as a function of k and incident energy, so does the Turing number for our Munro matrix. Figure 2.8 shows the conditioning calculated using Cromer-Liberman ASF values for the cases of GeBr₄ studied by

¹²Other definitions of the partial structure factors give different ratios; however, the most heavily weighted partials are always the Ge-Ge and Mo-Ge partials while Mo-Mo is the least heavily weighted partial.

Ludwig [28] and discussed briefly in Section 2.1.2, MoGe₃ in this case (Mo₂₇Ge₇₃, to be more precise) as well as Mo₁₄Ge₈₆ and Mo₄₂Ge₅₆, some of the compositions studied by Kortright [2]. The conditioning for the MoGe₃ system is similar to that of the GeBr₄ system.¹³ For MoGe₃, the *calculated* matrix conditioning begins at T = 224at k = 0 and decreases to T = 21 by k = 10 Å⁻¹. The *actual* matrix conditioning using experimental ASFs is slightly better at T = 192 at k = 0 Å⁻¹ and T = 19 at k = 10 Å⁻¹.



Figure 2.8: The calculated Turing number as a function of k for several different systems. The differences for the GeBr₄ system were taken between 11003 and 11098 eV below the Ge edge and between 13374 and 13469 eV below the Br edge, and the final measurement was taken at 20000 eV. The differences for the Mo-Ge system were taken between 11003 and 11088 eV below the Ge edge and between 19900 and 19985 eV below the Mo edge, and the final measurement was taken at 19900 eV. The Cromer-Liberman ASFs were used for these calculations.

¹³As noted in Section 2.1.2, Ludwig used incorrect matrix elements in calculating the Turing number and obtained T = 45 at k = 0 for the Munro matrix solved for the GeBr₄ structure. The correct value is near 195 at k = 0.

It is interesting to note that, of the sample compositions $(0 \le x_{Mo} \le 0.65)$ studied by Kortright [1], the Mo₄₂Ge₅₆ sample gives the best conditioning.¹⁴ However, he was unable to extract reliable partials. His measurements for that sample were acquired during two different experimental runs. This difficulty emphasizes the importance of taking measurements in a single run to ensure that systematic errors are as similar as possible for all of the data below a given edge.

We can take a closer look at the matrix decomposition for Sample 2 following the SVD analysis by Ludwig [30]. The singular values, σ_i , of the matrix are the positive square roots of the eigenvalues and the columns of **V** are the eigenvectors of $\mathbf{M}^T \mathbf{M}$. For the Munro matrix we have constructed at k = 0, we find

$$\mathbf{M} = \left(\begin{array}{rrrr} 762.5 & 1759.9 & 373.5 \\ -0.1 & 102.3 & 42.4 \\ 86.0 & 134.8 & 0.3 \end{array}\right)$$

This gives

$$\mathbf{V} = \begin{pmatrix} 0.37 & -0.77 & 0.51 \\ 0.90 & 0.21 & -0.38 \\ 0.19 & 0.61 & 0.77 \end{pmatrix} \text{ and } \mathbf{\Sigma} = \begin{pmatrix} 1962.7 & 0 & 0 \\ 0 & 60.4 & 0 \\ 0 & 0 & 10.2 \end{pmatrix}$$

These indicate that the experimental results are most sensitive in the 33-direction, the Mo-Mo direction, and the errors in the solutions will tend to take the form of the third column vector of \mathbf{V} . Thus, we find that the Mo-Mo PSF will be about twice as sensitive to error than the Ge-Mo PSF. In addition, errors in the Ge-Mo PSF will be opposite in sign to errors in the Mo-Mo and Ge-Ge PSFs. The Ge-Ge PSF is expected

¹⁴For the Mo-Ge system at the energies chosen, optimum conditioning occurs at $x_{Mo} = 0.46$.

to be about 30% more sensitive to error than the Ge-Mo PSF; however, since there are about three times more Ge about Ge than Mo about Ge in the sample, we may expect the *relative* accuracy of the Ge-Ge PSF to be near that of the Ge-Mo PSF.

2.6 Conditioning, Regularization and Modelling

There are several mathematical regularization methods for countering the effects of *ill-conditioning* on the PSF extraction problem. These methods reduce the influence of noise on the solution by forcing the solution to conform to certain boundary conditions. In spite of some impressive results (for examples, see references [33, 68, 69, 70, 71, 72]), there remains some hesitation about using these methods: In forcing physical behavior in certain regions, they have the potential for introducing distortions in others. In other words, there is some error introduced into the solution by the regularization procedure itself [71]. In addition, the resulting solutions will appear deceptively well-behaved even with errors present because the constraints applied are generally also those used to judge the quality of the function. The application of the methods is not without complications as well: The statistical precision of the experiment must be determined in order to choose the appropriate regularization parameter, λ . A value of λ too large results in incorrect solutions while λ too small gives the least squares solution. Finally, regularization techniques can stabilize systems with significant random error but can not successfully treat systematic errors which are likely to be present in experimental data [33, 34, 73] (hence the improvement in moving from the Keating to the Munro approach). Because of the potential pitfalls, regularization methods should not be viewed as a panacea for the ill-conditioned problem of PSF extraction. We believe reliance on regularization techniques should be minimized by first obtaining the cleanest experimental elastic scattering data possible. To the author's knowledge, well-behaved PPDFs yielding new structural information, without resort to regularization methods, have not been obtained prior to this work.

A second resource in extracting useful physical information from structure factors or distribution functions is modelling. Reverse Monte Carlo simulations, in particular, have been frequently used to determine real-space models that best reproduce the experimental structure factors. (See, for example, references [74, 75, 76].) These methods also have limitations. Naturally, simulations do not provide a unique physical arrangement of atoms for given experimental structure factors or distribution functions. Reverse Monte Carlo simulations, for example, tend to produce the most disordered physical arrangement of atoms that fits the experimental functions. Having good quality PSFs or PPDFs for an amorphous system, however, provides more explicit local structure information than typically is available and considerably reduces the field of possible solutions.
Chapter 3

Sample Preparation

The specifics of the deposition process impact the structure of amorphous films prepared by vapor phase deposition: The kinetics involved in condensation of the vapor onto the substrates at extremely rapid quench rates play a critical role in establishing the structure and properties of the film. As such, the sample preparation techniques established in the work of Jeffrey Kortright [1, 2] and Michael Regan [3, 4, 77] were closely followed to allow interpretation of the present results in the context of their work. The goal was the production of a free-standing amorphous Mo-Ge alloy film with a composition near 25 at% Mo of sufficient thickness to give reasonable mechanical stability and x-ray scattering signals. The details of sample preparation are given in this chapter.

3.1 Sputtering

All samples for this work were prepared in the 3-inch sputtering system (described in reference [1]) at the Vapor Phase Synthesis Lab in the Center for Materials Research at Stanford University. Mo (99.95% or purer) and Ge (99.999%) were cosputtered

sample	Mo gun (A)	Ge gun (W)	rate $(\text{Å}/s)$
1	0.105	400	1.26
2	0.135	400	1.79
3	0.140	400	2.04

Table 3.1: Sample deposition: gun parameters and deposition rates.

from 2" diameter, 1/8" thick elemental targets¹ using dc and rf magnetron sputtering, respectively. By controlling the rf and dc power, the relative sputtering rates, and therefore the composition of the final film, could be adjusted. For this work, the rf power to the Ge target was held at 400 W while the dc current to the Mo target was varied from 0.1 to 0.2 A. Table 3.1 contains sputtering parameters for the three samples nearest the target composition of MoGe₃.

The sputtering chamber was equipped with a cryopump yielding base pressures typically in the mid- 10^{-7} torr range and never exceeding 8.0×10^{-7} torr. The argon sputtering pressure was 2 mtorr. A sputter-down geometry was employed with the targets mounted in water-cooled sputter guns above the substrates. A shutter shielded the substrates during startup of the guns. The substrates (secured on the sample table by mounting rings which permitted deposition over a 2.5 inch diameter circle) were rotated at a rate of 3 revolutions/second. This is a sufficient rotation rate to ensure that the samples undergo several rotations under both sputter guns per deposited monolayer preventing multilayer structures. Both stationary and swivel sputter guns were available for the 3-inch system. The swivel guns allowed a certain degree of focussing of the sputtered material so that the highest deposition rate occurs

¹The feasibility of sputtering from an alloy target was investigated; however, the high cost and difficulties in achieving stoichiometry near 25 at% Mo (compositions tended toward MoGe₂) were prohibitive.



Figure 3.1: The target and substrate configuration for the magnetron sputtering deposition system.

over a larger area of the rotating sample table. Figure 3.1^2 is a schematic of the sputtering system indicating source-substrate distances and the tilt angle of the guns. All samples analyzed were taken from a 2.5 inch swath on the substrate table centered at a radial distance of approximately 4.5 inches.

A UTI Model 100C quadrapole mass analyzer was frequently used to verify that there were not significant quantities of contaminant gasses. Water desorbing from the chamber walls was the primary contaminant present. Samples typically $5\mu m$ or thicker were produced from 8 to 10 hours of continuous sputtering. These thicknesses were necessary in order to obtain films of sufficient mechanical stability that the Si substrate could be etched away to produce free-standing films. All films grown under these conditions demonstrate a stress gradient as evidenced by the slight curvature of the free-standing films released from the substrates.

Although the chamber was not equipped with a quartz crystal rate monitor, the

²after Kortright's Ph.D. thesis p. 31 [1].

deposition rates could be determined by masking off a small area of a substrate during timed sputtering and subsequently using an Alphastep profilometer to determine thickness. By measuring deposition rates of each element individually, the appropriate parameters for the desired composition were determined. Because of interactions between plasmas during cosputtering, individually determined rates are only approximate. A rough estimate of the composition of the film was determined using the deposition rates of the pure elements and the final film thickness, but compositions had to be verified by other means (see below).

There were no provisions for heating or cooling of the sample table, and there were no means available for measuring or controlling substrate temperature during deposition. Both the table and substrates were commonly warm to the touch ($\sim 40^{\circ}$ C) at the end of a deposition run.

3.2 Substrates

Films were initially deposited on a variety of substrates including glass slides, 0.001" Kapton film (DuPont) and 3-inch (100) p-type Si wafers. Although thinner Kapton films are available, they do not have enough mechanical rigidity to allow easy handling during or after sputtering. Small pieces of glass slide also were used as substrates for electron microprobe analysis. Various substrate cleans were carried out to ensure good film adhesion since the processing conditions generally yield films in compression.

Kapton is a polyimide film well known for its excellent stability over a wide temperature range. In addition, it has a smoothly varying scattered intensity as a function of scattering vector magnitude, and it shows a peak at a scattering vector magnitude below that of the sample. As such, the substrate scattering can be subtracted with reasonable success; however, we found that the Kapton-backed samples were more useful during early data collections as a means of verifying and, if necessary, adjusting the edge energy to account for shifts due to thermal loading on the monochromator. The Kapton was cleaned in soapy water, rinsed in deionized water and dried under a dry N_2 gun prior to deposition. Glass slides were soaked in acetone followed by methanol, rinsed in deionized water and dried in dry N_2 . Samples on glass could only be studied in the reflection scattering geometry due to the thickness of the glass substrate.

The p-type (100) prime Si wafers became the substrate of choice for their compatibility with the KOH etch described below and were used as-received with good adhesion of sputter-deposited films. They were kept under dry N_2 after opening. Surface contaminants on the Si wafer that may remain on the alloy film after etching of the Si were assumed to be negligible.

3.3 Free-Standing Films

As many sources of error as possible must be eliminated in order to obtain reliable partial distribution functions. By collecting x-ray scattering data from free-standing films, we avoid the potentially significant errors introduced in subtracting substrate contributions from the total scattering. The free-standing films resulting from the procedure described below are the primary samples used in this work and doubled as the edge energy calibration samples between scans in final data collections as well.

To produce free-standing films [78], the Si wafers were etched from under the alloy films using a KOH etch which anisotropically etches Si in the $\langle 100 \rangle$ direction. An etch of 33 wt.% KOH (45%, IC grade) in deionized H₂0 was prepared and held at 80°C in a

water bath. Approximately 4 hours were necessary to etch the 15 mils (0.015 inches) of Si underlying the alloy film. The end result was large pieces of film floating in the KOH bath. These were thoroughly rinsed in deionized water to remove the KOH. The fragile pieces of film were mounted in aluminum supports for transmission x-ray studies. From prior work done on the Mo-Ge system [78, 77], it has been determined that the KOH etch does not severely attack the alloy films so that no carbon etch stop or protective capping layer was added to the Si substrate/alloy film samples. Visual inspection indicated no change upon etching; films remained smooth and reflective. Although previous work by Lane Wilson on free-standing Ge/Mo multilayer films found evidence for precipitates presumably formed by reaction of Si with the KOH etchant, no crystalline diffraction peaks or visual evidence of precipitates were found in the present work.³

3.4 Preliminary Characterization

Following deposition, visual inspection of samples was immediately carried out to ensure that the samples showed no obvious signs of crystallization (flaking), surface particulates or oxidation. Most films appeared smooth and shiny as desired. Using a profilometer, preliminary thickness measurements (from the same radial distance as the center of the substrates) identified which samples were thick enough to provide mechanical stability upon removal of the silicon substrate. In order to confirm that the appropriate sample compositions had been achieved prior to requesting valuable synchrotron beamtime, sample compositions were determined to $\sim \pm 2 \ at\%$ using electron probe microanalysis (EPMA), commonly referred to as electron microprobe.

³It is possible that the precipitates on Wilson's multilayer films were deposited in the RCA clean of the Si wafers rather than by reaction between the KOH etchant and the Si substrate as he has suggested.

For the electron energies used, the depth sampled was a few microns. Table 3.2 contains the values from these initial characterizations. Most of the analysis has been carried out on Sample 2 as discussed in Chapter 5.

Table 3.2: Preliminary measurements of composition and thickness. Composition was determined by electron microprobe and thickness, by profilometer.

sample	$at\%$ Mo $\pm 2\%$ (µprobe)	$t_{prof} \pm 10\% ~(\mu m)$
1	20.52	6.6
2	24.04	6.5
3	30.10	6.9

Chapter 4

Experimental Procedures

The anomalous x-ray scattering technique is notoriously difficult. The experimental requirements for successfully carrying out an AXS experiment to obtain differential and partial distribution functions are extremely demanding. Excellent alignment, beam stability, mechanical stability, careful design and an exact knowledge of all instrumental parameters are necessary. We sought to optimize the experimental conditions taking into account the need for reasonable count rates, energy resolution, energy stability and removal of inelastic scattering. These considerations led to the construction of a 2-circle analyzer system mounted on a standard diffractometer and employing a variable-sagittal-focus graphite analyzer and a linear position-sensitive detector. By dispersing the scattered energies onto a detector, low background and sufficient resolution in energy were obtained to isolate the elastic scattering from the inelastic scattering over most of the k-range investigated. Experimental elimination of inelastic scattering gives a significant gain in the accuracy of the distribution functions as discussed in Chapter 6. This chapter describes the experimental optics and resulting energy resolutions as well as the procedures followed.



Figure 4.1: The x-ray optics of BL 10-2. (after Figure 3.1 in Reference [80])

4.1 Synchrotron Beamline

Scattering data were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) in the rear hutch of beamline (BL) 10-2, a 30-pole wiggler beamline (1.45 Tesla, 12.85 cm device period). Its rear hutch is equipped with a 6-circle Huber diffractometer and associated electronics. The 2-circle analyzer system built for these experiments (and described in more detail below) is mounted on the 2θ arm. A data collection program, SUPER [79], controls the relevant parameters for the scattering and absorption experiments including the monochromator energy, diffractometer table motion and diffractometer angles. The data presented here were taken with nominal ring energy and current of 3 GeV and 100 mA at beamfill which occurred every 24 hours.

BL 10-2 was chosen for its high cut-off energy, large flux to the sample and large hutch size. In order to attain the maximum range of k-space, the 2θ arm of the x-ray diffractometer (at the end of which the analyzer crystal and linear detector arm are mounted on a 2-circle goniometer) must be able to swing through nearly 180°. Due to energy resolution considerations, the total length of the 2θ arm with detector is quite long requiring the large hutch size.

The photon path is shown in Figure 4.1. The broad spectrum of photons emerging from the source pass through vertical and horizontal acceptance slits to reduce beam divergence before impinging on a Pt-coated bent cylindrical mirror with a cut-off energy of 22 keV (corresponding to a reflectivity drop of 50%). The mirror focusses the x-rays horizontally and vertically and results in approximately 0.5° increase in the angle of the reflected beam relative to the plane of the storage ring electron orbit. A water-cooled, non-dispersive, double crystal monochromator is tuned to select the energies for the experiment. For the present work, Si(220) monochromator crystals were used to pass energies near the Ge and Mo edges at 11 and 20 keV. (Si(220) crystals were chosen for the improved energy resolution over Si(111) crystals. The disadvantage is the increased power loading of the first crystal due to the higher incident angle.) The second monochromator crystal was slightly detuned—rotated out of parallel alignment with the first crystal—to reject higher-order harmonic reflections with minor loss of intensity. The resulting monochromatic x-rays enter the experimental hutch.

4.2 X-ray Scattering Setup

In the experimental hutch, the focussed beam of x-rays from the wiggler passed through slits as shown in Figure 4.2 to define the beam footprint on the sample. A piece of Kapton film positioned at an angle of 45° to the incident beam reflected a tiny fraction of the x-rays into a photomultiplier tube (located at I_o in Figure 4.2) to monitor the incident intensity before the beam reached the sample mounted in the center of the Huber 6-circle diffractometer. Figure 4.3 illustrates the angular relationships between the incident beam, scattered beam and scattering vector.

Scattered intensity was collected as a function of the magnitude of the scattering vector, $|\bar{k}|$ (in general, written as k in this work). This was achieved by symmetric



Figure 4.2: The experimental optics: Focussed and defined beam strikes the transmission sample in the center of the diffractometer and is scattered onto a bent graphite analyzer crystal resulting in dispersion of scattered intensity along the position sensitive detector.



Figure 4.3: The transmission scattering geometry used in this work. The scattering vector, \bar{k} , lies in the plane of the sample.

scans using the ϕ -circle (acting as θ) and the 2θ -circle of the diffractometer. The other angles were not employed since there is no crystallographic reason to orient the amorphous sample in a particular direction with respect to the incident beam.¹ The scattered radiation was Bragg-reflected from a bent graphite analyzer crystal to disperse it along a linear position sensitive detector (PSD).

The flight path to the sample was evacuated, and the sample was mounted in a "can" filled with He to reduce air scatter. The analyzer crystal can and flight path from the analyzer to the PSD were also He-filled; however, it was not practical to mount a He-filled flight path from sample to analyzer crystal. Scatter slits were mounted in front of the PSD, and an aluminum horizontal scatter shield was placed just above the transmitted beam to absorb any air-scattered photons that might find their way to the analyzer crystal.

4.2.1 Analyzer Scattering Geometry

The analyzer geometry used in this experiment, the von Hámos geometry [81], takes advantage of the dispersive parafocussing properties of a mosaic crystal such as graphite. The mosaic spread of the graphite crystal (FWHM value of $\omega_m = 0.3^{\circ}$ for the analyzer used in this work) provides a bandpass large enough at the energies used that both elastic and inelastic scattering can be detected simultaneously. At the Mo edge, the bandpass is nominally 1100 eV; at the Ge edge, 340 eV. The ideal parafocussing geometry is illustrated in Figure 4.4 for a sample acting as a point source. Different wavelengths of radiation are dispersed by the graphite analyzer crystal according to Bragg's Law to different positions on the detector. These focal points

 $^{^{1}}$ It is not always the case, however, that anorphous samples have the same average structure in all directions as Mike Regan [3, 77] illustrated in his work on phase-separation in amorphous films. Particularly in deposited films, anisotropy can be present in the growth direction.



Figure 4.4: Dispersive parafocussing by a mosaic crystal analyzer for a point source of x-rays at the sample position. This ideal parafocussing geometry requires a 1:1 magnification where F_1 is the focal length and r_R is the radius of the Rowland circle for radiation of wavelength λ_o . Different wavelengths of radiation are dispersed to different focal points.

of the meridional focussing fall along the curve delineated by sweeping out a circle centered at the graphite analyzer with radius equal to the focal length, F_1 . The actual scattering geometry differs from the ideal geometry in that the crystal used in this work does not lie completely on the Rowland circle which results in some meridional focussing error. The crystal is instead bent to focus radiation in the sagittal plane which results in higher count rates than a flat analyzer crystal. This is illustrated in Figure 4.5.

4.2.2 Analyzer

Different wavelengths (energies) of radiation Bragg-reflect at different angles from a set of planes with a given d-spacing according to Bragg's Law,

$$n\lambda = 2d_{hkl}\sin(\theta_B)$$
 where $\lambda = \frac{hc}{E}$. (4.1)



Figure 4.5: Dispersion of scattered radiation by the graphite analyzer crystal. The upper schematic is a side view of a scattering plane. It illustrates the meridional focussing of different wavelengths of radiation to different positions on the detector. The lower schematic is a top view looking down on the experiment, and it illustrates the sagittal focussing provided by the variable crystal bend which allows the collection of a range of scattering planes. Note that there will be some meridional focussing error since the crystal is not bent to lie on the Rowland circle.

Thus, an analyzer crystal, or exit-beam monochromator, can be used to disperse scattered intensity as a function of wavelength. (See Figure 4.5.) A linear PSD placed downstream of the analyzer records the scattered intensity. Position along the PSD corresponds to the energy of the x-rays as a result of the dispersion of scattered radiation by the analyzer crystal.

Highly oriented pyrolytic graphite (HOPG) has been used in high-flux x-ray monochromators and analyzers for decades [82]. Ice and Sparks [83] described a fixed-radius bent graphite analyzer for successfully resolving inelastic background. More recently, Freund, Munkholm and Brennan [84] developed and characterized a variable-curvature bent graphite analyzer. We have used this analyzer as a dispersive exit-beam monochromator to collect anomalous scattering data.

HOPG is comprised of crystallites having relatively well-aligned c-axes (out-ofplane) and randomly oriented a-axes. In one dimension, therefore, HOPG is a nonperfect single crystal with "mosaic blocks" in a range of orientations defined by the mosaic spread in degrees. The mosaic quality of graphite allows a larger bandwidth of radiation to pass than would a perfect crystal so that greater count rates may be obtained from amorphous samples. For the analyzer and energies used, the full width at half max (FWHM) of the mosaic spread is about 0.3° , and the peak reflectivities are 45 - 55%. The lower peak reflectivity of the mosaic crystal in comparison to a single crystal is more than compensated by the increased *integrated* peak reflectivity.

The combination of a focussing analyzer and linear detector has been used successfully in the past to obtain good energy resolution and low background in diffuse x-ray scattering experiments [83, 85]. Previously, focussing analyzers have been created by hot-pressing thick sheets of HOPG into molds to a fixed radius of curvature. The bent graphite analyzer used in the present work has variable curvature allowing it to



Figure 4.6: Schematic of the bent graphite analyzer.

be bent to a minimum radius of 10 cm. This freedom gives a distinct advantage in an experiment involving data taken below different absorption edges. Since the proper radius of curvature is $R = F_1 \sin \theta_B$, the sagittal focus can readily be adjusted for different energy photons scattering from the graphite analyzer. The analyzer was constructed by cleaving a thin (200 μ m) sheet of HOPG and affixing it to a spring steel plate. Parallel grooves were machined into the top of the HOPG to allow the sheet to be bent without cracking the HOPG. The spring steel plate was mounted atop two supports. By adjusting the distance between the supports via two screws, the plate can be bent to approximate a parabolic cylinder with the desired focal length. Figure 4.6 illustrates the bending mechanism.

The bent analyzer is rotated to Bragg-reflect the elastically scattered radiation near the center of the PSD. By adjusting the bending mechanism, the focal point is set at the PSD using visible light through a pinhole at the center of the diffractometer. The graphite (002) reflection was used for data taken at both the Ge and Mo edges. (The original intention was to use the (004) reflection for the Mo edge data to collect the scattered intensity over a greater solid angle; however, in addition to the low elastic intensity passed by the graphite (004) planes, the Ge fluorescence was passed by the (002) planes resulting in a large peak in close proximity to the elastic peak.)

For experiments that are not limited by photon flux, narrower bandpass analyzers can be used. We did initially consider a simple single crystal analyzer² and a point detector, but ultimately decided against it for several reasons: First, data can be collected more efficiently from a *range* of scattering vectors in the plane of the transmission sample using a wide bandpass, bent, mosaic crystal analyzer. Second, the long arm upon which the detector is mounted (following the analyzer) may have some flexure if not very carefully designed. Any mechanical bending would mean a risk of the detector not measuring the peak of elastic scattering. In addition, any motion of the analyzer crystal itself as a function of scattering angle would lead to errors in the measured elastic intensity. Finally, a single crystal analyzer would require careful readjustment of the Bragg angle at each incident energy below even a single absorption edge. For these reasons, a wide bandpass, focussing analyzer and linear detector have proven a better choice for our experiments since the entire energy spectrum can be monitored even if it shifts slightly in position on the linear detector as the incident energy is changed by 5-100 eV or as the 2θ arm bends slightly.

4.2.3 Detector

The linear position sensitive detector (PSD) is a "jeu de jacquet" or "backgammon" style detector [86]. It consists of an anode wire along the length of the detector and a cathode plate divided into two half-cathodes electrically separated from each other by a narrow saw-tooth-shaped insulating gap. The two half-cathodes thus form a backgammon-board pattern giving the detector its name. The anode wire and

²Such a system is available on Beamline ID01 at the European Synchrotron Radiation Facility, for example.

cathode backplate are enclosed in a gas-filled chamber with a beryllium window to allow photons to pass. Figure 4.7 is a schematic of the detector. A photon entering the chamber ionizes the gas freeing electrons which accelerate toward the anode wire ionizing more gas molecules along the way. The ionization cascade at the anode causes an image charge on the half-cathodes at the position of the photoionization event. The induced charge signal in each of the half-cathodes is measured individually as Q_1 and Q_2 . For a small saw-tooth pitch relative to the induced charge distribution, the ratios of $\left(\frac{Q_1}{Q_1+Q_2}\right)$ and $\left(\frac{Q_2}{Q_1+Q_2}\right)$ are linearly proportional to the position along the anode wire axis of the centroid of the induced charge distribution.



Figure 4.7: One-dimensional backgammon design for position-sensitive detection of photons. Differences in charge signal from the two half-cathodes are used to locate the photoionization event along the anode wire.

Because the scattered intensity in our experiment is passed through the bent graphite analyzer crystal before reaching the detector, position along the length of the detector corresponds to energy. The exact correspondence depends on the path length from sample to detector, but it can easily be determined by using an incident energy above the absorption edge to compare the position of the elastically scattered and fluorescence peaks or simply scanning the incident energy and monitoring position on the PSD. In this manner, both elastic and inelastic scattering are recorded and can be separated in the spectra obtained from the PSD.

The position of the elastic peak intensity on the PSD moved by as much as 1.0 mm during an individual scan through the entire 2θ range due to mechanical bending. Because of the method of elastic peak integration described below (Section 4.4), this slight motion of the PSD did not effect the final data.

The linear PSD (Reflection Imaging, Inc.) has a 2-inch-long window, 90 μm spatial resolution at 8.1 keV and a deadtime of 5 μs . The PSD chamber is sealed with a counter gas of 90% xenon - 10% (proprietary) quenching gas at 4 atmospheres.

4.3 Incident and Detected Energy Resolutions and Energy Dispersion

Because the experimental incident and detected energy resolutions are important for later data interpretation, the various energy widths in the scattering experiments are considered here. It is shown that the incident energy resolution is considerably smaller than the detected energy resolution at the PSD due to geometric considerations in the experimental optics; however, the detected energy resolutions are sufficient for separating the elastic and inelastic resonant Raman scattering at the experimental energies.

4.3.1 Incident Energy Widths

For photons of a single energy at a given scattering angle, the magnitude of the scattering vector $|\bar{k}|$ is constant; however, the angular acceptance of the analyzer crystal defines a range of k-vector directions, \hat{k} , that are probed in the sample (see Figure 4.8). For an isotropic, amorphous sample, this range of directions does not



Figure 4.8: The acceptance of the analyzer crystal defines bounds for the range of directions that the scattering vector, \bar{k} , can take. \bar{k}_i and \bar{k}_s are the incident and scattered wave vectors.



Figure 4.9: The divergence of x-rays exiting the monochromator determines the range of incident energies of the x-rays striking the sample which, in turn, establish the range of magnitude that the scattering vector takes.

result in a loss of information due to the spherical symmetry of the atomic structure. For the sample and wavelengths probed, the assumption of isotropy is valid.

On the other hand, a spread in the incident energy of the photons leads to a variation in the *magnitudes* of the k-vectors probed (see Figure 4.9), and this gives a broadening or "smearing out" of the measured intensity versus $|\bar{k}|$ data. The spread in scattering vector magnitudes correspond to an energy width as follows:

$$dk = \frac{4\pi}{hc} \sin \theta \, dE$$
$$\frac{dk}{k} = \frac{dE}{E}$$

Therefore, since k varies with sin θ , Δk also varies with sin θ .

The maximum spread of energies arriving at the sample is equal to that passing the monochromator. The angular divergence of the radiation is first defined by acceptance slits upstream of the Pt-coated mirror. The focussing action of the mirror then causes a coupling of the horizontal and vertical divergences before the beam reaches the monochromator. The intrinsic width of a Bragg reflection from the Si(220) monochromator crystals, the Darwin width, will be significantly smaller than the vertical divergence arriving at the monochromator and, since the divergences add in quadrature, the divergence due to the Darwin width can be ignored. ($\omega_D = 12.5 \ \mu$ rad at the Mo edge and 23.3 μ rad at the Ge edge.) The energy spread of the beam incident upon the sample is calculated below.

Bragg's law can be differentiated to give an expression for energy resolution of the monochromator

$$\lambda = 2d \sin \theta$$
$$\frac{\Delta \lambda}{\lambda} = \Delta \theta_{mono} \cot \theta = -\frac{\Delta E}{E}$$

where $\Delta \theta_{mono}$ is the vertical divergence of the beam at the monochromator and θ is the Bragg angle on the monochromator crystals.

For the bent-cylindrical Pt-coated mirror, the geometry of the mirror (see Figure 4.10) introduces a divergence given by

$$\Delta \theta_{focus} \approx \frac{2\theta_{mirror} \Delta \theta_{horz}^2}{8\theta_{mirror}^2 + \Delta \theta_{horz}^2}$$

where $\Delta \theta_{horz}$ is the horizontal acceptance of the mirror and θ_{mirror} is the angle of incidence on the mirror [87]. This vertical divergence is combined in quadrature with the vertical acceptance of the mirror to yield the vertical divergence at the monochromator:

$$\Delta \theta_{mono}^2 = \Delta \theta_{vert}^2 + \Delta \theta_{focus}^2$$

The vertical and horizontal acceptances are set by slits upstream of the mirror. For our experiment, $\Delta \theta_{mono} = 245 \ \mu \text{rad.}^3$

The resultant energy widths for the Mo and Ge edges are

. .

$$\Delta E_{inc}^{Mo} = 30.8 \text{ eV}$$
 and $\Delta E_{inc}^{Ge} = 8.9 \text{ eV}.$



Figure 4.10: The x-ray optics determining the vertical divergence at the BL 10-2 monochromator.

4.3.2 Factors Affecting Width of Detected Peaks

Due to the scattering geometries utilized in this experiment, there are a number of factors affecting the width of the elastic and inelastic peaks eventually measured at the linear detector. In general for independent sources of uncertainty with Gaussian distributions, the total uncertainty is the square root of the independent errors summed

³Unfortunately, there is no simple means of determining $\Delta \theta_{mono}$ from the nominal mirror slit settings on BL 10-2, so the experimental absorption edge width of Mo was compared to a measurement not limited by energy resolution (courtesy of Dr. Graham George, SSRL). The incident energy width was deconvolved to calculate $\Delta \theta_{mono}$.

in quadrature. Assuming such uncertainties, we can write the energy resolution as

$$\Delta E = \left(\sum_{i} \Delta E_{i}^{2}\right)^{\frac{1}{2}}$$

where ΔE_i represents the uncertainty from a single source. Each of the relevant contributions is discussed below frequently following the more thorough analyses of Ice and Sparks [83].

Energy width of incident radiation

The energy widths of the incident radiation for the Mo and Ge edges are given in the previous section.

Intrinsic width from analyzer crystal

Variation in *d*-spacing of the graphite (002) planes gives rise to an intrinsic energy resolution [84] of $\frac{\Delta E}{E} = 1.94 \times 10^{-4}$ due to the range of *k*-vector magnitudes which satisfy the Bragg condition for a single incident energy. For the edges of interest, this yields

$$\Delta E_{intr}^{Mo} = 3.88 \text{ eV}$$
 and $\Delta E_{intr}^{Ge} = 2.15 \text{ eV}$.

Error due to extended source size

The graphite crystal sees scattering from the portion of the sample illuminated by x-rays. In order to obtain reasonable count rates necessary to carry out anomalous scattering experiments in the lifetime of a graduate student, the rectangular slits upstream of the sample defined a beam size of 1.0 mm horizontal x 1.0 mm vertical. These slits establish the effective source size seen by the graphite analyzer. In the

parafocussing geometry, the effective source is imaged so that each point on the image is a focal point. As long as the convergence angle, $\beta =$ (source height / focal length), is less than the mosaic width, the entire source can be imaged in a single energy of radiation, and no geometric correction for partial imaging is needed. (In this particular case, $\beta = 0.066^{\circ}$ which is much less than the FWHM mosaic width, $\omega_m = 0.3^{\circ}$.) The image of the beam on the sample elongates as the scattering angle θ_B increases. This, in turn, results in a range of foci falling in a plane (for a planar sample) which may not be coincident—or, in general, even parallel—with the wire of the linear detector depending on whether the focus is in front of or behind the detector and depending on the size of the beam on the sample. The intersection of the detector wire with the first-converging, then-diverging rays which form the image gives a spatial distribution of radiation on the detector – a broadening of the peak for a single incident energy. This is illustrated in Figure 4.11. For a detector placed perpendicular to the second focal distance and at a distance from the graphite analyzer, $F_2 = F_1$, the focal length for parafocussing, this broadening is given by

$$D = \frac{\Delta y}{\cos \theta} \frac{\Delta \theta_a}{2}$$

where $\Delta \theta_a$, the vertical angular range accepted by the analyzer, is given by

$$\frac{\Delta\theta_a}{2} = \sin^{-1}\left(\frac{l_{gr}}{2}\frac{\sin \theta_{gr}}{\sqrt{F_1^2 + \left(\frac{l_{gr}}{2}\right)^2 - l_{gr}F_1\cos\theta_{gr}}}\right),$$

where Δy is the vertical slit height, θ is half of the scattering angle in the sample, l_{gr} is the length of the graphite crystal, F_1 is the focal length for parafocussing and θ_{gr} is the Bragg angle for the graphite (002) reflection in the analyzer crystal. For



Figure 4.11: An (exaggerated) extended source is imaged by parafocussing. Because the graphite analyzer is actually a flat crystal, there are additional focussing errors for a single energy from positions off the Rowland circle.

the transmission scattering geometry, the largest source size occurs at high scattering angles.

The peak broadening is $D^{Mo} = 0.0055$ mm and $D^{Ge} = 0.0099$ mm at the maximum scattering angle. These values correspond to negligible maximum energy broadening of $\Delta E_{source}^{Mo} = 0.76$ eV and $\Delta E_{source}^{Ge} = 0.42$ eV (using experimentally measured dispersion values).

Additional sources of error

Other errors that affect energy resolution of the graphite crystal analyzer are focussing errors, penetration of the x-rays into the crystal, surface roughness of the crystal and some mixing of sagittal and meridional focussing due to the bent-cylinder geometry (in the same manner as that resulting from the bent Pt-coated mirror upstream of the sample). For a detector anode wire at the focal point for parafocussing, additional errors due to parallax should be considered [83]. Finally, the linear resolution of the detector must be taken into account (in this case, 90 μm). In fact, all of the energy widths due to the sources of error described above in this section are significantly smaller than the effect (described below) of placing the linear detector in front of the meridional focus.

4.3.3 Effect of Defocussing on Detected Energy Resolution

Ideally, one chooses a long focal length, F_1 , for good separation of energies on the detector and places the detector at the focal point for the incident (and elastically scattered) energy. For the present experiments, the experimental hutch size for BL 10-2 limited the range of motion for a long $F_1 = F_2$, and a compromise was made: F_1 was chosen for reasonable dispersion, and $F_2 < F_1$ was chosen to retain maximum angular range of the 2θ arm of the Huber diffractometer (necessary to obtain the full range of k-space available for any given energy). Since $F_2 < F_1$, the detector was located at a defocussed position, and the parafocussing geometry led to a finite spot size for a detector placed off the focal plane. The resulting geometry is shown in Figure 4.12. Shown schematically are the combined effects of defocussing and extended source size (greatly exaggerated for purposes of illustration).

Theoretical dispersion and defocussing

The dispersion at the focus for parafocussing geometry is given by

$$N = \frac{\Delta E}{F_1 \Delta (2\theta_{gr})} = \frac{E \cot \theta_{gr}}{2 F_1}$$

where E is the incident energy, θ_{gr} is the Bragg angle on the analyzer crystal, F_1 is the meridional focal length and $\Delta(2\theta_{gr})$ is the angular dispersion of the energy by the analyzer. Accounting for geometry, $N^{detector} = N^{focus} (F_1/F_2)$. For $F_1 = 85.1$ cm



Figure 4.12: The effects of positioning the linear detector at a defocussed position and extended source size. The solid lines on the detector indicate schematically the width of the peak resulting from scattering of two wavelengths of x-rays.

and $F_2 = 68.6$ cm, the theoretical dispersions are

$$N_{theor}^{Mo} = 157.2 \text{ eV/mm}$$
 and $N_{theor}^{Ge} = 48.0 \text{ eV/mm}.$

Since the detector was not at the focus, the defocussed spot diameter must be found geometrically using the mosaic width to define the convergence cone:

$$s = 2(F_1 - F_2) \tan \frac{\omega_m}{2}$$

which gives s = 0.86 mm corresponding to

$$\Delta E_{theor}^{Mo} = 120 \text{ eV} \text{ and } \Delta E_{theor}^{Ge} = 37 \text{ eV}.$$

Measured peak width and dispersion with defocussing

The nominal experimental dispersion was measured from PSD spectra at energies above the K-shell absorption edge (or near enough to the edge to excite resonant Raman inelastic scattering). Note that since the curve of foci for different wavelengths is approximated by a line (the detector wire), the true dispersion varies slightly over the wire. At the Mo and Ge edges, the following dispersion values were measured:

$$N_{expm}^{Mo} = 151.9 \text{ eV/mm}$$
 and $N_{expm}^{Ge} = 42.6 \text{ eV/mm}$

These agreed well with those calculated above.

FWHM values of the elastically scattered peak were

$$\Delta E_{expm}^{Mo} = 130 \text{ eV}$$
 and $\Delta E_{expm}^{Ge} = 42 \text{ eV}$

The measured values agreed fairly well with those calculated above indicating that although the sagittal focus was at the detector, the defocussing in the meridional direction dominated the physical spread for a given energy.

The peak widths and dispersions attained were sufficient for separating the elastic scattering and inelastic resonant Raman scattering in this experiment although simultaneous fits were needed at energies near the absorption edges due to slight peak overlap. These procedures are discussed in Chapter 5.

4.4 Scattering Data Collection

Scattering data from the sample nearest the MoGe₃ composition (Sample 2 at 26.8% Mo) were collected over the following k-ranges: $k = 1 - 10 \text{ Å}^{-1}$ at energies below the

Ge edge and $k = 1.6 - 18 \text{ Å}^{-1}$ at energies below the Mo edge. The lower and upper k values were set by the minimum and maximum attainable 2θ angles. These angles were limited by the presence of components (evacuated flight path, photomultiplier tube, slits and beamstop) up- and down-stream of the sample.

Because amorphous samples are weak scatterers even in the high intensity of synchrotron radiation, k-space scans require long counting times. This experimental setup has additional losses of signal due to the analyzer crystal and the limited efficiency of the linear detector at the Mo edge energies. In order to reduce the effects of beam motion, beam fills and monochromator heating while still obtaining sufficient counts for good statistics, several scans were taken over the same k-space range for a given energy. Near the Mo edge at 20 keV, the incident count rate on the sample was particularly low because the wiggler critical energy is near 9 keV. (BL 10-2 has a mirror cut-off energy of 22 keV.) There are simply less photons available at these higher energies and this fact, coupled with the poor detector efficiency near 20 keV, led to much longer data collection times near the Mo edge than near the Ge edge.

The limited lifetime of the electrons orbitting in the ring requires that data be taken in *constant signal mode*. Often, synchrotron data are acquired in constant time mode or constant dose mode by fixing the count time or monitor counts for each point in k space; however, by instead fixing the total detected counts at each k value (constant signal mode), the counting statistics are uniform over the entire k-range explored, and the effects of decaying current in the storage ring (and thus decaying incident counts per second) are eliminated.⁴ Intensity data were analyzed in units of [detected counts / monitor counts] vs. k. Even for the highest signal

⁴A further improvement suggested for future studies is the use of a single channel analyzer set to exclude most of the K_{β} resonant Raman scattering for energies near the absorption edge. Thus, the detected *elastically-scattered* counts are uniform over the *k*-range explored.

count rates, there were sufficient monitor counts so that statistical fluctuation in the monitor counts was negligible. Obtaining sufficient signal-to-noise at each energy is a concern since the final "signal" to be analyzed in AXS is often a difference between two similarly-valued I versus k scans.

Beamfills, to refill the decaying current in the synchrotron storage ring, occurred once a day for the data presented here. They present a problem since the thermal loading on the monochromator (upstream of the experimental hutch) varies during a fill and the precise beam position on the monochromator can change between fills. Thus, a scan interrupted by a beamfill must usually be discarded.

Thermal distortion of the monochromator, due to the large flux density of photons impinging on the first crystal, was another experimental problem encountered. This can lead to gradual small changes in the incident energy as a function of time and beam fill. To compensate, the position of the absorption edge nearest the incident energy at which data was to be acquired was checked between every scan of intensity versus k (symmetric $\theta - 2\theta$ scans). Since the edge positions in energy are constant for a given sample, any shift of the edge energy indicated a shift in the incident energy which was then adjusted. These incident energy checks were carried out in a procedure similar to the more careful absorption measurements described below. The monochromator energy was rapidly scanned through the edge energy (11.103 keV for the Ge edge and 20.000 keV for the Mo edge) while recording the transmitted intensity. A routine written into SUPER takes the second derivative of the intensity vs. energy data to determine the nominal edge energy from the zero-crossing.⁵ A single command allows the user to move the monochromator to that energy; subsequent commands move the energy a fixed number of electron volts below or above the nominal edge

⁵The algorithms for determining derivatives are given by Savitzky and Golay [88]. Corrections have been published by J. Steiner et al. [89] and by H.H. Madden [90].

energy.

Linearly interpolating to obtain the zero-crossing of the second derivative rather than simply looking at the maximum of the first derivative ensures that the energy increments of the edge determination algorithm are significantly smaller than the limiting energy step, dE, of the monochromator stepper motor. The limiting dE of the monochromator at, for example, the Ge edge energy of 11103 eV can be calculated from the steps/degree for the monochromator motor, 8000 steps/degree on BL 10-2. For Si (220) monochromator crystals, $d_{Si(220)} = 1.92011$ Å giving $\theta_B = 16.9048806^{\circ}$. One monochromator step corresponds to $d\theta = 1^{\circ}/8000$, and the resulting dE is 0.080 eV. At the Mo edge, dE is significantly larger at 0.95 eV. This step size is a good reason not to work at energies too near the absorption edge.

Finally, for removal of systematic error via differences below the absorption edges in the sample, all data must be taken during the same beamtime for identical experimental conditions. A large and contiguous amount of experimental time at SSRL was thus necessary to collect the data.

4.5 X-ray Absorption Data Collection

The x-ray absorption as a function of incident energy provides information vital to this work: the anomalous scattering factors. To collect these data, the same sample used for scattering data was simply rotated to $\theta = 0^{\circ}$ so that the x-rays hit the sample at normal incidence. The χ -circle of the diffractometer was positioned so that the plane of the circle was parallel to the incident beam—out of the paths of the incident, transmitted and, for scattering experiments, elastically scattered beams. SSRL-standard 6-inch ion chambers filled with nitrogen were mounted on either side



Figure 4.13: Schematic of the equipment for absorption data collection.

of the χ -circle to monitor the incident and transmitted intensities as the x-rays passed through the sample. See Figure 4.13. Scans of incident energy were taken through both the Ge and Mo K absorption edges of all samples. The absorption is normally plotted as incident energy, E, versus $\ln(\frac{I_o}{I})$ where I_o and I are the intensities before and after the sample.

As discussed in Chapter 2, the same sample must be used in absorption measurements to obtains ASFs as was used in the scattering measurements (rather than theoretical ASFs or measured ASFs from another sample) because of chemical shifts in the edge energy and shape of the absorption spectrum. In addition, we have found that it is vital that these data be collected during the same experimental run as the scattering data. In that way, the measured f'' as a function of energy are representative of the experimental incident energy resolution, and the ASF values inserted



Figure 4.14: Schematic of f' for two different incident energy resolutions. (Values given are σ).

in the matrix equation to solve for the PSFs are properly weighted over the distribution of incident energies. Consider, for example, x-ray absorption scans collected with $\sigma = 3.8$ eV versus $\sigma = 9$ eV where σ is the Gaussian standard deviation of the incident energy width. The resulting f' curves are shown schematically in Figure 4.14. First, the K edge energy determined by the inflection point is 2 eV lower in the lower resolution measurement. Second, measurements taken at the same energy on the absolute scale give different f' values: At 11098 eV, the higher resolution measurement gives f' = -8.49 electrons while the lower resolution measurement gives f' = -8.22 electrons. Therefore, it is very important that the same incident energy resolution be used for collection of both the scattering and x-ray absorption data.

Chapter 5

Data Analysis

Scattered intensity versus scattering vector magnitude, the raw data from an amorphous material, do not immediately reveal physically meaningful information about the system. In order to extract real-space results in the form of distribution functions, a significant amount of data analysis must be carried out. The data analysis procedures are particularly important to the partial (and differential) distribution functions in which two large-valued functions are subtracted to obtain a small difference containing the desired structural information.

The data analysis steps are crucial to obtaining quality distribution functions since it is here that the data are corrected and normalized. A brief roadmap of the steps taken in moving from raw data to a real-space distribution function follows:

- Determine sample constants (composition, thickness, anomalous scattering factors and μt absorption coefficients).
- Extract the elastic scattering from raw data.

- Correct for experimental effects (detector non-linearity, absorption, polarization, multiple scattering and substrate scattering, if necessary).
- Normalize the corrected, elastic scattering to an absolute scale to calculate structure factors.
- Fourier transform structure factors to obtain real-space distribution functions.

This chapter describes each of these steps, the impact of experimental limitations on the final data and the damping function applied in the Fourier transform to real space. Finally, a description is given of the computer code used to carry out these critical steps.

5.1 Sample Constants

There are several quantities intrinsic to the samples probed which must be determined and entered into the analysis. These include the exact sample composition and thickness as well as the absorption coefficients (μ) and anomalous scattering factors or ASFs (f', f'') at each energy probed. These quantities can be obtained by fitting absorption data with calculated atomic absorption curves and assuming an average sample density. Each sample constant is discussed in more detail below.

5.1.1 Composition

Preliminary measurements of sample composition by electron probe microanalysis are described in Chapter 3. The edge jump method of determining sample composition in transmission synchrotron x-ray experiments (Wilson [78]) samples the entire film thickness and is, therefore, a better technique for composition determination. Using the edge jump method, the x-ray absorption through an absorption edge is measured via ion chambers recording the intensities before and after the sample as incident photon energy is scanned. The transmitted intensity I can be written as a function of the incident intensity I_o , the linear absorption coefficient μ and the sample thickness t through which the x-rays have passed:

$$I = I_o \, \exp(-\mu t) \tag{5.1}$$

More explicitly, we can sum over each element in the sample and add a detector function, C(E), to describe the effect of slight variations in detector response between the two ion chambers:

$$I = I_o \ C(E) \ \exp\left(-\sum_{\alpha} \sigma_{\alpha} m_{\alpha}(\rho t)_{\alpha}\right)$$
(5.2)

where σ_{α} is the absorption cross-section $\left[\frac{cm^2}{g}\right]$, $(\rho t)_{\alpha}$ is the areal number density $\left[\frac{1}{cm^2}\right]$ or the number of α atoms in a unit area of sample, and m_{α} is the atomic mass of atom α . Rewriting the expression yields

$$\ln\left(\frac{I_o}{I}\right) = \sum_{\alpha} \sigma_{\alpha} m_{\alpha}(\rho t)_{\alpha} + C'(E).$$
(5.3)

The detector function, C(E) is a slowly varying function of x-ray energy, so $C'(E) = \ln(C(E))$ is an even more slowly varying function of energy.

Each sharp jump in the absorption as a function of energy is due only to the absorption cross-section σ of the element corresponding to the edge in question since the other σ_{α} are smoothly varying with energy. Thus, the detector function and absorption from other edges can be combined in a background function, B(E), and
the measured intensities near an edge can be written as

$$\ln\left(\frac{I_o}{I}\right) = \sigma_\alpha m_\alpha(\rho t)_\alpha + B(E) \tag{5.4}$$

where the background function is fit well by the functional form

$$B(E) = \sum_{n=0}^{3} C_n E^{-n}.$$
(5.5)

From the areal densities of each atom, $\rho_{\alpha}t$, the overall sample composition is given by

$$\mathbf{x}_{Mo} = \frac{\rho_{Mo}t}{\rho_{Mo}t + \rho_{Ge}t} \tag{5.6}$$

(±1% based on application of the method to molecular liquids). constants for each sample and each edge, the absorption edge data were fit simultaneously in the regions outside the edge region (100 eV below to 500 eV above the Ge edge and 200 eV below to 500 eV above the Mo edge). The slowly varying background B(E) was fit and removed, and the absorption data were normalized to theoretical values for the free atom absorption cross-section from the Cromer-Liberman calculations [46, 47, 48]. Fitting far above and below the edge ensured that the sample-specific EXAFS and near edge structure-induced variations in absorption were not included in the fit. To remove B(E) and to normalize the experimental data to the Cromer-Liberman values far from the edge, the program **fppfit.m** was used (Matlab version, Hope Ishii; original FORTRAN version FPPFIT.FOR, Karl Ludwig with modifications by Lane Wilson). Section 1 of Appendix A describes the algorithms involved. **fppfit.m** was modified to also read in Kissel's values [35] (with bound-bound transitions removed

and absorption edge energies shifted to experimental values) for fitting far from the edge. The Cromer-Liberman values provide a better fit to the experimental data taken at the Ge edge, and the Kissel and Cromer-Liberman values give similar quality fits at the Mo edge. Thus, the tried-and-true Cromer-Liberman values were used for all calculations.

Table 5.1 contains the sample compositions determined by preliminary electron microprobe measurements as well as by the edge jump method. The discrepancies between composition values from the two methods may arise from several sources. Although the nominal error in composition from electron microprobe is about 2%, the accuracy is worse because the software program used for analysis calculates the density of the sample based on a weighted average of the *crystalline* elemental densities. As a result, the presumed Mo density is too high, and we expect Mo composition values from this technique to be too low. Indeed, they are lower than the values obtained by the absorption edge jump method. In addition, electron microprobe samples only the top micron or so of a 6-7 μm thick film, whereas the x-ray edge method samples the entire film.

Table 5.1: Initial and final measurements of composition and thickness. Compositions were determined by electron microprobe and x-ray edge jump measurements and thicknesses, by profilometer and by edge jump.

sample	$at\%$ Mo $\pm 2\%$	$at\%$ Mo $\pm 1\%$	$t_{prof} \pm 0.5 \; (\mu m)$	$t_{edge} (\mu m)$
	(μprobe)	(edge)		-
1	20.52	22.59	6.6	5.11
2	24.04	26.87	6.5	6.62
3	30.10	33.11	6.9	8.42

Since the edge jump values are consistantly higher than the microprobe values, the question of uniformity of the film composition profile arises. Due to the changing shape profiles of the targets as they are sputtered away, the relative amounts of the two elements may change slightly during sputter deposition. All targets were presputtered to remove any surface contamination and to initiate sputtering grooves. More important than target shape profile, the target thins as sputtering progresses which would tend to increase the magnetic field and, thus, the flux of Ar^+ ions on the target. The sputtering power, however, was held constant, and neither of these considerations were expected to have a significant effect on the sample composition. Microprobe results indicates that oxygen did not account for more than 1 at.% of the overall composition.

In fact, an advantage of using wide-angle x-ray scattering is that even with a sample of overall composition slightly off that of the MoGe₃ phase endpoint (and assuming the MoGe₃ composition is a homogeneous phase as prior work indicates), the scattering signal from the potential second phase (*a*-Ge) is negligible. Sample 2 at ~ 27 at% Mo is nearest to the 25 at% Mo of the MoGe₃ phase. Due to slow x-ray scattering data collection rates for amorphous samples, particularly at the Mo edge, Sample 2 alone is used for all of the analysis in the chapters that follow.

5.1.2 Thickness

Once the areal densities were determined by the edge jump method described above, the thicknesses could be calculated by assuming an average density for the film:

$$t = \frac{\rho_{Mo}t + \rho_{Ge}t}{\rho_{ave}} \tag{5.7}$$

The average amorphous sample density was assumed to be 95% of the weighted average of the number densities for crystalline Ge and α -MoGe₂ [91]. The assumption

that the amorphous density is 95% of the linear combination of the crystalline densities is widely used and has proven to be reasonable. The resulting distribution functions in Chapter 6 show physically reasonable behavior. At distances less than the first nearest neighbor distance, the neighboring atoms repel each other, and the distribution functions should be, and are, essentially zero. An average density too high or too low would yield a positive or negative slope in the low-r region below the first nearest neighbor peak. The average density can be obtained via a fit to the low-r region of the reduced distribution functions, $4\pi r[\rho(r) - \rho_o]$, following all data analysis. This method was used to validate the densities initially chosen. Table 5.1 contains the thicknesses of the films determined by profilometer and by edge jump measurements. The thicknesses measured by these two methods differ, sometimes significantly, because the preliminary profilometer measurement was carried out on a test piece positioned at a specific radial position on the sample table corresponding to the center of the silicon substrate while the actual sample on which all x-ray measurements were made may have been as much as 1.25 inches from that radial position. Deposition rates varied by 18% radially over one inch near the center of the substrates. Thicknesses from edge jump measurements (estimated accurate to within a few percent) were used in the data analysis.

5.1.3 Anomalous Scattering Factors

As discussed in Chapter 2, at energies near the absorption edge of an atom in the sample, the free atom scattering factor, f_o , must be modified to include real and imaginary correction terms, the anomalous scattering factors (ASFs). By fitting the edge jumps to Cromer-Liberman theoretical values far above and below the α atom's K absorption edge energy and extracting the areal densities, we obtained the absorption

Table 5.2: Experimental anomalous scattering factors (ASFs) for the energies probed obtained by scaling the absorption data to theoretical values far from the edge and applying a Kramers-Krönig transform. ASFs are given in electron units.

Energy	Ge f'	Ge f''	Mo f'	Mo f''
11.003 keV	-4.3212	0.5096	-0.4749	1.5807
$11.088~{\rm keV}$	-6.5367	0.5678	-0.4875	1.5592
$11.098~{\rm keV}$	-8.0797	0.8526	-0.4890	1.5567
$19.900~{\rm keV}$	0.2739	1.4411	-4.6910	0.5523
$19.995~{\rm keV}$	0.2764	1.4291	-7.5026	1.6963

cross-section, σ_{α} , in the region of the absorption edge. The absorption cross-section is related to the imaginary ASF, f'', by the optical theorem (See Equation 2.28.) A Kramers-Krönig transform of f'' yields the real ASF, f', and the full atomic scattering factor is then

$$f = f_o + f' + if''$$

as described in Chapter 2, Section 2.1.3. The ASF values used in this work are given in Table 5.2. The Kramers-Krönig transform was carried out using a second program, **kramkron.m** (Matlab version, Sean Brennan; original FORTRAN program FPCL.FOR, Karl Ludwig [30]). This program evaluates the integral via the method described by Hoyt and coworkers [41]. Section 2 of Appendix A describes the algorithm for implementing the transform. Using this technique, uncertainties in absolute f' values due to extrapolation on the energy axis are of the order of 0.2 electrons.

5.1.4 Absorption Coefficient

The μt product is necessary to correct for the effects of absorption of incident and scattered x-rays in the sample. A simple method for determining the μt constant is

Table 5.3: Sample 2 μt constants obtained by θ -scans compared with those obtained by back-calculating μ from the edge jump and assuming theoretical amorphous densities. c_{abs} is the multiplicative absorption correction.

Sample 2	11.000 keV	$19.900~{\rm keV}$	$19.985~{\rm keV}$
$(\mu t)_{exp} \ [cm^{-1}]$	0.1887	0.1557	0.1634
$(\mu t)_{calc} \ [cm^{-1}]$	0.1874	0.1562	0.1654
difference in c_{abs} at k_{max}	0.16%	0.08%	0.23%

to place the transmission sample in the x-ray beam and rock the sample in the beam so that the beam pathlength varies as the angle is changed. The directly-transmitted intensity is related to the incident intensity and the angle θ between the incident beam vector and the surface normal by

$$I = I_o \exp^{-\left(\frac{\mu}{\cos\theta}\right)}.$$
(5.8)

Thus, a plot of $\ln(\frac{I}{I_o})$ versus $\frac{1}{\cos \theta}$ can be fit with a line of slope $-\mu t$. Fitting in this manner removes the effects of differences in detector response and absorption by the ambient gasses. θ -scans were carried out on the sample at a few representative energies.

The linear absorption coefficient μ can also be determined from the imaginary part of the scattering factor, f''. μ is related to f'' through the optical theorem:

$$\mu = \sum_{\alpha} \frac{2 \ \rho_{\alpha} e^2 hc}{m_e c} \frac{f_{\alpha}''}{E} \ [cm^{-1}]$$
(5.9)

Thus, from the f'' values (obtained from the full EXAFS measurements at each energy of interest and the theoretical amorphous densities), the absorption coefficient can be calculated. Absorption corrections using μt constants determined by this method differ from those using μt constants extracted from θ scans by less than 0.5% at the highest attainable k (where error would be greatest) and result in at most 0.1% error in the intensity at high k. Table 5.3 contains the μt values from both methods at select energies. Note that the correction is applied by multiplying it with the intensity at each k value. As the correction is largest at high k where the intensity is smallest, the potential overall effect is small. Since θ -scans were not carried out at every energy of interest, the absorption coefficients used in the analysis are those obtained from the f'' values assuming theoretical amorphous atomic densities.

5.2 Extraction of Elastic Scattering

With the appropriate sample constants in hand, the elastic portion of the x-ray scattering can be extracted. The experimental removal of inelastic scattering, made possible by the diffracted-beam graphite analyzer and position sensitive detector (PSD), has proven to be a tremendous improvement to the AXS technique. As discussed in Chapter 2, there are two sources of inelastic scattering which must be excluded: Compton and resonant Raman scattering.

The Compton scattering has a low, broad distribution in energy, and the total intensity integrated over all energies increases with scattering angle. Section 2.2.2 discusses this process in more detail. In a typical AXS experiment, the Compton scattering is calculated using parameterized values appropriately weighted for the sample composition, corrected for absorption and subtracted from the total experimentallymeasured scattering. Detector sensitivity to different energies of Compton scattered photons is usually assumed to be a constant. Errors resulting from this method can impact the normalization, described later, of the RDFs and DDFs. The highly sensitive PPDFs are expected to be strongly effected by such errors.

Resonant Raman scattering appears in the spectra as well-defined peaks at constant energy differences ΔE below the incident energy. As the incident energy approaches the edge energy for an element in the sample, the resonant Raman scattering evolves into the characteristic x-ray fluorescence for that element. In a typical AXS experiment with very limited energy resolution, the K_{\beta} resonant Raman and elastic scattering intensities are both collected together as a single integrated intensity, and the K_{\alpha} resonant Raman scattering is recorded separately. The ratio of K_{\alpha} to K_{\beta} fluorescence is then applied to calculate the expected K_{\beta} resonant Raman contribution which is subtracted from the measured intensity. See Section 2.2.1 for a discussion of the resonant Raman scattering process.

By recording an energy spectrum (corresponding to position on the linear detector wire) of sufficient energy resolution at each k-value, both Compton and resonant Raman scattering have been excluded down to $k \approx 3 \text{ Å}^{-1}$ for energies near the Ge K edge and $k \approx 5 \text{ Å}^{-1}$ near the Mo K edge. The raw intensity versus position data were imported into Matlab, and the resonant Raman and elastic peaks were simultaneously fit by Gaussians to select the boundaries for a 3.5σ peakwidth within which the *experimental* data were integrated. It was determined that the resonant Raman scattering does not contribute to the signal in this peakwidth. Since the peak in Compton scattering shifts away from the elastic peak position in energy (see Figure 2.5), the significant Compton contributions at high k were sufficiently far away from the elastic peak that they were completely excluded. At k values for which the Compton shift was less than the elastic peak width on the PSD, the Compton intensity was small enough that we neglect it. (Even in data taken at energies just *above* the absorption edge of the element of interest, the fluorescent and elastic peaks



Figure 5.1: Signal versus position on the PSD (corresponding to energy of the scattered radiation) for three incident energies below the Ge K absorption edge at $k = 8.5 \text{ Å}^{-1}$. As the incident energy approaches the edge energy, the resonant Raman peaks increase in intensity. Data are from Sample 2.

can be distinguished; however, the detector response is strongly non-linear for such high count rates. In addition, the sample would be absorbing more than it would be scattering so that elastic count rates would be very low.) In this way, we exclude most of the inelastic contributions from Compton and resonant Raman processes without relying upon calculated values.

Examples of signal vs. position spectra from the PSD are shown in Figure 5.1. The K_{α} and K_{β} resonant Raman peaks are clearly visible at 5 and 15 eV below the Ge K absorption edge. The low, broad Compton distribution is difficult to distinguish. Note that the detector function, the transmission and detection efficiency of scattered intensity by the analyzer crystal and PSD, is not a constant as a function of energy. It is a strongly peaked function of the energy of the scattered x-rays with the peak position determined by the scattering angle of the analyzer crystal. As a result, inelastic x-ray intensity is strongly and increasingly damped as the energy decreases below the incident x-ray energy. This is evident in the $K_{\beta}:K_{\alpha}$ ratio in Figure 5.1 which is much larger than the 0.15 value expected.

5.3 Corrections

In general, the elastic scattering must be corrected for several experimental effects:

- detector non-linearity
- substrate scattering, when relevant
- absorption
- polarization
- multiple scattering



Figure 5.2: Comparison of data before (dashed line) and after (solid line) corrections have been applied for Sample 2 (27 at% Mo).

These corrections are discussed separately below. The combined effect of corrections is illustrated in Figure 5.2 for elastic scattering [detected counts / monitor counts] from Sample 2 (27 at% Mo) collected below the Ge K absorption edge.

5.3.1 Detector Non-Linearity

When the measured count rate is not proportional to the incident count rate, the detector response is non-linear, and the detector is said to have a *deadtime*. This rate limitation is largely due to the shaping time of the amplifier: A photon arriving in the detector sends a pulse into the shaping amplifier. For a period of time τ , the deadtime, any additional pulses arriving may be corrupted or lost in a phenomenon called *pileup*. As a result, the detector behaves non-linearly at high count rates. Using an incident count rate monitor that provides an accurate measurement of incident photon rate (without energy resolution), data can be corrected for counts lost due to pileup.

data are fit to the form

$$I_{meas} = I_{true} \exp(-\tau I_{true}) \tag{5.10}$$

where I_{meas} is the measured scattered intensity (in counts per second, cps), I_{true} is the true intensity and τ is the detector deadtime. The correction function $\frac{I_{true}}{I_{meas}}(k)$ is thus determined iteratively. For the present data, the linear position-sensitive detector deadtime was $\tau = 5 \,\mu s$. Figure 5.3 illustrates the detector nonlinearity for a $5 \,\mu s$ deadtime.



Figure 5.3: Nonlinearity of the linear position-sensitive detector used in the present experiments. The deadtime is $\tau = 5 \,\mu s$.

5.3.2 Substrate Scattering

For the samples initially studied on Si substrates in reflection scattering geometry, a substrate correction was necessary. The high energy synchrotron x-rays were not absorbed and diffracted completely by the film, and scattering from the underlying substrate also contributed to the final detected signal. To determine the contribution from the substrate, scattering from a bare substrate can be measured and adjusted for the absorption of the incident intensity travelling through the film. This correction relies on accurate knowledge of the absorption of the film and can be the source of significant error. For the data presented here, the substrate was etched from beneath the films, and the free-standing films were measured in symmetric transmission geometry. As a result, no substrate correction was necessary for these data.

5.3.3 Absorption

Because incident and elastically scattered photons must travel through the sample before detection, a sample absorption correction must be applied. (If He-filled beam flightpaths are not used, the air absorption should also be accounted for.) Depending on the Bragg angle sampled, the path length travelled by the photon and the scattering volume in the sample vary. For symmetric transmission geometry, the measured intensity is modulated by a factor

$$A = t \ \frac{e^{\frac{-\mu t}{\cos\theta}}}{\cos\theta}$$

where t is the sample thickness, μ is the linear absorption coefficient and θ is the scattering angle. The correction function applied to the measured data is proportional to the inverse of this factor:

$$c_{abs} \propto \frac{\cos \theta}{t \ e^{\frac{-\mu t}{\cos \theta}}} \tag{5.11}$$

The absorption correction is a slowly varying function of k and strongly dependent on the μt constant for the sample. It is also the largest magnitude correction factor for these data, so obtaining accurate μt constants is well worth the investment of time and effort. Figure 5.4 contains the correction factor normalized to 1 at $k = 0 \text{ Å}^{-1}$ for several μt constants. Note that for the transmission scattering geometry used here, the largest x-ray pathlength (biggest magnitude correction) occurs at high k.



Figure 5.4: Normalized absorption correction factor for the Samples 1, 2 and 3 at 11 keV. (Only results from Sample 2 are presented in the following chapters.)

5.3.4 Polarization

The acceleration of electrons in a storage ring in the plane of orbit results in synchrotron x-rays with nearly-linear polarization. In fact, the polarization is elliptical with a very small vertical component (approximately 4% at SSRL after monochromatization at 11 keV $[92]^1$). This elliptical polarization leads to a correction term of

$$c_{pol} = \frac{1}{(1-v) + v \, \cos^2(2\theta) \, \cos^2(2\beta)} \tag{5.12}$$

where v = 0.04 is the fraction of vertical polarization present in the incident beam, θ is the scattering angle in the sample and β is the Bragg scattering angle for the incident energy photons on the exit beam graphite analyzer crystal. (Each additional scattering event in the vertical plane leads to a reduction in the vertical component by a cosine-squared term.) Figure 5.5 illustrates the behavior and magnitudes of the polarization corrections for incident energies of 11.0 and 19.9 keV.



Figure 5.5: Polarization correction factor for incident energies of 11 and 20 keV as a function of scattering vector magnitude, k, in the sample. (The correction is symmetric about 90° in scattering angle.)

¹The vertical component is somewhat dependent on the position from the center of the beam.

5.3.5 Multiple Scattering

The primary contribution to the detected scattered intensity is from x-rays scattered once by a volume element in the sample. However, there is also a small multiple scattering contribution from scattered x-rays that rescatter in additional volume elements: $I_{total} = I_1 + I_2 + \dots$ Scattering of order higher than two is negligible, so we consider only double scattering of x-rays. Warren and Mozzi [93] originally derived an exact expression (a double integral) for the ratio of the intensity of double scattering to single scattering (I_2/I_1) for an amorphous sample with effectively infinite thickness in reflection geometry using unpolarized radiation. They made the approximation that the scattered intensity from the sample equals the independent scattering $(\sum_{\alpha} x_{\alpha} f_{\alpha} f_{\alpha}^*)$ which contains no structural features. This assumption, while not strictly accurate, is reasonable for amorphous materials. For the case of unpolarized radiation, Dwiggens and Park [94, 95, 96] derived equations involving numerical integration over only a single variable for any thickness sample and various scattering geometries. They presented parameterized results in tabular form for symmetric reflection, symmetric transmission and asymmetric transmission. For the symmetric transmission case in which we are interested, the ratio of (I_2/I_1) is already small (less than 0.03 at $k = 10 \text{ Å}^{-1}$ for 11 keV incident photons) for unpolarized radiation.

Because complete rederivation is required to adjust the polarization factors, we turn to Malet and coworkers [97] who present a clear and concise derivation of the double to single scattering ratio for the symmetric transmission case. Their general derivation of the polarization factor has been simplified for linearly polarized incident radiation (see Appendix C of reference [80]). The resulting double integral was implemented in Matlab for the present work (**multscat.m**, Hope Ishii). The double to single scattering ratio (I_2/I_1) was calculated as a function of the scattering angle 2θ for the relevant samples and incident photon energies. These values were used to determine the multiple scattering correction which can be written as [98]:

$$c_{mult} = \frac{1}{(1 + I_2/I_1)} \tag{5.13}$$



Figure 5.6: Multiple scattering correction factors for Sample 2 and Sample 3 at different energies. The correction is larger (in relative magnitude) at 11.0 keV than at 19.9 keV.

Since the contribution of multiply-scattered x-rays is small, the correction factor also is small as shown in Figures 5.6 as a function of scattering angle 2θ . These corrections were included although they are small enough relative to the uncertainties in μt constants to be entirely negligible. It should be noted that the transmission geometry used here results in a much smaller multiple scattering correction than the reflection geometry. This reduces the impact of errors in the correction function on the normalization of the elastic scattered intensity.

5.4 Normalization

Normalization of the elastically scattered, corrected intensity is arguably the most difficult and most critical aspect of the data analysis. In order to extract structural data (number densities of atomic species as a function of radial distance), the data must be normalized to an absolute scale, independent of the data-collection techniques, by a multiplicative factor, K_{norm} . This absolute scale is chosen as the atomic structureindependent (coherent) elastic scattering for the particular composition of the sample $\langle ff^* \rangle$. In other words, the measured intensity is normalized to a 'per average atom' basis. There are two general historical approaches to this normalization:

The first approach is the method proposed by Warren [19]. Rexamining Equation 2.9 in Chapter 2, we note that, for an amorphous material, the excursion of the atomic density from the average density in the sample approaches zero rapidly with r: $[\rho(r) - \rho_o] \rightarrow 0$, and the $\frac{\sin(kr)}{kr}$ term oscillates with decreasing amplitude as k increases. Therefore, the experimental elastic intensity approaches the structureindependent coherent scattering as k increases $(S(k) \rightarrow 0 \text{ at high } k)$. The *large-angle normalization method* therefore constrains the experimental data to oscillate about the structure-independent elastic scattering $\sum_{\alpha} x_{\alpha} f_{\alpha}^2(k)$ at high k values. For data taken at lower energies, unfortunately, the available k-space often does not extend to the region where the structure-dependent oscillations have died out. This is certainly the case for data taken near the Ge K edge. In such cases, the normalization obtained is highly dependent on the exact range of k-space chosen.

The second approach is the method of Norman [99] and Krogh-Moe [100] which relies on the fact that there is no overlap in real space between neighboring atoms. Thus, the Fourier transform evaluated at r=0 of the structure-dependent term, S(k), represents the atomic distribution function at r=0 and must equal zero. Noting that $\frac{\sin(kr)}{kr} \to 1$ as $r \to 0$, we obtain

$$\rho(r) = \rho_o + \frac{1}{2\pi^2} \int_0^\infty k^2 S(k) \frac{\sin(kr)}{kr} dk$$
 (5.14)

$$\rho(0) = 0 = \rho_o + \frac{1}{2\pi^2} \int_0^\infty k^2 S(k) dk$$
(5.15)

This holds for any arrangement of atoms, so we can assume that each atom scatters independently. Following Norman, the following relationship for the normalization factor is obtained using the free atom scattering factors:

$$K_{norm} = \frac{\int_0^\infty k^2 [I_{coh}(k) + I_{inc}(k)] dk - (2\pi^2 \rho_o) (\sum_\alpha \mathbf{x}_\alpha Z_\alpha)^2}{\int_0^\infty k^2 I_{obs}(k) dk}$$
(5.16)

where $I_{coh}(k) + I_{inc}(k) = \sum_{\alpha} [x_{\alpha} f_{\alpha}^2(k)] + I_{inc}(k)$.² I_{coh} is the coherent (elastic) scattered intensity, I_{inc} is the incoherent scattered intensity and I_{obs} is the measured (corrected) intensity. In previous work, values for I_{inc} were commonly obtained from tables or calculated and then subtracted. By using a position sensitive detector, I_{inc} can be

$$D(r) = \int I(k)e^{-2\pi i k \cdot r} \frac{k^2}{2\pi^2} dk.$$

Since x-ray measurements typically do not go down to zero-angle, we subtract out that contribution where the entire sample acts as one particle of average density:

$$D_m(r) - D_o(r) = \int (I_m - I_o) e^{-2\pi i k \cdot r} \frac{k^2}{2\pi^2} dk$$

We can substitute in our expression for $I_m - I_o$ now and recognize that for spherical symmetry, the exponential term becomes $\frac{\sin(kr)}{kr}$. At r = 0, $\frac{\sin(kr)}{kr} \to 1$, $D_o(0) = \rho_o (\sum_{\alpha} x_{\alpha} Z_{\alpha})^2$, and $D_m(0) = 0$. The final result is equivalent to Equation 5.16:

$$0 - \rho_o \left(\sum_{\alpha} \mathbf{x}_{\alpha} Z_{\alpha} \right)^2 = \frac{K_{norm}}{2\pi^2} \int I_{obs} k^2 \ dk - \frac{1}{2\pi^2} \int \left(I_{coh} + I_{inc} \right) k^2 \ dk.$$

²For the interested reader: This arises from $K_{norm}I_{obs} = I_{coh} + I_{inc} + I_m - I_o$ where I_m is the structure-dependent term and I_o is the zero-angle scattering (which we must include in an integral over all k-space). Norman begins by writing an electron distribution function

excluded from the observed intensity down to very small k values.

Combining these two contraints, Fuoss [26, 27] developed a third normalization method which is applied in this work. Assuming the presence of significant background intensities, the scattering can be written as

$$I_{coh} + I_{inc} = K_{norm} \left[I_{obs} - I_b \right] \tag{5.17}$$

where I_b is a background intensity. From Warren's method, we have the relationship

$$K_{norm} = \frac{I_{coh}(k_{max}) + I_{inc}(k_{max})}{I_{obs}(k_{max}) - I_b}$$
(5.18)

And from Norman and Krogh-Moe, we can write

$$K_{norm} = \frac{\int_{k_{min}}^{k_{max}} k^2 [I_{coh}(k) + I_{inc}(k)] dk - 2\pi^2 \rho_o \sum_{\alpha} (\mathbf{x}_{\alpha} Z_{\alpha})^2}{\int_{k_{min}}^{k_{max}} k^2 [I_{obs}(k) - I_b] dk}$$
(5.19)

By solving these two equations simultaneously, we can obtain the two unknowns, K_{norm} and I_b . Figure 5.7 contains the corrected elastic intensity (collected below the Ge K absorption edge) normalized to the coherent independent intensity for Sample 2 (27 at% Mo).

It should be noted here that the correction functions discussed in Section 5.3 are all largest at high angles where the x-ray pathlength through the sample is largest. (This is true even for transmission data which, as discussed earlier, generally require smallermagnitude corrections decreasing the impact of potential errors in the correction process.) As a result, choosing the highest k-region available for the normalization is not necessarily the most prudent choice since this region will also be the most susceptible to the corrections applied to the data.



Figure 5.7: Normalized data (solid line) and the coherent independent intensity (dashed line) for Sample 2 (27 at% Mo).

In practice, the data taken at the highest energy, and therefore having the largest k_{max} , were normalized first. Since the experimental elastic intensity approaches the structure-independent coherent scattering as k increases, these data were more readily well-normalized. They were then used as a guide for normalizing data taken at lower energies. For example, the optimal k_{min} and k_{max} limits of integration for the large-angle normalization equation were selected by referring to the already-normalized high energy total structure factor, S(k).

5.5 Impact of Experimental Limits

While the data analysis is, in theory, straight-forward, complexities lie in the details. The majority of the inelastic scattering can be experimentally eliminated using our diffracted-beam analyzer and PSD setup, but we must consider the effect of the limited incident and detected energy resolutions discussed in Chapter 4. The limited detected energy resolution means the Compton scattering peak can be nominally removed only down to $k \sim 3 \text{ Å}^{-1}$ for energies near the Ge K edge and $\sim 5 \text{ Å}^{-1}$ near the Mo K edge. The K_{β} resonant Raman (RR) scattering and elastic scattering are also broadened by the limited resolution. As a result, they must be fit simultaneously for energies near the absorption edges since the tails of the peaks overlap. With an improvement in the degree of parafocussing between sample and PSD, the detected energy resolution can be sharpened. This will, however, result in some loss of dispersion of energies on the PSD because the total length from sample to PSD is limited by the experimental hutch at the present beamline.

The final potential source of background scattering in the collected data is true fluorescent radiation. One means by which fluorescence finds its way into the elastic peak is when the monochromator crystals are not sufficiently detuned to prevent the passage of higher-order harmonics in the incident beam. Another means arises when the incident energy is close to the edge energy and the incident energy resolution is not sufficient to prevent some sampling above the edge energy. This is the situation at 5 and 15 eV below the Mo K edge energy for the incident energy resolutions obtained experimentally. Figure 5.8 illustrates schematically the two situations encountered.



Figure 5.8: Possible distributions of incident photons near an absorption edge: a) The entire distribution lies below the threshold energy and b) the centroid of the distribution lies close enough to the threshold energy that part of the distribution is above the edge resulting in fluorescence as well as resonant Raman scattering.

100 eV below the Mo K edge is given by case a) where the entire incident energy distribution is below the edge energy, so photons are mostly scattered elastically and inelastically. For energies nearer the K absorption edge, some photons produce resonant Raman peaks with widths related to ΔE_{inc} , the incident energy peakwidth. For each discrete incident energy located dE below the edge energy, there is a corresponding resonant Raman peak located dE below the fluorescent line energy. For a distribution of incident energies, a distribution of resonant Raman energies results. 15 and 5 eV below the Mo edge are given by case b). (Recall that the FWHM incident energy peakwidth below the Mo edge is ~ 31 eV.) Here, the centroid of the incident energy is close enough to the edge energy that part of the distribution lies above the edge. Those photons that are above the edge contribute to fluorescent radiation occurring in narrow lines. The result is a broad peak of resonant Raman scattering beneath a sharper, more intense peak due to true fluorescence. Although these inelastic and fluorescent peaks occur at lower energies than the elastic peak, the limited detected energy resolution of this experiment requires simultaneously fitting them with the elastic peak rather than simply windowing them out. This illustrates the importance of experimentally measuring the incident energy resolution and considering its width in selecting energies at which to collect data as discussed in Section 2.3.3.

To explore whether the inelastically scattered intensities (and fluorescence) have been completely eliminated, we must see if I_b is negligibly small. This is the case 100 eV below the Mo edge where I_b is at most 1% of the normalized scattering at k_{max} . Data taken 15 and 5 eV below the Mo edge display significant background intensity that increases as the incident energy approaches the edge. This is most likely due to the influence of fluorescent radiation on the two-peak Gaussian fits of the elastic and K_β resonant Raman scattering. Due to the relatively wide peakwidth of the incident energy at the energies near the Mo edge (see Chapter 4), some fluorescence was excited by the upper tail of the incident energy peakwidth lying above the K absorption edge. This fluorescence atop the K_{β} resonant Raman peak can shift the peak fits giving extra counts in the elastic peak.

15 and 5 eV below the Ge edge, I_b is only a few percent at k_{max} , but the data taken 100 eV below the Ge have a larger background of 11% at k_{max} . This significant background so far below the Ge edge is puzzling. Although the incident energy resolution at the Ge edge was narrow enough that no fluorescence should have been excited, it is possible that a higher-order harmonic was able to pass the monochromator crystals at that energy. In that case, K_{β} fluorescence (~ 120 eV below the K edge) would be indistinguishable in energy from the elastic peak (100 eV below the K edge) at the present detected energy resolution.

These considerations have led to the redesign of the experimental setup for improved parafocussing at the PSD. Additional experiments will allow the assessment of the quality of the PPDFs extracted from still-cleaner, elastically scattered intensity obtained with narrower incident energy resolution. Further discussion of experimental improvements may be found in Chapter 8.

5.6 Solution for Distribution Functions

The elastically scattered, corrected and normalized intensities are now used to obtain total or differential structure factors or inserted into the Munro matrix (Equation 2.24) to solve for the partial structure factors at each k point. It would seem that a Fourier transform is all that is required to produce the real space distribution functions. However, the upper integration limit in k in the sine Fourier transform from reciprocal space to real space is intrinsically limited by the data taken below the lowest absorption edge, in this case, the Ge K edge: $k_{max} = 4\pi/\lambda$. This, in turn, limits the real space resolution of the PPDFs: The experimental $k_{max} = 10 \text{ Å}^{-1}$ implies a real space resolution of $\Delta r = 0.16 \text{ Å}$. The limited k-space data (missing high frequencies) yield real space termination oscillations that can obscure physical information. These effects can be mitigated to some degree by multiplying k S(k) by a damping function before applying the sine Fourier transform.

5.6.1 A Comparison of Damping Functions

Determining the appropriate damping function is important since too little damping results in high amplitude termination oscillations that obscure the true structural peaks and too much damping unnecessarily degrades the *r*-space resolution of the distribution functions. In addition, the choice of damping function and degree of damping (damping factor) effects not only oscillations about a peak but also nominal peak position. This can result in erroneous conclusions if damping is not *uniformly* applied.

Gaussian damping

The simplest damping function is a Gaussian, $D_G(k) = e^{-\alpha k^2}$, where the strength of damping is determined by α : The larger α , the stronger the damping effect. (This functional form does not guarantee that the function being damped approaches zero at k_{max} .) Increasing the strength of α smears out the distribution function rapidly. An indication of this is the behavior of the low-r region below the first peak and the first peak itself. As α is increased, the termination oscillations quickly die out below



Figure 5.9: Simple Gaussian damping functions $D_G(k)$ with various values of α are shown on the left and the resulting RDFs are shown on the right.

the first peak, but the onset of the first peak comes earlier as the peak broadens and loses height. Since real space peaks in distribution functions are generally not comprised of a single Fourier component, an additional effect of any damping function is some shift in the real space peak position. For the Gaussian function, increasing α from 0 to 0.02 results in an upward shift in first peak position by 0.07 Å in $4\pi r\rho$. Figure 5.9 illustrates the effect of this form of damping on the RDF.

Delayed-onset damping

A second damping function is designed to remain at unity until a k_{min} value at which damping begins: $D_2(k) = e^{-\alpha(k-k_{min})^2}$. To investigate the behavior of this delayedonset function, a value of α was chosen and the k_{min} values were varied. In other words, the shape of the damping function was not changed, but its position was shifted along the k-axis: As k_{min} increases, the damping function at k_{max} reaches



Figure 5.10: Delayed-onset Gaussian damping functions $D_2(k)$ with $\alpha = 0.02$ and various k onset values are shown on the left and the resulting RDFs are shown on the right.

larger positive values. The effect (shown in Figure 5.10) is very similar to simply decreasing α in the $e^{-\alpha k^2}$ case.

Variable- α damping

A third damping function establishes the damping factor, α , depending on the chosen values of k_{min} and k_{max} : $D_3(k) = e^{-\alpha(k-k_{min})^2}$ where $\alpha = \log(100)/(k_{max}-k_{min})^2$. The advantage of setting α in this manner is that the damping function always approaches zero at k_{max} . Figure 5.11 illustrates this for different k_{min} values. Again in this case, however, setting k_{min} to anything greater than zero only increases the termination oscillations. Disadvantages to using the D₃ damping function are (1) comparisons of data from two different k-ranges have different damping and (2) this damping function is very strong - unnecessarily so, particularly for high-Z element edges.



Figure 5.11: Variable- α damping functions $D_3(k)$ with various k onset values are shown on the left and the resulting RDFs are shown on the right.

Consider the effect of setting k_{min} to a value greater than zero in the D₃ damping function by examining the total function that is multiplied by S(k) prior to the sine Fourier transform: k times the damping function, D₃(k). For a damping function that begins far above k = 0, $k D_3(k)$ rises linearly and then begin falling discontinuously as seen in Figure 5.12. This leads to spurious features in the distribution functions rendering interpretation suspect. As a result, damping is applied over the *entire* k-range in this work.

Lorch damping

A frequently used damping function that, like the simple Gaussian damping function $D_{\rm G}(k)$, is applied over the entire experimental k-range is the Lorch function: $D_{\rm L}(k) = \frac{k_{max}}{\pi k} \sin(\frac{\pi k}{k_{max}})$. Recent work by Laaziri and coworkers [101] indicates that this form of damping yields errors in coordination numbers similar in magnitude to the Gaussian



Figure 5.12: k times $D_3(k)$, the variable- α damping function, with several k onset values: Discontinuity occurs for k_{min} much greater than 2 Å^{-1} .

damping function for $k_{max} < 30 \text{ Å}^{-1}$. Based on these comparisons, the best choices for reducing termination oscillations while maximizing real-space resolution are the Gaussian and Lorch functions, $D_{G}(k)$ and $D_{L}(k)$.

5.6.2 To Real Space

Because its effect in the Fourier transform is readily understood, the simple Gaussian damping function is used in this work with a carefully-chosen α for sufficient damping. For all work presented in the following chapters, the $k S_{\alpha\beta}(k)$ in all integrands of Equations 2.12, 2.15 and 2.22 are multiplied by the Gaussian damping function, $D_{\rm G}(k) = e^{-0.02k^2}$, prior to the Fourier transform to real space. This function broadens a delta function to a real space peak with FWHM of 0.38 Å for $k_{max} = 10 \,\text{\AA}^{-1}$. Figure 5.13 demonstrates this effect.



Figure 5.13: The broadening of a delta function at r = 2.7 Å by the Gaussian damping function $D_{\rm G}(k)$ with $\alpha = 0.02$ and $\Delta k = 0.025$ Å⁻¹. For the extraction of PPDFs, $k_{max} = 10$ Å⁻¹.

5.7 Data Analysis Code

The data analysis for anomalous scattering from amorphous samples described in this chapter is quite complex due to the vast quantities of data necessary for statistically-relevant results, the numerous corrections applied and the many variables in the normalization process. The analysis could not be completed in a graduate student's lifetime without the use of computer programs to accomplish these tasks in the appropriate order carrying through the relevant variables. All data analysis in this work has been carried out using Matlab (The MathWorks, Inc.), an advanced mathematical programming language. Programs of executable commands (macros) are referred to in this work as **filename.m**. Appendix B contains a flowchart of the data analysis macros with brief descriptions of each.

Many of the fundamental x-ray diffraction macros accessed by the anomalous scattering code have been written, transferred from other programming languages, rewritten, expanded and updated by Sean Brennan [102]. Students in the Bienenstock group have written much of the code for analysis of scattering from amorphous materials in FORTRAN. That code was later moved into Matlab and expanded by Ritva Serimaa, a postdoc in the group in the early 1990s [69, 103]. The students who followed continued to expand and refine the Matlab code. I have made several modifications including adding a master program to make the data analysis more straightforward and transparent to the user.

Chapter 6

Results

The results of the synchrotron experiment and data analysis described in the previous chapter are the total, differential and partial structure factors and pair distribution functions. The improvements in experimental data collection have produced much higher quality partial pair distribution functions (PPDFs) than previously obtainable by anomalous x-ray scattering (AXS) without using regularization methods. The complete chemical specificity of the PPDFs offers extremely valuable information frequently unattainable by other techniques.

This chapter presents the structure factors and distribution functions of increasing degree of chemical specificity for the sample with composition nearest a-MoGe₃ (Sample 2 at 27% Mo). The total and differential structure factors are shown to fit in the appropriate order in the progression of these functions with composition produced by Kortright [2] in his earlier work on the amorphous Mo-Ge system.

6.1 SF and RDF

The total structure factor, SF, for *a*-MoGe₃ is shown in Figure 6.1 for data taken 100 eV below the Mo K absorption edge. These data extend to $k_{max} = 18 \text{ Å}^{-1}$. At this large k_{max} , the oscillations in the SF have damped nearly to zero, so proper normalization of the data to a per atom basis is more easily accomplished than in the data taken below the Ge edge. The SF has been smoothly extended from $k = 1.6 \text{ Å}^{-1}$ to k = 0 with a cubic function. (Previous workers have frequently linearly extrapolated to k = 0, and we find negligible differences in the radial distribution functions resulting from the two extrapolations.)



Figure 6.1: The SF from data taken 100 eV below the Mo edge (19.900 keV).

The radial distribution function, RDF, describes the average coordination of an atom in the sample and is the sine Fourier transform of the SF plotted above. Figure 6.2 contains the RDF from data taken 100 eV below the Mo edge with two different

damping factors giving a real space resolution of 0.33 Å for $\alpha = 0.020$ and 0.20 Å for $\alpha = 0.005$. The low- α RDF is plotted to illustrate the improved real space resolution. Since the PPDFs are terminated at the $k_{max} = 10 \text{ Å}^{-1}$ associated with the lower energy Ge K edge, they are subject to larger termination errors. As such, all data comparisons will be made using the stronger of these damping factors, $\alpha = 0.020$. The average number density of the sample is taken to be $\rho_0 = 5.585 \times 10^{-22} \text{ cm}^{-3}$ as discussed in Section 5.1.2.



Figure 6.2: The radial distribution function from data taken 100 eV below the Mo edge (19900 eV). The solid line is the RDF obtained with a damping factor $\alpha = 0.020$ in the Fourier transform; the dashed line, with $\alpha = 0.005$.

The simplest measure of quality of the real-space distribution functions is the low-r behavior. Physically, there should be no atomic density at distances less than the first nearest neighbor (NN) distance. The low-r region of the RDF is smooth and flat, an indication of good quality.



Figure 6.3: The radial distribution function obtained 100 eV below the Ge edge (11003 eV) is plotted as a solid line. Overlaid as a dashed line is the radial distribution function from 100 eV below the Mo edge (19900 eV) cut off at the same k_{max} of 10 Å^{-1} as the data taken below the Ge edge. Ideally, these functions would overlay exactly.

Figure 6.3 shows the RDFs taken 100 eV below the Ge and Mo K edges where the normalized reciprocal space data have been truncated at the same k_{max} of 10 Å^{-1} .

Ideally, these functions would overlay exactly. The disagreement is most likely caused by the lower quality of the Ge edge normalization. Since there are still significant oscillations about the coherent independent scattering at $k_{max} = 10 \text{ Å}^{-1}$, the best normalization constants are difficult to determine. For normalization of the Mo edge data to a per atom basis (prior to truncation at $k = 10 \text{ Å}^{-1}$), the data extended to $k_{max} = 18 \text{ Å}^{-1}$ where oscillations about the coherent scattering have largely died out. Thus, the data collected below the Mo K edge are expected to be better-normalized. The differences in the first peak area and position are 3% and 0.01 Å respectively and provide some indication of the uncertainties in the RDF. (These are in good agreement with the uncertainties in RDFs found by Ludwig in a study of *l*-GeBr₄ [28] discussed in the following chapter.)

The lack of complete agreement between the RDFs from the two absorption edges points to the presence of systematic errors in normalization of lower-energy measurements (lower-Z elements). Such errors are particularly troublesome when present in the final row of the Munro matrix which does *not* involve a difference of measurements below an edge. For this reason, measurements taken at higher energy (higher k_{max}) should be chosen for that final row when solving for the PSFs and PPDFs. Since the two RDFs described above should be identical, a potential means of improving normalization for data taken below the lower-energy edge may be to iteratively vary the normalization parameters so as to minimize the differences between the two RDFs. It should be emphasized, however, that because the lower-energy measurements are typically included as a difference, the same limits for normalization should be applied to both measurements comprising the difference.
6.2 DSFs and DDFs

The differential functions provide a means of corroborating results from the partials and allow for direct comparison of the present scattering results with those obtained by Kortright (discussed below in Section 6.4). The DSFs for *a*-MoGe₃ are shown in Figure 6.4. DSF_{Mo} is from measurements taken 100 and 5 eV below the Mo K absorption edge, and DSF_{Ge} is from measurements 100 and 15 eV below the Ge edge. DSF_{Ge} is offset vertically for visibility, and both structure factors oscillate about zero. The Γ values used in the weighting function, W(k), were initially chosen to match the mole fractions of the respective elements. (The choice of Γ has almost no effect in the Mo differential functions; however, increasing Γ results in changes in the magnitude of oscillations in the Ge DDF, an effect similar to what one would expect from an improvement in real-space resolution. This added variable of Γ leads to some arbitrariness in the Ge DDF.) The Mo DSF is much noisier than its Ge counterpart due to 4-5 times fewer counts at the Mo edge.

The DDFs calculated via sine Fourier transforms are shown in Figure 6.5. The standard damping factor of $\alpha = 0.02$ was included in the transform. Due to the different k_{max} values for the two DDFs, the Mo DDF has better real space resolution than the Ge DDF; however, it is of somewhat lower quality exhibiting some oscillations at low-r below the first NN peak.

Although these oscillations are not of sufficient magnitude to interfere with physical interpretation of the Mo DDF, it is nevertheless desirable to investigate their origin in order to improve the design of subsequent experiments. By sine Fourier transforming only the low-r region between r = 0 and r = 1.5 Å, the results in Figure 6.6 were obtained. This gives the general form of the error causing the low-roscillations, and a close look at the Mo edge DSF in Figure 6.4 confirms that the



Figure 6.4: The differential structure factors, DSF_{Ge} and DSF_{Mo} , from measurements taken 100 eV and 15 eV below the Ge edge ($k_{max} = 10 \text{ Å}^{-1}$, $\Gamma = 0.25$) and 100 eV and 5 eV below the Mo edge ($k_{max} = 18 \text{ Å}^{-1}$, $\Gamma = 0.75$).



Figure 6.5: The Ge (dotted line) and Mo (solid line) differential distribution functions, DDFs, from the DSFs plotted above in Figure 6.4 ($\alpha = 0.02$).



Figure 6.6: The S(k)-like function resulting from a sine Fourier transform of the low-r region from r = 0 - 1.5 Å of the Mo DDF. This function indicates that error in the DSF was not fully removed by the Fuoss normalization.

structure oscillations follow a broad curve peaking near $k = 6 \text{ Å}^{-1}$. At first glance, one might suspect a polarization correction error that has been partially-compensated by the Fuoss normalization. (Partial compensation of error is discussed in more detail in the following chapter.) A comparison of Figure 6.6 with Figure 5.5 reveals that the peak ($k = 14 \text{ Å}^{-1}$) for a pure polarization correction error occurs at the wrong position in, for example, the data taken nearest the Mo edge. A difference of the polarization corrections for the two energies involved has a peak near $k = 10 \text{ Å}^{-1}$; however, it is possible that partial compensation of a polarization correction error with background and normalization constant errors might shift the peak to lower k. Another possibility is that the error is an artifact due to insufficient statistics in the scans taken below the Mo edge. The low incident count rates and low detector efficiency at these high energies precluded collection of more data. Sufficient statistics are particularly important in calculating the DSFs (and PSFs) which involve subtraction of similarly-valued functions. The most probable source of the error in the Mo edge DDF, however, is Compton scattering. Although the Compton scattering peak is nominally eliminated down to $k = 5 \text{ Å}^{-1}$, the peak shape is low and broad in energy. While the Compton scattering *peak* may be excluded, some Compton intensity from the high energy tail can still be included in the energy window of interest. In data collection of intensity as a function of k, the entire Compton peak would be included in the energy window at low k. Above some k value, the Compton scattering would begin to be excluded as the peak moves to progressively lower energies. Far from the edge (100 eV below), only the elastic peak must be fit by a Gaussian, but for the data collected nearest the Mo edge, a wider range including both the elastic and K_{β} resonant Raman scattering were fit by two Gaussians. It is possible that this nominally-elastic intensity data from near the Mo K edge contained some Compton scattering that was not included in the intensity data taken 100 eV below the edge. Thus, partial Compton scattering may be contained in the difference below the Mo edge. Improved detected energy resolution can aid in eliminating this issue.

6.3 PSFs and PPDFs

The PSFs, $S_{\alpha\beta}(k)$, for *a*-MoGe₃ obtained by direct solution of the Munro matrix are shown in Figure 6.7. The Mo-Ge and Mo-Mo PSFs are offset vertically for visibility. Data taken at 19.900 and 19.995 keV comprise the difference below the Mo edge, data taken at 11.003 and 11.088 keV comprise the difference taken below the Ge edge, and the final measurement was taken at 19.900 keV. (The data taken at 19.900 keV as the final measurement provide better Munro matrix conditioning than would data taken at any intermediate energy far from both absorption edges.) The PSFs have also been smoothly extended to their low-*k* limits with a cubic function. Since the low-*k* limit for the entire matrix problem is the largest k_{min} from data collected at



Figure 6.7: The partial structure factors, $S_{\alpha\beta}(k)$, obtained by solution of the Munro matrix. Data taken at 19.900 and 19.995 keV comprise the difference below the Mo edge, data taken at 11.003 and 11.088 keV comprise the difference below the Ge edge, and the final measurement was at 19.900 keV.

both edges, it is clear that improving the experimental setup to allow collection of data below the current $k_{min} = 1.6 \text{ Å}^{-1}$ near the Mo K edge would be very valuable since, at present, the precise low-k behavior of the PSFs is unknown.

All three PSFs display the proper limiting behavior approaching the appropriate high- and low-k limits. A close examination of the Ge-Ge PSF reveals that, at high k, its average value is slightly less than zero. Since the Mo DDF is clearly the worstbehaved of the three distribution functions whose scattering data enter the Munro matrix, error introduced in the difference below the Mo edge (like partial Compton scattering discussed in the previous section) is likely to be a primary cause of errors in these PSFs and the final PPDFs. Note that because the high-frequency noise present in k-space influences the PPDFs primarily at large r beyond the region of study, no smoothing of the PSFs is necessary. In fact, smoothing is generally inadvisable since inadvertent introduction of lower frequencies may impact the region of study.

The PPDFs, $4\pi r^2 \rho_{\alpha\beta}(r)$, for *a*-MoGe₃ resulting from the sine Fourier transform of the PSFs (via Equation 2.24 as described in Chapter 2) are shown in Figure 6.8. The damping factor is again $\alpha = 0.02$ and $k_{max} = 10$ Å⁻¹. The average number densities of Ge and Mo used are $\rho_{Ge0} = 4.084 \times 10^{-22}$ cm⁻³ and $\rho_{Mo0} = 1.501 \times 10^{-22}$ cm⁻³ (obtained from the areal densities in Section 5.1.1). The Mo-Mo and Mo-Ge PPDFs are again offset for ease of viewing, and the dashed lines indicate the zero levels for the three PPDFs. To our knowledge, this is the first complete set of reasonable-quality PPDFs obtained from the Mo-Ge system and the first study of the fully-chemically-specific structure of the *a*-MoGe₃ phase in particular.

The quality of the PPDFs is, again, indicated by their low-r behavior. Although we do find some fluctuations below the first NN peak, especially in the Mo-Mo PPDF,



Figure 6.8: The partial pair distribution functions, $4\pi r^2 \rho_{\alpha\beta}(r)$ from the partial structure factors plotted above in Figure 6.7 ($\alpha = 0.02$).

these PPDFs, obtained by direct solution of the Munro matrix equation without regularization, are reasonably well-behaved, and we may expect to extract some physical results from them. This is a significant improvement in the capabilities of the AXS technique that will be discussed further below.

With PSFs and PPDFs in hand, we can now return to the predictions of SVD analysis from Section 2.5. We find that those predictions are in excellent agreement with the results. The Mo-Mo PPDF, predicted to be most sensitive to error, contains the most non-physical negative atomic density. In addition, a small amount of *mirroring* is present between the Ge-Ge and Mo-Ge PPDFs as expected from the SVD analysis. The agreement of these predictions with the PPDF behavior indicate that the remaining prediction that the Mo-Ge PPDF is the most reliable of the PPDFs can also be expected to be true. We will use these SVD results in the following chapter in interpreting the coordination results from a-MoGe₃.

6.4 Comparison with Previous X-ray Scattering Results

Kortright [1, 2] carried out AXS on Mo-Ge sputtered amorphous alloys over a wide range of compositions and presented the early evidence for phase separation in the system. He measured total and differential structure factors for a range of compositions. Figures 6.9 and 6.10 were scanned from Kortright's PhD thesis, relabelled and overlaid with the properly scaled results from the current sample with composition near a-MoGe₃. They show 1) that the current sample (26.9% Mo overlaid in red) falls in the proper position in the composition progression of Kortright's SFs and DSFs (in black), and 2) that comparisons with Kortright's work on the amorphous sputtered Mo-Ge alloy system are valid.



Figure 6.9: The total structure factor from the present sample overlaid on those from Kortright's work [1].

The progression of Mo DSFs shows little change between 14 and 42% Mo indicating that the Mo environment does not change drastically. The progression of Ge DSFs, in particular, illustrates how the scattering profile for the present 26.9% Mo sample is nearly identical to Kortright's 42% Mo sample and completely unlike *a*-Ge. The disappearance near 23-25% Mo of the tetrahedral distance characteristic of *a*-Ge is in agreement with the disappearance of phase separation in Ge-rich compositions at $\sim 25\%$ Mo seen using small angle x-ray scattering (SAXS) on this amorphous alloy system by Regan [3, 4].



Figure 6.10: The differential structure factors (DSFs) from the present sample overlaid on plots of the Mo and Ge DSFs from Kortright's work [1].

Chapter 7

Discussion

In the previous chapter, the total, differential and partial structure factors and pair distribution functions were presented for Sample 2 which, at 27% Mo, is nearest to the MoGe₃ endpoint composition for the amorphous phase separation. The present data were also shown to agree well with earlier work done by Kortright on the system.

In this chapter, we demonstrate that the extracted PSFs satisfy the original Munro matrix equation and then illustrate the improvements in the PPDFs extracted without regularization procedures by comparisons to previous results. The neighboring crystalline compounds are presented, and tests for the presence of *a*-Ge show that the sample is not a phase-separated mixture of *a*-Ge and *a*-MoGe₂. The physical coordination results from the alloys are presented and compared with those obtained by Kortright using EXAFS to illustrate the utility of the AXS technique for amorphous alloys with high static disorder. The stability of the coordination results with respect to introduced errors is explored, and estimates of the coordination number uncertainties are presented. Finally, the role of the MoGe₃ composition in the amorphous alloy system is addressed.

7.1 Internal Comparisons

An important first step is to verify that the extracted PSFs satisfy the original matrix problem. This verification of the internal consistency of the data can be carried out by constructing various structure factors from the appropriately-weighted sum of the partial structure factors (PSFs). This allows us to confirm that the extracted PSFs are solutions of the original matrix problem. These *constructed structure factors* and the resulting real space distribution functions can then be compared with *measured structure factors* and the resulting distribution functions. Comparisons are made only over the experimental k-range.

7.1.1 Sum of PSFs to Give SF

The total structure factor (SF) can be written as a weighted sum of partial structure factors (PSFs) by combining Equations 2.14 and 2.16:

$$S(k) = C_{AA}(k) S_{AA}(k) + C_{AB}(k) S_{AB}(k) + C_{BB}(k) S_{BB}(k)$$
(7.1)

$$C_{AA}(k) = \frac{\mathbf{x}_A |f_A|^2}{\langle f \rangle^2}$$
$$C_{AB}(k) = \frac{2\mathbf{x}_A \Re (f_A f_B^*)}{\langle f \rangle^2}$$
$$C_{BB}(k) = \frac{\mathbf{x}_B |f_B|^2}{\langle f \rangle^2}$$

This sum, calculated at the appropriate incident energy, is compared to a measured SF. The results are illustrated in Figure 7.1 where the constructed SF is overlaid as a dotted line on the measured SF at 100 eV below the Mo edge. The agreement



Figure 7.1: The total structure factor measured at 19.900 keV (100 eV below the Mo edge) is shown in the solid line, and the total structure factor constructed from the weighted sum of partial structure factors is overlaid as the dotted line. The difference in the magnitudes is plotted at the bottom on an enlarged scale.

between the measured SF and that constructed from the PSFs is excellent. The RDFs resulting from the measured and constructed SFs at 19.900 keV are shown in Figure 7.2. Again, the agreement is superb.



Figure 7.2: The RDFs from the measured and constructed SFs at 19.900 keV (100 eV below the Mo edge).

It is informative to plot the k-dependence of the three weighting factors for the PSFs as shown in Figure 7.3. Although the factor of $\langle f(k) \rangle^2$ approximately removes the k-dependence of the scattering factors in the total structure factor, it also contributes to gradual changes in the relative weighting of the partial structure factors

within the total structure factor as a function of k. Thus, the RDF gives only an approximate picture of the physical atomic distribution.¹



Figure 7.3: The k-dependence of the weighting factors for the three PSFs comprising the SF for a-MoGe₃ at 19.900 keV.

7.1.2 Sum of PSFs to Give DSFs & Testing the DSF Approximation

The differential structure factors (DSFs) can be similarly expressed as weighted sums of the appropriate partial structure factors (PSFs):

$$\Delta S_A(k) = D_{AA}(k) \, S_{AA}(k) + D_{AB}(k) \, S_{AB}(k) \tag{7.2}$$

¹Note that the Ge-Mo PSF is more heavily-weighted than the Mo-Mo PSF in this alloy. In typical 80:20 transition metal-metalloid glasses such as $Ni_{80}P_{20}$ or $Pd_{80}Si_{20}$, the metal-metal interactions overwhelmingly dominate the RDF.

$$D_{AA}(k) = \frac{\Delta_A [\mathbf{x}_A | f_A |^2]}{W}$$
$$D_{AB}(k) = \frac{\Delta_A [2\mathbf{x}_A \Re (f_A f_B^*)]}{W}$$

where W is defined in Equation 2.20. The constructed DSFs are compared to the measured DSFs in Figure 7.4 and 7.5 for the same energies and Γ values. The constructed DSFs are overlaid as dotted lines on the measured DSFs below each absorption edge.



Figure 7.4: The measured DSF at the Ge edge (100 and 15 eV below the edge) is plotted in grey, and the constructed DSF from the appropriate PSFs and weighting factors is plotted as the dashed line.

The DDFs resulting from Fourier transform of the above DSFs are again indistinguishable by eye. Like the RDF, the DDF is also an approximation of the sum of PPDFs involving a given element; however, the DDF is even less accurate due to the added factor of Γ .



Figure 7.5: The measured DSF at the Mo edge (100 and 5 eV below the edge) is plotted in grey, and the constructed DSF from the appropriate PSFs and weighting factors is plotted as the dashed line.

The capability to construct the DSF from the extracted PSFs allows the testing of the approximation inherent in the definition of the DSF. The DSF involves taking a difference of two measurements below an element's absorption edge and assuming that those pair correlations that do not involve that element will cancel out so that those contributions can be ignored completely. See Section 2.1.2. (It is not necessary to make this assumption in extracting PSFs.) By comparing the DSF constructed according to Equation 7.2 with the same constructed DSF including the additional term

$$D_{BB}(k) = \frac{\Delta_B \left[\mathbf{x}_B | f_B |^2 \right]}{W},$$

we test how sensitive the DSF and DDF are to the normally-neglected third pair correlation. For the sample composition and energies used here, including the $D_{BB}(k)$ term gives DSFs differing by at most 0.6% from the the DSF without the $D_{BB}(k)$ term. The difference is not discernable to the eye for the energies explored in the DSFs or DDFs; however, as one might expect, the DSF constructed with all three terms is in better agreement with the measured DSF than the DSF constructed with only two terms. ($D_{BB}(k)$ itself is at most of the order 10^{-3} for the present sample and k-range. It has the largest contribution at low k for the Mo DSF and at high k for the Ge DSF.)

Figure 7.6 shows the relative strengths of the weighting factors for PSFs used to construct the DSFs over the k-range available. The third weighting factor, normally neglected in the definition of the DSF, is also included for comparison. As shown above, the third weighting factors are completely negligible in the DSFs at both edges.



Figure 7.6: The weighting factors that are multiplied by the relevant PSFs to construct the DSF are plotted here for each element edge, Mo and Ge. The third weighting factor is nearly zero and completely negligible for the sample composition and all energies studied here.

7.2 Comparison with Results from l-GeBr₄

The improved quality of the PPDFs obtained with experimental elimination of inelastic scattering is evident upon comparison with the careful studies of l-GeBr₄ carried out by Ludwig and coworkers [28]. They studied a molecular liquid, l-GeBr₄, as a model system with well-defined local structure. They were thus able to evaluate the AXS techniques for obtaining state-of-the-art DDFs and PPDFs at that time. The high accuracy of first NN positions and coordination numbers was confirmed for the differential functions, but they found that some of the PPDFs were completely unreliable, as discussed below. The a-MoGe₃ studied here and l-GeBr₄ are similarly conditioned for the energies selected (as illustrated in Section 2.5.2), and both were solved using the Munro matrix (Equation 2.24). It should be emphasized that both the present a-MoGe₃ data and the l-GeBr₄ data were not subjected to any regularization methods.

Ludwig's data [30, 28] were collected using a Ge solid-state detector with sufficient energy resolution to discriminate against the K_{α} resonant Raman scattering but not against the K_{β} resonant Raman or Compton inelastic scattering. His data were corrected for detector nonlinearity, air scattering, absorption, multiple scattering and 4% vertical polarization of the incident beam. It is not clear from his writing whether Ludwig subtracted a calculated Compton intensity; however, it was common practice at the time to do so with the assumption that the detector collected elastic and inelastic photons with equal efficiency. By using Fuoss' normalization procedure discussed in Section 5.4, Ludwig removed a constant (after correction for absorption) representing the contribution of the K_{β} resonant Raman scattering and obtained a scaling constant to place the coherent intensity on a per atom scale.

The present data, on the other hand, were obtained using a graphite analyzer

crystal and a position-sensitive detector that provided sufficient energy resolution to discriminate against the K_{β} resonant Raman scattering and against most of the Compton scattering - in particular, against the significant Compton contribution at high k values. Thus, no subtraction of K_{β} resonant Raman or Compton scattering was necessary.

Figure 7.7 gives a side-by-side comparison of the PPDFs obtained from the two systems. Ludwig found that the Br-Br PPDF agreed well with the GeBr₄ molecule, but the Ge-Ge and Ge-Br PPDFs showed rotation of results in solution space, the *mirroring* effect that is a symptom of systematic error present in the matrix problem. This leads to regions of negative atom density, a non-physical result. (Ludwig estimated the error levels to be 30% and 100% for the Ge-Br and Ge-Ge PPDFs, respectively.) These regions of negative atom density reach amplitudes up to 75% of the height of the first nearest neighbor peak in the Ge-Br PPDF.

The *a*-MoGe₃ PPDFs also show some regions of non-physical behavior. The worst offender is the Mo-Mo PPDF; however even there, the negative atom density amplitude has been greatly reduced to 22% of the height of the first nearest neighbor peak. We attribute this improvement to the removal of most of the inelastic scattering in the experiment and believe that further efforts to achieve even cleaner data will yield further improvements.

It should be noted that the use of the Fuoss normalization procedure on data contaminated with significant inelastic contributions from more than one source or with correction errors is risky. The Fuoss normalization assumes that there is a constant background signal (a fluorescence-like signal) contaminating the nominally elastic scattering. Other errors with k-dependent behavior may be partially-compensated



Figure 7.7: On the left are the PPDFs from a-MoGe₃, and on the right, the PPDFs from l-GeBr₄ obtained by Ludwig et al. [28] and a model of the GeBr₄ molecule. The arrows indicate the largest magnitude of non-physical negative atom density relative to the magnitude of the first nearest neighbor peak in each set of PPDFs. The GeBr₄ PPDFs have been scaled to approximately match the ordinate and abscissa of the MoGe₃ PPDFs.

by the scaling factor resulting in an incorrect overall shape for the final normalized elastic intensity. Examples of potential pitfalls include incorrect or incomplete removal of Compton scattering, application of the wrong absorption correction to the elastic scattering (or to the K_{β} resonant Raman scattering if it is calculated and subtracted based upon the K_{α} contribution), incorrect polarization correction and alignment problems. An incorrect shape for the normalized elastic intensity will lead to unreliable PSFs and PPDFs, and thus, the cleaner the *initial* elastic signal, the better the results.

7.3 Crystals of Neighboring Compositions

As a basis for comparisons, the nearby crystal structures are presented here. Crystalline Ge has the diamond-cubic structure, and there are two crystal structures for MoGe₂. The lower symmetry α -MoGe₂ phase displays a large range of near neighbor distances and is thus inherently more structurally disordered, even as a perfect crystal, than the high temperature, high symmetry β -MoGe₂ phase. The crystal structures [104, 105] and crystalline PPDFs are shown in Figures 7.8, 7.9 and 7.10. In β -MoGe₂, Mo has 4 Mo nearest neighbors at 3.32 Å and 10 Ge nearest neighbors at 2.72 Å. Ge has 5 Mo nearest neighbors at 2.72 Å and 5 Ge nearest neighbors also at 2.72 Å. The α -MoGe₂ nearest neighbor coordination is not so simple. Mo in the α phase has 4 Mo near neighbors near 3.5-3.6 Å and 2 more at 4.0 Å. It has 10 Ge near neighbors distributed between 2.4 and 3.4 Å. Ge in the α phase has 10 Ge near neighbors lying between 2.8 and 3.5 Å and 5 Mo near neighbors between 2.4 and 3.4 Å.



Figure 7.8: The crystal structure and crystal PPDFs for the α phase of c-MoGe₂.



Figure 7.9: The crystal structure and crystal PPDFs for the β phase of *c*-MoGe₂.



Figure 7.10: The crystal structure and crystal RDF for c-Ge.

7.3.1 Testing for Phase Separation

Since no MoGe₃ crystalline analogue to the amorphous state exists, one might expect an amorphous sample of this composition to be phase-separated into *a*-Ge and *a*-MoGe₂. Phase separation, however, is not supported by prior anomalous small-angle scattering or EXAFS studies [1, 2, 3, 4] which indicate that MoGe₃ is the endpoint for phase separation in the amorphous sputter-deposited system. Despite this evidence to the contrary, we must address the question of whether Sample 2 studied here ($\sim 27\%$ Mo) is actually a phase-separated mixture of MoGe₂ and Ge as would be expected from the equilibrium phase diagram.

A simple and often-useful first approach for understanding the structure of an amorphous alloy is to consider the local structures of nearby equilibrium compounds. (See, for example, [106] and [107].) This is sometimes referred to as the *quasi-crystalline* (qc) model and falls between what can be considered two extremes of amorphous material models: dense random packing of hard spheres which ignores any short range chemical ordering and the microcrystalline model which assumes the material is comprised of very small, well-defined crystals with random orientations.

The foundation for the qc model was first explicitly described by Warren [108] in his work confirming Zachariasen's continuous random network model for network glasses [109] such as silica. In silica, the strong atomic interactions lead to a basic structural unit (a "building block") identical to that found in the crystal, the SiO₄ tetrahedron. The qc model, therefore, assumes that the local bonding within the amorphous alloy is similar to that found in the nearby crystal(s). For the metal-metalloid systems that display hybridized bonding with preferred bond orientation, this is often a reasonable approach. Crystalline PPDFs may be broadened by a function representing the increasing disorder with distance in the system to yield qc-PPDFs. For a hypothetical, phase-separated mixture of Ge and MoGe₂ with an overall composition of Mo_xGe_{1-x} , the Mo-Mo PPDF is equal to the Mo-Mo PPDF from $MoGe_2$, and the Mo-Ge PPDF is equal to the Mo-Ge PPDF from MoGe₂. (There are no Mo-Mo or Mo-Ge correlations contributed by pure Ge.) The Ge-Ge PPDF is equal to $\frac{2x}{(1-x)}$ times the Ge-Ge PPDF from MoGe₂ plus $\frac{(1-3x)}{(1-x)}$ times the Ge-Ge RDF from Ge where x is the atomic fraction of Mo atoms in the sample. These relationships are given below in terms of the number densities:

$$\rho_{MoMo}(Mo_{x}Ge_{1-x}) = \rho_{MoMo}(MoGe_{2})$$

$$\rho_{MoGe}(Mo_{x}Ge_{1-x}) = \rho_{MoGe}(MoGe_{2})$$

$$\rho_{GeGe}(Mo_{x}Ge_{1-x}) = \frac{2x}{(1-x)}\rho_{GeGe}(MoGe_{2}) + \frac{(1-3x)}{(1-x)}\rho_{GeGe}(Ge)$$

$$(7.3)$$

As will be shown in the following sections, the local structure in this amorphous system differs from the local structure in the crystalline MoGe₂ phases. As such, comparisons of the experimental PPDFs with quasi-crystalline mixtures of equivalent total composition can not be used to determine whether phase separation is present. (Such comparisons demonstrate only that the experimental *a*-MoGe₃ structure is inconsistent with a phase-separated mixture of qc-Ge and $qc-\alpha$ -MoGe₂ or with a phase-separated mixture of qc-Ge and $qc-\beta$ -MoGe₂.) We can, however, verify whether the experimental Ge-Ge PPDF is consistent with the presence of *a*-Ge, an indicator for phase separation. Pure *a*-Ge has 4 nearest neighbors and, using Equation 7.3, we expect to find 1.0 Ge atom at the tetrahedral distance 2.45 Å in the PPDF if the experimental data are representative of a phase-separated mixture of Ge and MoGe₂. (This peak arises at 2.47 Å in $4\pi r \rho_{GeGe}(r)$, the function which is fit with Gaussians.) Because disorder in the amorphous sample quickly washes out the correlations with distance, and the third peak in the crystalline Ge RDF is not present in amorphous Ge, we focus only on the low-*r* region.

Using this approach, the best fit depends on the *r*-range included in the fit. Table 7.1 contains the results of fitting the Ge-Ge PPDF with two Gaussians, one constrained to lie at the tetrahedral Ge distance. A sample of the two-peak fit is shown in Figure 7.11. With a low-*r* limit of 2.2 Å and varying the upper limit between 3.3 and 3.1 Å, we find that the number of near neighbors at the tetrahedral distance varies from 0 to 0.7 atoms, considerably less than the expected average coordination number for Ge in *a*-Ge for a phase-separated mixture of *a*-Ge and *a*-MoGe₂. These results are not consistent with phase-separation into *a*-Ge and *a*-MoGe₂ in agreement with the previous work using anomalous small-angle scattering and EXAFS.

Since the possibility of phase separation has been considered and found inconsistent with these and previous results, we can be confident of an interpretation of coordination results for a-MoGe₃ assuming a single phase.

Table 7.1: Results of fitting two Gaussians to the first peak of the GeGe PPDF divided by radial distance $(4\pi r \rho_{GeGe}(r))$ for a variety of r_{max} values. $r_{min} = 2.2$ Å. Areas are the area of the Gaussian multiplied by the peak position. The number 1 refers to the Gaussian at the tetrahedral Ge distance (2.54 Å in the PPDF), and the number 2 refers to the second Gaussian at a longer distance. (A goodness of fit parameter is not presented since it simply reflects the *r*-range included in the fit.)

r_{max}	$d1_{NN}$	area1	FWHM1	$d2_{NN}$	area2	FWHM2
(Å)	(Å)	(atoms)	(Å)	(Å)	(atoms)	(Å)
3.1	2.47	0.69	0.58	2.98	6.5	0.78
3.2	2.47	0.48	0.61	2.98	7.0	0.84
3.3	2.47	0.01	0.27	2.97	7.9	0.95



Figure 7.11: The two-Gaussian fit to the first peak of $4\pi r \rho_{GeGe}(r)$ over the range r = 2.2 - 3.1 Å. The solid line is the experimental Ge-Ge PPDF for *a*-MoGe₃, dashed lines are the two Gaussians, and the dotted line is the residual.

7.4 Coordination Results

Having verified that 1) the extracted PSFs solve the initial Munro matrix equation, 2) the PPDFs are more reliable than those obtained previously on a similarly-conditioned system and 3) there is no evidence for phase separation, we now turn our attention to the interpretation of the PPDFs. To our knowledge, this is the first time physical interpretation of amorphous alloy structure has been feasible from a complete set of PPDFs obtained by AXS without regularization.

Table 7.2 contains the local coordination parameters for *a*-MoGe₃. The area under a peak in a PPDF gives the number of near neighbors (NNs) at that distance, the peak position. The local coordination parameters were obtained by fitting the first nearest neighbor peak in each function, $4\pi r \rho_{\alpha\beta}(r)$, to single Gaussians to extract the NN position, d_{NN} , coordination number, N, and the full-width at half-max, FWHM_{tot}. The intrinsic peak width, FWHM, was obtained by removing, by quadrature, the experimental broadening (0.38 Å) caused by the finite integration limit and damping function. (The Ge-Mo coordination number is given by $\frac{\mathbf{x}_{Mo}}{\mathbf{x}_{Ge}}$ multiplied by the Mo-Ge coordination number.)

Figure 7.12 shows examples of single Gaussian fits to the first peaks of the experimental PPDFs and the residual. The Mo-Ge and Mo-Mo PPDFs display a distinct, well-defined first NN peak. The first NN peak in the Ge-Ge PPDF, however, is broad and poorly defined on the high-r side. As such, it will be more difficult to interpret. All three peaks display apparent asymmetry evidenced by the negative dip in the residual on the low-r side of the first peak. Since there are small magnitude oscillations at low-r below the first peaks in the PPDFs, one may be suspicious of an assertion of peak asymmetry; however, the fact that all three are broader on the high-r side of the first NN peak, which occurs at different distances, lends support

Table 7.2: Local coordination parameters for a-MoGe₃. The numbers of nearest neighbors, N_1 and N_2 , are obtained by two different means. Note that $PPDF_{MoGe}(r) = \frac{x_{Ge}}{x_{Mo}} PPDF_{GeMo}(r)$. The error estimates given are based solely upon the variability of each parameter with the range included in the fit. (Uncertainties in N1 are discussed further in Section 7.6.4.)

$a-Mo_{27}Ge_{73}$	d_{NN}	$N1^a$	$FWHM^{b}$	$N2^c$
$\approx a$ -MoGe ₃	$(\text{\AA} \pm 0.02)$	(atoms ± 0.1)	$(\mathrm{\AA}\ \pm 0.02)$	(atoms)
$DDF_{Mo} (\Gamma = 0.75)$	2.66	7.6		10.81
$\text{DDF}_{Ge} \ (\Gamma = 0.25)$	2.73	8.3		11.65
$DDF_{Ge} \ (\Gamma = 0.55)$	2.72	8.5		11.71
$PPDF_{GeGe}$	(2.96)	(7.9)	(0.86)	8.34
$PPDF_{GeMo}$	2.67	3.0	0.39	3.40
$PPDF^*_{MoGe}$	2.67	8.0	0.39	9.24
$PPDF_{MoMo}$	3.21	1.8	0.35	1.67

^{*a*}N1 is obtained from a single Gaussian fit to the first peak in $4\pi r\rho(r)$ multiplied by the nearest neighbor distance, (d_{NN}), the position of this Gaussian. Parentheses indicate that the coordination values were strongly dependent on the *r*-range included in the Gaussian fit due to the broad and asymmetric shape of the Ge-Ge first NN peak.

 b FWHM is obtained from the Gaussian fit and has been corrected for the experimental broadening caused by finite k-range and damping.

^cN2 is simply the area under $4\pi r^2 \rho(r)$ (the PPDF) from r = 0 to 3.7 Å with the appropriate density, $\rho_{\alpha\beta}$ or ρ_o .



Figure 7.12: Representative single Gaussian fits (dashed lines) to the first near neighbor peaks of the experimental PPDFs (solid lines) and the residual (dotted line). The exact parameters depend on the range fitted, and the central values for the best fits are in Table 7.2 above.

to the assertion. The exact coordination parameters for each PPDF depend on the r-range fitted, and the central values for the best fits are given in Table 7.2 above. The Ge-Ge PPDF coordination parameters are strongly dependent on the r-range included in the single Gaussian fit due to the broad high-r side of the first peak. This is a clear indication that there are numerous Ge-Ge NN distances present.

The final coordination number included in Table 7.2 is N2, the area under the PPDF from r = 0 - 3.7 Å. N2 provides a common basis for comparing the present data with Kortright's earlier scattering work on the system. In addition, the areas under the DDFs can be shown to be consistent with the areas under PPDFs for identical r-ranges as expected from the internal consistency tests in Section 7.1: The sum of N2 for the Ge-Ge PPDF and Ge-Mo PPDF gives 11.7 near neighbor atoms for Ge which agrees well with N2 for the Ge DDFs, 11.7 atoms. Similarly, the sum of N2 for the Mo-Mo PPDF and Mo-Ge PPDF is 10.9 atoms which is in good agreement with the 10.8 atoms from the Mo DDF. The Mo DDF, as expected, shows the sharp, well-defined Mo-Ge correlations at low r followed by the Mo-Mo correlations about 0.5 Å further out in r. The Ge DDF, on the other hand, is comprised of broad Ge-Ge correlations and sharper Mo-Ge correlations, and it shows an average first NN distance intermediate to the Mo-Ge distance and the nominal Ge-Ge distance. The high number of near neighbors for both Mo and Ge indicate that a-MoGe₃ is quite densely packed relative to the open tetrahedal network found in a-Ge.

The Mo-Ge first NN distance is the shortest distance present in the alloy and is well-defined. This is consistent with the strong attractive interaction known to exist between Mo and Ge from the Mo-Ge equilibrium phase diagram which contains many line compounds exibiting negligible solid solubility of both Mo and Ge. The Ge-Ge first NN distance is intermediate to the other NN distances and is very broad indicating a large degree of disorder in the local Ge-Ge NN distances. The Mo-Mo first NN distance is the longest, concurrent with Mo-Mo avoidance, and this distribution is also relatively well-defined. The Mo-Mo coordination is most likely determined by the constraints of the strong Mo-Ge interactions. Kortright was able to successfully extract the Mo-Mo PPDF from a 65% Mo sample [1]. (It was the most heavily weighted partial and least sensitive to error). The Mo-Mo first NN distance for that alloy composition is $d_{NN}^{MoMo} = 2.78$ Å $\approx 2 \cdot r_{metallic}^{Mo}$ indicating the presence of Mo-Mo first NN distance is $d_{NN}^{MoMo} = 3.21$ Å $> 2 \cdot r_{metallic}^{Mo}$. This lends further credence to the assumption that the Mo-Mo coordination is determined by the Mo-Ge interaction in a-MoGe₃.

From the singular value decomposition analysis described in Section 2.5.2, the Mo-Ge distribution is expected to be the least sensitive to error and most trustworthy. The Mo-Mo PPDF is expected to be most prone to error. In addition, the error in the Mo-Ge PPDF is expected to be opposite in sign to the error in the Mo-Mo and Ge-Ge PPDFs. With this in mind, the puzzle of the local structure can approached by beginning with the Mo-Ge PPDF.

The most definitive feature of the Mo-Ge distribution is the sharp NN peak (FWHM=0.39 Å after correction for broadening from finite k-range and damping). The position, 2.67 Å, and area of the peak (N1=8.0 Ge atoms) are consistent with a regular eight-fold coordination of Mo by Ge. This is less than the regular ten-fold coordination of Mo by Ge found in crystalline β -MoGe₂ at 2.72 Å. The a-MoGe₃ Mo-Ge coordination is more regular than that of the lower symmetry α phase which has 10 Ge NNs over distances ranging from 2.4-3.4 Å.

This decrease in the Mo coordination from 10 to 8 Ge atoms in going from crystalline MoGe₂ to amorphous MoGe₃ is counterintuitive and not yet fully understood. There are several possible ways to arrange 8 Ge atoms about Mo. One can consider regular arrangements such as a cube or tetragonal antiprism or even completely nonregular arrangements such as in the $Mo[CN]_8^{4-}$ complex in which four ligands lie at 34° from a vertical axis and four at 73° . Looking to the crystal structures for possible clues to explain this counterintuitive trend, we find that the β -MoGe₂ structure is characterized by repeated trilayers consisting of sheets of Mo atoms sandwiched between two sheets of Ge atoms as drawn schematically in Figure 7.13 a). The two sheets of Ge atoms above and below a Mo sheet give rise to 8 of the 10 Ge NNs to Mo. The final 2 Ge NNs reside in neighboring trilayers. We may consider pulling the trilayers apart and, in the process, losing the two Ge NNs from the neighboring trilayers as illustrated in Figure 7.13 b). This leaves 8 Ge NNs to Mo which can relax and reorganize within the trilayer. The Mo-Ge distance in the amorphous alloy is about 0.05 Å shorter than in the β -MoGe₂ crystal, a significant, measurable difference. As a final step, the layered structure is disordered, and additional Ge is added to reach the $MoGe_3$ composition shown schematically in Figure 7.13 c). Evidence that a layered structure is not retained in a-MoGe₃ include an average Mo-Ge-Mo bond angle (74°) > 70.5°, a Mo-Mo NN distance d_{MoMo} > 3.08 Å, and a Mo-Mo coordination number $N_{MoMo} < 4$ where the values cited are those expected for the layered structure. (The Mo-Ge-Mo bond angle is determined from the experimental Mo-Mo and Mo-Ge distances.) In addition, previous work [3, 4] shows that the Ge atoms are uniformly distributed throughout these materials. Although this is a very simple, initial picture, it offers some useful insight into the 8-fold coordination of Mo

by Ge in the a-MoGe₃ phase.


Figure 7.13: Schematics illustrating the possible transition from (a) 10-fold coordination of Mo by Ge atoms in the trilayer structure found in β -MoGe₂ through an intermediate structure (b) in which the trilayers are pulled apart so that Mo loses two of its Ge nearest neighbors to the final structure (c) in which the layer structure is disrupted by disorder and the insertion of additional Ge atoms to achieve the 8-fold coordination of Mo by Ge atoms and the total composition of *a*-MoGe₃.

Interestingly, Kortright obtained similar coordinations for Mo. Since the first peaks in the Ge and Mo DDFs occur at the same position, he was able to infer that the first peak in his Mo DDFs corresponded to the Mo-Ge coordination and found about 8 or 9 Ge atoms about Mo in samples of 14 and 42% Mo. These compositions bracket both the *a*-MoGe₂ and *a*-MoGe₃ compositions indicating that 8-fold coordination of Mo by Ge is a characteristic of these sputter-deposited Ge-rich amorphous alloys.

This eight-fold coordination of Mo by Ge, in turn, necessarily implies that the average Ge has 3.0 Mo neighbors at the same distance (provided the material is not phase separated, an assumption tested above). Determining the precise Ge coordination from the PPDFs has not been possible thus far because the initial Ge-Ge peak at ~ 3.0Å is broad and poorly resolved on its high-r side. In β -MoGe₂, each Ge is coordinated by 5 Mo and 5 Ge atoms at 2.72 Å. This implies that excess Ge can be accomodated by additional Ge neighbors and fewer (3.0) Mo neighbors about Ge.

If the Ge atoms coordinating a Mo atom were arrayed on a cube, the Ge-Ge separation would be 3.08 Å. When the first Ge-Ge peak is fit with two Gaussians, one constrained to lie at 3.08 Å, we find 3.5 Ge atoms at that distance and 3.0 Ge atoms at 2.69 Å (close to the Mo-Ge NN separation of 2.67 Å). This implies that the average Ge nearest neighbor coordination (3.0 Ge atoms plus 3.0 Mo atoms) is less than its ten-fold value in β -MoGe₂. There are a number of ways this could be achieved through various combinations of Ge coordinations, and further elucidation of the Ge coordination will require modelling.

The first Mo-Mo distance at 3.21 Å corresponds well to the shortest Mo-Mo distance, 3.32 Å, in β -MoGe₂. The peak is rather sharp (FWHM=0.35 Å) with an area of about 1.8 atoms (examined in Section 7.6.4). As discussed earlier, the Mo-Mo coordination is thought to be determined by the attractive interaction between Mo and Ge.

For a three-dimensional representation of this chemically-specific one-dimensional data, a modelling method like Reverse Monte Carlo (RMC) will be required. While RMC modelling can provide a physical model for this structure that agrees with the scattering data, it will not be a unique solution, and it will tend to be the most disordered solution that agrees with the data as discussed in Section 2.6. The present PPDFs provide a much more detailed set of initial conditions for such modelling than the RDFs typically available for an amorphous structure, and they considerably narrow the field of solutions available.

7.5 Comparison of PPDF Results with Previous EXAFS Results

Because of the relative ease of sample preparation and experiment, EXAFS is a more widely used technique for examining the atomic-scale, local structure of amorphous materials than the anomalous x-ray scattering techniques. The results from this technique have frequently been questioned, however, because of its limitations in dealing with disorder and asymmetry in atomic near neighbor distributions. (For examples, see Reference [110] and citations therein.) Kortright and coworkers [1, 2] carried out a systematic study of the amorphous sputter-deposited Mo-Ge system over Mo concentrations ranging from 0% (a-Ge) to 70% Mo using both EXAFS and DDFs from AXS. In this section, the results from the experimental PPDFs of a-MoGe₃ are compared with Kortright's EXAFS results.

Although both AXS and EXAFS yield chemically-specific coordination information, the results are frequently complementary because the techniques access different

k-ranges as discussed briefly in Section 2.4.1. Scattering from an amorphous material generally consists of a few strong peaks at low k containing information about distant and disordered coordinations and a more-or-less single frequency oscillation at high karising from the first NN distance [1]. For the anomalous x-ray scattering techniques, the available k-range is between $\sim 1 \text{ Å}^{-1}$ and k_{max} . This region encompasses the low-k region, but the extent of the high-k region available depends on the energy at which data are collected since $k_{max} = \frac{4\pi}{hc}E$. For the present work, $k_{max} = 10 \text{ Å}^{-1}$. Kortright's EXAFS data encompass the high-k region extending from $k = 6 - 30 \text{ Å}^{-1}$ where k is the scattering vector as defined in AXS. ($k = 2k_{EXAFS}$ since the backscattered photoelectron in EXAFS travels twice the distance to a neighboring atom.) These differences in the collected k-range lead to different sensitivities: The EXAFS is primarily sensitive to very near neighbors in narrow, well-defined coordination shells. The lack of low-k data means that information about more distant coordination shells is missing entirely. Oscillations from a broad, disordered or asymmetric first coordination shell are strongly damped in the k-range sampled by EXAFS so that information may be lost even about the first coordination shell. Anomalous scattering samples the overall shape of the atomic distribution functions but, lacking the high-k data, the sharper detail of the features are missing. Kortright found that, for a short, well-defined first coordination shell such as that present in a-Ge, the EXAFS and DDFs gave nearly identical results for NN distances and coordination shell widths. For the amorphous Mo-Ge alloys, however, EXAFS results generally indicated shorter and narrower coordinations than the DDFs. Kortright surmised that those differences were due to asymmetric first coordination shells about Mo and Ge. Difficulties in studying amorphous materials with broad or asymmetric coordinations have been noted by previous workers [110, 111].

Like the DDFs, EXAFS provides information about the nearest neighbors of a given species. Unlike the DDFs, this information can be obtained by modelling of the EXAFS oscillations directly in k-space as well as through a Fourier transform to real space. The absorption data, collected at both elements' edges, is normalized to the Cromer-Liberman values far from the edge. Using only the data above the edge energy, the data are converted to k-space by

$$E - E_o = \frac{\hbar^2 k^2}{2m}$$

where E_o is the zero of the photoelectron energy scale and k, in this context, refers to k_{EXAFS} . The data are then weighted by k^n (where n = 3 in Kortright's work) to emphasize the high-k oscillations. Polynomial fits are subtracted leaving only the oscillations or EXAFS, $k^3\chi(k)$. The EXAFS are then fit with the following equation:

$$k^{n}\chi_{\alpha}(k) = k^{n-1}\sum_{\beta} \frac{N_{\beta}}{R_{\alpha\beta}^{2}} e^{-2\sigma_{\alpha\beta}^{2}k^{2}} |f_{\beta}(\pi,k)| \sin\left(2kR_{\alpha\beta} + \phi_{\alpha\beta}(k)\right)$$
(7.4)

The absorbing atom is designated α and the backscattering atom, β . $R_{\alpha\beta}$ is the distance between α and β , N_{β} is the number of β atoms at a distance $R_{\alpha\beta}$ from α , $\sigma_{\alpha\beta}$ is the Gaussian standard deviation of the coordination shell due to static and thermal broadening. The backscattering amplitude of the β atom is given by $f_{\beta}(\pi, k)$, and the total phase shift of the backscattered photoelectron, by $\phi_{\alpha\beta}(k)$. Kortright allowed R, N and σ^2 to vary using Gaussian shells to model the data. Gaussians are appropriate for materials with symmetric, relatively-narrow coordination shells. Mean free path, many-body and multiple-scattering effects were neglected in Kortright's analysis. These effects were expected to cause the coordination numbers, N, to be smaller than the actual coordination numbers.

Table 7.3: The coordination parameters from EXAFS from Kortright's 25% Mo sample. The best self-consistent fits were a two-shell fit of Ge and Mo to the Ge EXAFS and a one-shell fit of Ge to the Mo EXAFS.

	R(Å)	N_{Mo}	FWHM $(Å)^a$	Σ^{b}
Ge-Ge	2.69	0.75	0.279	
Ge-Mo	2.59	0.64	0.178	0.128
Mo-Ge	2.59	3.59	0.212	0.043

^{*a*}FWHM is obtained from Kortright's σ^2 values.

 ${}^{b}\Sigma$ represents the goodness of the fit defined as the sum of squares of the residuals between the model and data divided by the sum of squares of the data.

At the Ge K edge, Kortright found that the best self-consistent fit to the data was a two-shell fit with one Mo shell and one Ge shell. For his 25% Mo sample, the Mo shell had a distance of 2.6 Å, a coordination number of 0.6, and a narrow FWHM of 0.19 Å. The Ge shell was located at 2.7 Å with 0.8 atoms and a much wider FWHM of 0.28 Å. Mo continued to be the nearest neighbor to Ge from 25% Mo to at least 65% Mo. Below 23% Mo, the Ge EXAFS was well-fit by a narrow first shell of Ge atoms at 2.45 Å, the tetrahedral Ge distance, a piece of the evidence for phase separation in the Ge-rich compositions.

At the Mo K edge, Kortright found a one-shell fit of Ge atoms gave the best selfconsistent fit to the data for the 25% Mo sample. He found a nearest neighbor distance of 2.6 Å for the 3.6 Ge atoms about Mo. The FWHM of this Mo-Ge shell, at about 0.21 Å, was much smaller than the Ge first shell about Ge. These results are given in Table 7.3 with the results for the Ge K edge EXAFS described above. Kortright found that the Mo nearest neighbor environment remained the same between ~ 25 and $\sim 42\%$ Mo. Below 23% Mo, the 2.6 Å distance to Ge nearest neighbors was still present, but the number of Ge atoms about Mo increased with decreasing Mo

a-Mo ₂₇ Ge ₇₃	d_{NN}	$N1^a$	$\mathrm{FWHM}_{tot}{}^{b}$
$\approx a$ -MoGe ₃	$(\text{\AA}\pm0.02)$	(atoms ± 0.1)	$(Å \pm 0.02)$
$PPDF_{GeGe}$	(2.96)	(7.9)	(0.94)
$PPDF_{GeMo}$	2.67	3.0	0.54
$PPDF^*_{MoGe}$	2.67	8.0	0.54
$PPDF_{MoMo}$	3.21	1.8	0.52

Table 7.4: Local coordination parameters for a-MoGe₃ excerpted from Table 7.2 and with total FWHM values not corrected for experimental broadening.

^{*a*}N1 is a single Gaussian fit to the first peak in $4\pi r\rho(r)$, and the nearest neighbor distance (d_{NN}) is obtained from the position of this Gaussian. Parentheses indicate that the first peak was not fit well by a single Gaussian distribution.

 ${}^{b}\text{FWHM}_{tot}$ is obtained from the Gaussian fit and has NOT been corrected for the experimental broadening.

content.

For direct comparison with Kortright's EXAFS coordination results in Table 7.3, a portion of Table 7.2 which contains the coordination parameters for the present a-MoGe₃ sample is reproduced in Table 7.4 with FWHM_{tot} not corrected for experimental broadening. These comparisons are presented below.

Of the possibilities, the Mo-Ge coordination shell, with the shortest NN distance in the amorphous alloy and one of the narrower NN peak widths, should be best represented by modelling the EXAFS. A comparison of Tables 7.3 and 7.4 shows that the EXAFS predicted a coordination shell $2\frac{1}{2} - 3$ times narrower than in the PPDFs obtained by anomalous scattering. Kortright showed that the experimental broadening of his EXAFS and RDF were nearly the same (0.42 Å and 0.38 Å) for *a*-Ge, and the experimental broadening for the present PPDFs is 0.38 Å as well. So, the narrower coordination obtained by EXAFS is not due simply to differences in experimental broadening but likely arises because the EXAFS sees only the low-*r* part of this somewhat broad, likely-asymmetric coordination shell. As a result, the peak width is too narrow, and the position, perhaps too short by 0.1 Å.

The situation worsens for the Ge-Ge coordination shell. Here, the Ge-Ge PPDF clearly shows a broad, highly disordered first coordination shell. It has a poorly defined high-r side making it difficult to fit with a single Gaussian. Since it is quite asymmetric (broader on the high-r side), it is no surprise that the EXAFS gives a NN distance significantly shorter than the PPDF distance by 0.3 Å. The EXAFS peak width is three times narrower than the scattering peak width indicating that the EXAFS misses all but the sharper, low-r side of the coordination shell.

The Mo-Mo coordinations seen in the PPDFs near 3.2 Å are evidently too far away for the EXAFS to reproduce reliably. In addition, the coordination numbers from the EXAFS analysis are far too small to be accurate for any of the coordinations discussed. In modelling tests on Ge and Mo_3Ge , Kortright found that the coordination numbers he obtained were 30-56% too low due to neglected effects and, perhaps, error in calculated values of the backscattered amplitudes. As such, we ignore the EXAFS coordination numbers.

Thus, in part *because* the EXAFS and AXS techniques sample complementary regions of k-space, Kortright's EXAFS results do not give an accurate representation of the local and intermediate structure in a-MoGe₃, a material with high static disorder because of the broad, probably asymmetric (certainly asymmetric in the case of Ge-Ge) first NN coordination shells. Rigorous modern analysis methods [57, 112, 113] of EXAFS data incorporating lower k data (strongly affected by the effects, such as multiple-scattering, neglected in Kortright's analysis) and permitting asymmetry of distributions are now available, and the efficacy of these methods has been tested by comparing EXAFS and neutron diffraction studies of a-Ge [113]. The Mo-Ge alloys, however, display much longer and less well-defined coordination shells than a-Ge. In fact, Kortright found reasonable agreement between the coordination distances from his EXAFS and DDFs for a-Ge. Although it is likely that more rigorous EXAFS analyses would yield improved agreement between the scattering and EXAFS coordination results for a-MoGe₃, it is not clear how complete the agreement would be. Such a study is beyond the scope of the present work; however it offers the interesting possibility of comparing the information about coordination widths and asymmetry from EXAFS to that obtained from high-quality PPDFs on a sample with large average static disorder like a-MoGe₃.

7.6 Stability of Coordination Results with Respect to Error

It is no simple task to determine how errors in the elastic intensity, which is measured in k-space, propagate into the PPDFs in real space, but we hope to be able to determine how sensitive the coordination results from the extracted PPDFs are to error in the intensity measurements. To do so, we observe the effect of error *purposefully introduced* into the intensity measurements.

There are two types of easily introduced error: an error in the normalization constant and an error in the background constant. Note that both of these types of errors should ideally be removed by the Fuoss normalization discussed in Section 5.4; however, the precise normalization parameters depend on the k-ranges selected for the integral and large-angle normalization equations. As such, small errors are possible in both background and normalization constants even using the Fuoss normalization. There are, of course, other k-dependent errors potentially present in the elastically scattered intensity from any given AXS experiment. (For example, using a wide detected energy window can lead to Compton scattering that is only partially discriminated against. This would give rise to an error that increases and then decreases as a function of increasing k.) One of the dangers of the Fuoss normalization method mentioned earlier in this chapter is that some error with a different k dependence may be partially-compensated yielding an incorrect overall shape for the final normalized intensity. As such, beginning with the cleanest possible elastic scattering data is vital. Since the functional form of such k-dependent errors is very specific to the experimental setup, only the normalization constant and background constant errors are explored here.

The corrected and normalized experimental intensity, I_o (assumed to be relatively error-free for the purpose of addressing the question of coordination result stability), is modified to include an introduced error as follows:

$$I_{mod} = I_o(1+\delta) + b.$$

For simplicity, only the cases of $\delta = 0, b \neq 0$ and $\delta \neq 0, b = 0$ are considered. This error-contaminated intensity can then be introduced into the Munro matrix to observe the impact on the final PPDFs.

7.6.1 Background Error

It is clear that applying identical background errors in both of the intensities comprising the difference below the Mo or Ge edge will have no effect on the final PPDFs since the backgrounds will simply subtract out. Non-equal background errors in the intensities comprising a difference are expected to have the same effect as a background error in the final row of the Munro matrix (see Equation 2.24) which does not involve a difference, so we apply a background error only in the final row of the Munro matrix while keeping $\delta = 0$.

A background error of $\pm 1\%$ of the maximum intensity in the final row of the Munro matrix results in $\pm 3\%$ change in N1 (the number of near neighbors from a Gaussian fit to the first peak) for the Mo-Mo PPDF and $\pm 1\%$ change for the Mo-Ge PPDF. (Since the Ge-Ge first near neighbor peak is not well-fit by a single Gaussian, it is not considered here.) The first peak position, d_{NN} , does not change for the Mo-Ge PPDF with this low level of background error, but d_{NN}^{MoMo} varies by ± 0.01 Å. Figure 7.14 shows the effect of a background error on the total structure factor measured 100 eV below the Mo edge: a smoothly varying function, $b/\langle f \rangle^2$, is added to the structure factor. The magnitude of error seen for a $\pm 1\%$ background error could easily arise if inappropriate limits of integration were chosen for normalization of data that does not extend to high k where the elastic scattering approaches the coherent scattering. The graph on the left in Figure 7.15 contains the three PPDFs extracted from the Munro matrix with $\pm 1\%$ background error. The visual appearance of the PPDFs is not strongly affected by this level of background error.

Increasing the background error to $\pm 3\%$ of the maximum intensity results in a dramatic degradation of the quality of the PPDFs. Both the Mo-Mo and Ge-Ge PPDFs have such strong oscillatory behavior that fitting a single Gaussian to the first NN peak is not meaningful. The Mo-Ge PPDF has a $\pm 5\%$ change in N1 and a ± 0.03 Å change in d_{NN}^{MoGe} . The graph on the right side in Figure 7.14 shows the obvious impact of this large error on the normalization of the total structure factor. The graph on the right side in Figure 7.15 contains the three PPDFs extracted from



Figure 7.14: The total structure factor 100 eV below the Mo K edge obtained for positive, negative and no purposefully-introduced background error in the intensity. $\pm 1\%$ background error is on the left side and $\pm 3\%$, on the right.



Figure 7.15: The PPDFs extracted from the Munro matrix containing the background-error-contaminated intensity in the final row of the Munro matrix. Positive, negative and no background error are considered. $\pm 1\%$ background error is presented in the graph on the left side and $\pm 3\%$, on the right.

the Munro matrix with this error-containing intensity in the final row of the Munro matrix. The lower sensitivity of the Mo-Ge PPDF to error, and the mirroring between the Mo-Ge PPDF and the Mo-Mo and Ge-Ge PPDFs are now very clearly seen.

7.6.2 Normalization Constant Error

An error in the normalization constant will have the effect of adding a factor of $(\delta I_o(k))/\langle f \rangle^2$ to the structure factor. Unlike an error in the background constant, this error is not a simple, smoothly-rising function of k: It will be modulated by the oscillations of the intensity as a function of k. As before, we begin by applying this type of error only in the final row of the Munro matrix. A normalization constant error of $\pm 1\%$ corresponds to $\delta = 0.01$ and gives a $\pm 3\%$ change in N1 for the Mo-Ge PPDF and $\pm 5\%$ for the Mo-Mo PPDF. The first peak position, d_{NN} , does not change for the Mo-Ge PPDF with this level of normalization constant error, but d_{NN}^{MoMo} varies by ± 0.02 Å.

Increasing the normalization constant error to $\pm 3\%$ naturally increases the errors seen in the PPDFs (relative to the experimental PPDFs). The number of near neighbors in the first coordination shell, N1, from the Mo-Ge PPDF changes by $\pm 10\%$. For the Mo-Mo PPDFs, the change is $\pm 16\%$. d_{NN} varies by only ± 0.01 Å for the Mo-Ge PPDF, but d_{NN}^{MoMo} varies by ± 0.06 Å. As with the background constant error, the Mo-Ge PPDF is demonstrably least sensitive to introduced normalization constant error, and the mirroring between the Mo-Ge PPDF and the Mo-Mo and Ge-Ge PPDFs is evident.

Another possibility to explore is the presence of a normalization constant error in the intensities comprising one of the differences below an edge. Since identical limits of integration are usually chosen for normalizing data taken below a given edge, it



Figure 7.16: The total structure factor 100 eV below the Mo K edge obtained for positive, negative and no purposefully-introduced normalization constant error in the final row of the Munro matrix. $\pm 1\%$ normalization constant error is presented in the graph on the left side and $\pm 3\%$, on the right.



Figure 7.17: The PPDFs extracted from the Munro matrix containing the intensity contaminated by a normalization constant error in the final row of the Munro matrix. Positive, negative and no normalization constant error are considered. $\pm 1\%$ normalization constant error is presented in the graph on the left and $\pm 3\%$, on the right.

is most likely that a normalization constant error would be present in the intensities from both energies below that edge. Introducing $\pm 1\%$ normalization constant error in the intensities below the Ge edge results in $\pm 2\%$ error in N1 for the Mo-Ge PPDF and $\pm 5\%$ error in N1 for the Mo-Mo PPDF. d_{NN}^{MoGe} does not change, and d_{NN}^{MoMo} changes by ± 0.02 Å. Increasing the error to $\pm 3\%$ gives $\pm 7\%$ change in N1 for the Mo-Ge PPDF and $\pm 10\%$ change in N1 for the Mo-Mo PPDF. The change in NN distances also increases: ± 0.01 Å for the Mo-Ge peak and ± 0.04 Å for the Mo-Mo peak. Figure 7.18 contains the PPDFs extracted from the Munro matrix with the two levels of introduced normalization constant error in both intensities measured below the Ge edge.



Figure 7.18: The PPDFs extracted from the Munro matrix containing the intensities contaminated by a normalization constant error. Positive, negative and no normalization constant error are considered. The error is introduced into both of the intensities comprising the difference below the Ge K edge. $\pm 1\%$ normalization constant error is presented in the graph on the left and $\pm 3\%$, on the right.

7.6.3 Conclusions about the Impact of Introduced Error

It is gratifying to note that nearly all errors introduced lead to a degradation of the quality of the final PPDFs extracted from the Munro matrix. If a variation in the background or normalization constants had yielded a significant improvement in PPDF quality, it would suggest that the optimal values had not been used in the earlier analyses. Possible exceptions are the addition of +1% normalization constant error in the final row of the Munro matrix and -1% normalization constant error in both intensities comprising the difference below the Ge edge. Although the catalog of errors tested is by no means complete, we may estimate the coordination number uncertainties to be ~ 3% for the Mo-Ge PPDF and ~ 5% for the Mo-Mo and Ge-Ge PPDFs based upon the variation of coordination number with these 1% normalization constant errors.

The uncertainties for the various introduced errors are only valid for the specific Munro matrix equation studied here, but the trends in PPDF behavior response to the introduced errors allow us to draw some general conclusions about the impact of errors. First, the differences of intensities below each edge are highly effective at removing background constant errors, and they greatly reduce the impact of normalization constant errors provided the two intensities in the difference have been normalized similarly. Errors in the final row of the Munro matrix (which does not involve a difference of two intensities) are the biggest liability to PPDF reliability. Background constant errors in the final row have a strong negative impact on PPDF quality, but these errors are also easy to detect in the total structure factor, SF, for that intensity measurement and therefore are unlikely to be pass unnoticed into the Munro matrix. Normalization constant errors in the final row of the Munro matrix are less noticeable in the SF but have a strong effect on the PPDFs. It is thus best to use data collected at high energy in the final row of the Munro matrix since normalization to a per-atom basis is less ambiguous for data extending to high k_{max} .

7.6.4 A Conservative Estimate

A more conservative approach to uncertainty estimation considers the magnitude of the oscillations at distances shorter than the first NN peak. If the oscillations were to continue into the first peak, the maximum change they might cause in the first peak area is assumed to be the area of the largest oscillation (positive or negative peak) before the first NN peak. This gives ~ 4% uncertainty in the Mo-Ge coordination number, ~ 2% uncertainty in the Ge-Ge coordination number and ~ 14% uncertainty in the Mo-Mo coordination number. This Mo-Mo coordination number uncertainty is larger than cited above, and this results in 1.5 - 2 Mo atoms about the average Mo atom in *a*-MoGe₃. Thus, final conservative estimates of coordination number uncertainties are ~ 5% for the Mo-Ge and Ge-Ge PPDFs and ~ 15% for the Mo-Mo PPDF. These uncertainties are greatly reduced from those in previous work [28] on a similarly-conditioned system.

7.7 Role of $MoGe_3$

In the equilibrium Mo-Ge phase diagram, there are many line compounds with no appreciable solid solubility. Kortright's earlier comparisons of the Mo and Ge DDFs from > 23% Mo samples with the PPDFs of the crystalline line compounds led him to believe that the local order in the amorphous alloys was like that of the Ge-rich intermetallics. Perhaps then, there exists a unique MoGe₃ compound in the amorphous system. The present data offer sufficiently reliable, low uncertainty

coodination information that this question can be answered: Taken as a whole, the PPDFs for a-MoGe₃ are not indicative of a locally well-ordered amorphous compound. Although the attractive Mo-Ge interaction introduces some local short-range chemical ordering, as a whole, the alloy displays very high static disorder especially in the Ge-Ge correlations. While some of the intermetallics also have high local disorder, a more apt description of the structural information available for MoGe₃ is a solid solution of Ge and Mo in which the relaxation of crystallographic constraints allows a high range of solid solubility in the alloy. The MoGe₃ endpoint is then simply the solubility limit beyond which additional Ge added to the amorphous sputter-deposited alloy precipitates out as a second phase, a-Ge.

Chapter 8

Conclusions and Future Work

The original goals of this work were two-fold. We sought to improve the reliability of partial pair distribution functions obtained from anomalous x-ray scattering (AXS), and specifically, to elucidate the structure of *a*-MoGe₃, the endpoint for phase separation in Ge-rich amorphous sputter-deposited Mo-Ge alloy films. In the process, a number of specific questions have been answered:

- Can experimental removal of inelastic scattering improve the quality of partial pair distribution functions (PPDFs) obtained by anomalous x-ray scattering?
- Are these PPDFs, extracted without regularization methods, reliable?
- What can be said of the structure of *a*-MoGe₃?
- Does the MoGe₃ composition correspond to a new compound in the amorphous material with strong local ordering as suspected by previous workers?
- What new questions are raised by these results?

The answers to these questions are summarized in this chapter followed by a discussion of future work which will address the following two questions:

- What specific experimental improvements can be undertaken to obtain cleaner elastic scattering data from *a*-MoGe₃?
- Anomalous x-ray scattering experiments are notoriously difficult. How can the technique of PPDF extraction be made more universally-available in the future?

8.1 Experimental Removal of Inelastic Scattering

Although there are mathematical regularization methods designed to stabilize the illconditioned matrix equation which must be solved in order to obtain the final product, the PPDFs, these methods address only random errors and completely neglect systematic errors. In forcing physical behavior of the distribution functions in certain regions, they may distort the results in others. As such, it is preferrable not to rely on regularization methods as a means of extracting reasonable PPDFs. Such methods should instead be applied to reduce the impact of statistical errors on data already free of systematic errors.

By experimentally reducing the error in the initial data, much cleaner data requiring few corrections were obtained in these anomalous scattering experiments. The partial structure factors (PSFs) for *a*-MoGe₃ extracted from the Munro matrix without regularization were shown to be solutions of the original matrix equation by reconstructing the total and differential structure factors. The PPDFs were obtained by sine Fourier transform of the PSFs.

Experimental removal of inelastic scattering yields marked improvements in the reliability of these PPDFs obtained from anomalous x-ray scattering. Prior work relied on subtraction of calculated values of inelastic scattering which implicitly assume detector response is constant over all photon energies. Direct comparisons between an earlier PPDF study [28] using the Munro matrix on a similarly-conditioned system, *l*-GeBr₄, and the present study of *a*-MoGe₃ show that the maximum amplitude of non-physical atomic density is reduced from 75 to 22% of the height of the first nearest neighbor peak. The *l*-GeBr₄ study involved subtracting calculated values for Compton scattering which assume the detector is equally efficient at collecting all energies of scattered photons. In addition, the K_{β} resonant Raman scattering was removed as a constant in the Fuoss normalization. Neither of these systems were solved using regularization methods. Since there remain additional modifications that can be implemented in the experimental system, it is expected that the quality of the PPDFs can be even further improved through experimental improvements alone.

Key steps in the collection and analysis of the scattering data which contributed to the improved quality of the PPDFs are summarized below:

- Use of a graphite analyzer crystal and position-sensitive detector allowed collection of energy-resolved scattered intensity as a function of the scattering vector magnitude, k. Detected energy resolutions were $\Delta E^{Mo} = 130$ eV and $\Delta E^{Ge} = 42$ eV at energies below the Mo and Ge K absorption edges respectively. This energy resolution allowed the separation of the elastic scattering from the inelastic contributions at each k-point.
- Removal of the sample substrate prior to data collection eliminated the need for an additional correction.
- The appropriate edge energy was verified between scattering data collection scans to ensure good energy stability particularly when working close to the absorption edge where the anomalous scattering factors vary strongly with

energy.

- All data entering the matrix equation were collected during a single synchrotron experiment so that any systematic errors present were as similar as possible, and data interrupted by a beamfill were not included in the data analysis.
- Absorption data, which yield the anomalous scattering factors (ASFs), were collected on the same sample and with the same incident energy resolutions as the scattering data to minimize errors in the ASFs.
- Correction constants were carefully measured, and corrections for absorption, detector nonlinearity, polarization and multiple scattering were applied to the elastically scattered intensity data.
- The Fuoss normalization, which combines the methods of Warren and Norman/ Krogh-Moe, was applied to the corrected elastic scattering data. Data taken at the highest energy (having the highest k_{max}) were more readily well-normalized and were referred to in normalizing data taken at lower energies.
- Finally, a Gaussian damping function that acts smoothly over the entire k-range was applied in the sine Fourier transform to real space.

8.2 Coordination Results and Their Reliability

Although there remain regions of small, non-physical, negative atomic density (particularly in the Mo-Mo PPDF) and some mirroring as predicted by singular value decomposition analysis, the magnitude of these effects is small enough that local coordination results can be extracted from the three PPDFs with small uncertainties. Because no MoGe₃ compound exists in the equilibrium phase diagram, tests were first conducted for the presence of a phase-separated mixture of *a*-Ge and *a*-MoGe₂ by fitting an *a*-Ge component in the Ge-Ge PPDF. The results were inconsistent with phase separation, and the coordination results from the PPDFs were interpreted as arising from a single phase as expected from previous studies on this system [2, 3, 4]. Comparisons of total and differential structure factors with those from Kortright's work [2] verified that the sample falls in the appropriate position in the progression of compositions in the amorphous, sputter-deposited Mo-Ge system. Thus, the present results were interpreted in light of the previous studies.

The coordination results are briefly summarized here: Simple Gaussian fits to the first nearest neighbor peaks in the PPDFs indicate that Mo is closely coordinated by about 8 Ge nearest neighbors at a distance of 2.7 Å. This short, reasonably-ordered Mo-Ge distance is consistent with the strong attractive interaction known to exist between Mo and Ge. The Mo-Mo coordination, the longest at 3.2 Å, is most likely determined by the constraints of the Mo-Ge interactions. Ge, on the other hand, has a very broad and disordered coordination by other Ge atoms peaking near 3.0 Å. Due to the large degree of disorder in Ge-Ge PPDF and limited real-space resolution inherent to the AXS technique applied near the Ge K absorption edge, more detailed structural information than that presented in Chapter 7 will require modelling.

Despite the local short-range order introduced by the attractive Mo-Ge interaction, all three PPDFs display apparent asymmetry in the first nearest neighbor peak, the Mo-Mo first near neighbor peak occurs at long distances, and the Ge-Ge first near neighbor peak is quite broad. These considerations lead to disagreement between coordination results from the PPDFs and from previous EXAFS studies carried out by Kortright and coworkers on sputter-deposited *a*-MoGe₃: Coordination distances given by EXAFS are too low and the coordination shell widths, too narrow. These effects are due to the differing k-ranges sampled by the two techniques and highlight the importance of quality PPDFs for determining the local and intermediate structure in highly-disordered amorphous materials having broad, potentially-asymmetric coordination shells.

Introduced errors in the PPDFs provide a measure of the uncertainties in the coordination numbers. Errors introduced in the row of the Munro matrix which does not involve a difference of two intensities were found to be most detrimental to PPDF quality, and normalization constant errors were more difficult to detect than back-ground constant errors in the normalization process. Based upon the normalization and background constant errors tested, we estimate the coordination number uncertainties to be $\sim 3\%$ for the Mo-Ge PPDF and $\sim 5\%$ for the Mo-Mo and Ge-Ge PPDFs. More conservative means of estimation give coordination number uncertainties of $\sim 5\%$ for the Mo-Ge and Ge-Ge PPDFs and $\sim 15\%$ for the Mo-Mo PPDF. These are remarkably low uncertainties for PPDFs obtained by AXS.

8.3 Relevance of the MoGe₃ Composition

Regan's work [3, 4, 77] on the amorphous, sputter-deposited Mo-Ge system indicated that at the Ge-rich compositions, samples were phase-separated into two phases with compositions of approximately pure Ge and MoGe₃ (23-27% Mo). Why do we find the MoGe₃ composition as the phase separation endpoint in the amorphous system rather than the MoGe₂ composition found in the crystal system? Is there a unique MoGe₃ compound with a distinct local atomic structure?

The amorphous, sputter-deposited a-MoGe₃ displays as its defining correlation the strong Mo-Ge interaction present in all of the crystalline Mo-Ge compounds. This observation led earlier workers to wonder if this composition corresponded to a unique MoGe₃ intermetallic compound present only in the amorphous system. We do not, however, find a distinct intermetallic compound with definitive local ordering. The PPDFs obtained by AXS on *a*-MoGe₃ indicate that, despite the local ordering of Ge about Mo, the alloy has a very high degree of static disorder not consistent with an intermetallic compound. A more appropriate view of the MoGe₃ endpoint for phase separation in the Ge-rich amorphous sputter-deposited Mo-Ge alloy films is that of a densely-packed alloy with a wide range of solid solubility for which ~ 75% Ge (~ 25% Mo) happens to be the solubility limit. The addition of more Ge results in the precipitation of a second phase of *a*-Ge. We speculate that such a wide range of solid solubility (30 - 75% Ge) in this system is made possible by the removal of crystallographic constraints and by the specific kinetics of the non-equilibrium deposition process.

8.4 New Questions

New questions are raised by these results on a-MoGe₃ that suggest new directions of research:

Since these amorphous alloy films are created by a highly non-equilibrium sputtering process, it would be interesting to see the effect of variations in deposition parameters or the deposition method on the phase separation endpoint in the system. Regan has already shown that the precise deposition parameters have an impact on the small angle x-ray scattering spectra obtained [77]. In addition, the critical composition for phase separation has been found to be different in the Fe-Ge amorphous system than in the Mo-Ge system [4]. The Fe-Ge system phase separates at a composition of 32 - 38% Fe nearer the digermanide compositions which is found in the equilibrium phase diagram. Since both Mo and Fe have partially-filled d shells, it would be interesting to investigate what leads to these differences in solid solubility in the amorphous systems.

Another interesting possibility for future work is a comparison of crystalline MoGe₂ with amorphous MoGe₂. The present results, when taken in context with Kortright's earlier work, indicate that the amorphous MoGe₂ alloy likely displays the 8-fold coordination of Mo by Ge atoms found in *a*-MoGe₃. This is in contrast to the 10-fold coordination in crystalline MoGe₂. Perhaps a 10-fold coordination is also possible in amorphous MoGe₂. Polymorphism or, more appropriately, poly*a*morphism is known to exist in many amorphous materials including ice and silica as well as some transition metal-metalloid alloys [114, 115]. A more direct, side-by-side comparison of the amorphous and crystalline forms of the same composition prepared using a variety of deposition parameters may provide insight into the different local environments possible in these alloys.

8.5 Future Work on *a*-MoGe₃

As noted in Chapter 6, the primary source of error entering the Munro matrix (from which the PPDFs were extracted) was the difference in intensities below the Mo edge. The functional form of this error suggested a few possible sources: incomplete removal of inelastic scattering due to have less-than-optimal detected energy resolution, a polarization correction error or an artifact introduced by insufficient statistics below the Mo edge. Specific improvements in the experimental design to produce cleaner elastic scattering data with higher statistics, better detected energy resolution and more accurate corrections are listed here. These improvements have, in fact, already been undertaken in a synchrotron experiment carried out in November and December of 2001.¹ The analysis of these data will provide a critical second test of the reliability of the PPDFs for a-MoGe₃.

Improved mechanical design of the post-sample instrumentation allows accurate and repeatable adjustment of the analyzer crystal position and curvature as well as the detector position. The total weight of the instrumentation is reduced, and the mechanical stability improved.

Due to limited hutch size, the position-sensitive detector (PSD) in the present work was placed at a defocussed position short of the focus. Working in parafocus geometry provides improved detected energy resolution without significant decrease in the dispersion of energies with position on the PSD. The improvement in detected energy resolution will allow the elimination of inelastic scattering down to lower kvalues and more complete separation of the K_{β} resonant Raman scattering peak from the elastic scattering peak for data taken near an absorption edge.

A second PSD optimized for efficiency at 20 keV provides better statistics at the incident energies below the Mo edge by allowing the collection of more data in less time. This will decrease the noise levels in the Mo DSF and, hopefully, the PSFs.

Collecting data over a wider k-range beginning at $k_{min} = 0.8 \text{ Å}^{-1}$ makes the extrapolation of structure factors to k = 0 a less variable process and increases confidence in the final real space distribution functions. In addition, the normalization

¹There was some concern about the stability of the sample since it was grown many years earlier; however, the preliminary RDFs look identical to those presented in Chapter 6. (Earlier scattering studies on Regan's samples also showed no crystallization or evolution of scattering profiles after 5-6 years of storage indicating that these amorphous alloys are very stable.)

for the data collected below the Ge edge can be improved by minimizing the difference between the resulting RDF and the RDF from data collected far below the Mo edge (assumed to contain negligible systematic error and to be well-normalized) cut off at the Ge edge k_{max} .

The conditioning of the Munro matrix is improved with scattering data taken 200 eV below the Mo edge instead of the 100 eV used in the present experiment. Figure 8.1 shows the improved conditioning expected. This will translate into smaller errors in the extracted PSFs and the PPDFs obtained by subsequent sine Fourier transform.



Figure 8.1: The condition number for the Munro matrix for various schemes of data collection at different sets of energies for MoGe₃. In the legend, the notation 'Mo d100-d15' refers to a difference in the Munro matrix between data taken at 100 and 15 eV below the Mo K edge, and 'Ge d100' refers to a single measurement taken 100 eV below the Ge K edge. Notice that using data taken at the Mo edge rather than the Ge edge for the 3rd equation in the Munro matrix problem gives a strong improvement in conditioning. Using an energy nearer the absorption edge as the high energy in the difference also provides rapid improvements.

The scattering plane was horizontal in the present experiment, but the percent horizontal polarization was a source of some uncertainty since the exact polarization of the synchrotron x-rays depends on the position from the center of the beam and the x-ray energy (through the scattering by the monochromator crystals). Measuring the polarization of the incident x-rays with the same experimental system during the same beamtime provides a check on the proper value.

Finally, the effect of errors in the ASFs entering the Munro matrix were not explored in this work; however, they clearly have an impact on the quality of the PPDFs obtained. Until now, the experimental errors have been significant enough that error due to the angular dependence of the ASFs has been negligible. Now that we have decreased the levels of error present in the PSF extraction problem, this may no longer be the case. See, for example, the discussion in Reference [116]. Future work may benefit from careful measurement of the angular dependence, particularly the change in f' which is of the order of 0.1-0.2 electrons, in addition to the traditionallymeasured energy dependence.

8.6 Improvements for Future AXS

Anomalous x-ray scattering for extraction of PPDFs has the potential to be an extremely powerful technique for structure determination in many systems. Because of its susceptibility to errors in experimentally-measured quantities, the experiment requirements are very stringent, and accurate knowledge of all instrumental parameters is necessary. As a result, the technique is not widely used, and experiments are often limited by necessary compromises and incomplete knowledge of the experimental instrumentation. This final section offers recommendations for future AXS experiments to make the technique more routinely available.

First, longer focal lengths (larger available hutch dimensions) than used in the present study would be advantageous. They will permit greater dispersion of energies on the PSD giving greater separation of the elastic and inelastic contributions to the scattering; however, additional care must be taken to eliminate air scatter through He or vacuum paths.

Second, anomalous scattering experiments can be more efficiently performed at brighter 3rd generation sources such as SPEAR3. Such sources offer more focussed flux density providing better scattering statistics in less time. The added flux density also will allow experimenters to work at narrower incident energy resolutions $\left(\frac{\Delta E}{E}\right)$ without resulting in unreasonable count times for the experiment. Coupled with good energy stability from the monochromator, this will permit measurements closer to the absorption edge energies for higher contrast. In addition, the higher energies accessible will provide higher resolution RDFs and allow the study of alloys containing heavier elements.

Because of the considerable amount of time required to set up the instrumentation for anomalous x-ray scattering experiments, the compromises that frequently must be made due to experimental limitations (such as hutch size) and the need for accurate knowledge of all instrumental parameters, experiments could be readily and repeatedly carried out at a dedicated beamline specifically designed for anomalous x-ray scattering at a 3rd generation source. To *benchmark* the progress made with these experimental improvements, a model compound such as l-GeBr₄ should be characterized.

Through optimization of the experimental instrumentation for energy resolution at a third generation source on a dedicated beamline, AXS may be used routinely in the future to extract PPDFs from binary alloys without the need for mathematical regularization methods.

Appendix A

Algorithms

Computer programs are essential to this work on anomalous scattering. The algorithms for carrying out the calculations necessary for data analysis have been in use for a few decades and have been ported and transferred and translated into various languages as more sophisticated programming languages have become available. The current code was moved from FORTRAN to Matlab which is especially efficient at matrix math. Because the original "intent" of the FORTRAN code, lacking sufficient comments, had to be deciphered in order to debug the present Matlab version, it is the purpose of this appendix to document the fundamental algorithms used so that future generations can easily decipher code – and potentially improve methods of calculation.

A.1 Fitting Experimental f''

The theory behind the fit has been described in Chapter 5. The Matlab version of this program is called fppfit.m and has a graphical user interface driver named fppfitg.m.

A.1.1 Input

• E vs. $\ln(I_o/I)$ – experimental data (energy versus natural logarithm of the ratio of the intensities upstream and downstream of the sample) about the K-edge of the atom of interest

- Z atomic number for the atom of interest
- region about the edge (in energy) to exclude from the fit to theoretical f''_{theor} values
- n maximum degree of polynomial to fit to the background,

$$B(E) = \sum_{n=0}^{3} C_n E^{-n}$$

which contains the natural logarithm of the detector function and the absorption tails from lower energy absorption edges. (1 < n < 6)

A.1.2 Fit

Theoretical values of f_{theor}'' (with units of electrons) are obtained for the atom and energies of interest. The equation

$$\ln\left(\frac{I_o}{I}\right) = C_1 + \frac{C_2}{E} + \frac{C_3}{E^2} + \dots + \frac{C_{n+1}}{E^n} + \frac{C_{n+2} f_{theor}''}{E}$$
(A.1)

is set up in matrix form where the coefficients, C_n , are sought:

$$\begin{pmatrix} \ln(\frac{I_o}{I})_{E_1} \\ \ln(\frac{I_o}{I})_{E_2} \\ \ln(\frac{I_o}{I})_{E_3} \\ \vdots \\ \ln(\frac{I_o}{I})_{E_{max}} \end{pmatrix} = \begin{pmatrix} 1 & \frac{1}{E_1} & \frac{1}{E_1^2} & \cdots & \frac{1}{E_1^n} & \frac{f_{theor}'(E_1)}{E_1} \\ 1 & \frac{1}{E_2} & \frac{1}{E_2^2} & \cdots & \frac{1}{E_2^n} & \frac{f_{theor}'(E_2)}{E_2} \\ 1 & \frac{1}{E_3} & \frac{1}{E_3^2} & \cdots & \frac{1}{E_3^n} & \frac{f_{theor}'(E_3)}{E_3} \\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots \\ 1 & \frac{1}{E_{max}} & \frac{1}{E_{max}^2} & \cdots & \frac{1}{E_{max}^n} & \frac{f_{theor}'(E_{max})}{E_{max}} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_{n+2} \end{pmatrix}$$
(A.2)

where the region near the absorption edge is excluded. (Note: Fitting the data to the theoretical values in this manner takes advantage of Matlab's matrix manipulation capabilities. Previous code has used linear least-squares methods.) The coefficients are now used to reconstruct the total fit and the background function. The background is then subtracted out of the experimental data, and the last coefficient is used to scale the data (multiplicative factor) to the per atom basis of the theoretical f''_{theor} values yielding f''_{exp} , the experimental f'' for the sample. From the optical theorem, the scaling factor also yields the areal number density of the atom in question for the sample:

$$\ln\left(\frac{I_o}{I}\right) - B(E) = \sigma_{\alpha}m_{\alpha}(\rho t)_{\alpha}$$
$$\sigma_{\alpha} = \left(\frac{2he^2}{m_ec}\right)\frac{1}{m_{\alpha}}\frac{f_{\alpha}''}{E}$$
$$(\rho t)_{\alpha} = \frac{m_ec}{2he^2}C_{n+2}$$
(A.3)

where σ_{α} is the mass absorption coefficient

A.1.3 Output

• E vs. $f_{exp}^{\prime\prime\alpha}$ – experimental values of the imaginary part of the ASF as a function of energy for the α atom in the sample [eV, electrons]

• $(\rho t)_{\alpha}$ – the areal number density of the α atomic species $[\text{\AA}^{-2}]$

The present code multiplies the C_{n+2} coefficient by $\frac{m_e c}{2he^2}$ to yield $(\rho t)_{\alpha}$ with units of $[\text{\AA}^{-2}]$. This output has been the source of some confusion in the past – primarily due to notation. n has been used to refer to the number density, and ρ has been used to refer to both mass and number densities. For example, in the expression for the mass

absorption coefficient, $\sigma = \frac{\mu}{\rho}$, ρ refers to a mass density, and in the expression for the linear absorption coefficient, $\mu = \frac{2he^2}{m_ec} \frac{f''}{E} \rho$, ρ refers to a number density. For this reason, the mass density is written expressly as $m_{\alpha}\rho_{\alpha}$ here. In addition, σ has been used to refer to both the absorption cross-section $[cm^2]$ and to the mass absorption coefficient $[\frac{cm^2}{g}]$.

A.2 Kramers-Krönig Transform

The Kramers-Krönig transform (or Kramers-Krönig dispersion relationship) is discussed in Chapter 2. The transform has the following form:

$$f'(\omega_o) = \frac{2}{\pi} \oint_0^\infty \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega$$
(A.4)

The Matlab version of the program which carries out this calculation is called *kramkron.m*. The procedure follows that outlined by Hoyt et al. [41]

A.2.1 Input

The user may input either

- E vs. $f_{exp}^{\prime\prime\alpha}$ experimental values of $f^{\prime\prime}$ as a function of energy for the sample and element of interest [eV, electrons]
- -or-

• E vs. $\ln(\frac{I_o}{I})$ – experimental x-ray absorption spectroscopy (XAS) data as a function of energy

-and-

• E vs. C(E) – the detector response function
as well as

- \bullet the sample composition
- Z the atomic number of the atom of interest

• region (in energy) over which to carry out the transform (f' values are only output from this region)

A.2.2 Calculation

The calculation of the transform involves integrating over a singularity at the edge energy. We first simplify the integral as much as possible:

$$f'(\omega_o) = \frac{2}{\pi} \oint_0^\infty \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega$$

$$= \frac{2}{\pi} \left[\underbrace{\int_0^a \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega}_{ans6} + \underbrace{\int_b^\infty \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega}_{ans5} + \underbrace{\oint_a^b \frac{\omega f''(\omega)}{\omega_o^2 - \omega^2} d\omega}_{A} \right]$$
(A.5)

$$\underbrace{\frac{2}{\pi} \underbrace{\oint_{a}^{b} \frac{\omega f''(\omega)}{\omega_{o}^{2} - \omega^{2}} d\omega}_{B}}_{B} = \underbrace{\frac{1}{\pi} \left[-\underbrace{\int_{a}^{b} \frac{f''(\omega)}{\omega + \omega_{o}} d\omega}_{ans3} - \underbrace{\oint_{a}^{b} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega}_{B} \right]}_{ans3} = \underbrace{\int_{a}^{a_{o} > a} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega}_{ans1} + \underbrace{\int_{b_{o} < b}^{b} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega}_{ans2} + \underbrace{\oint_{a_{o}}^{b_{o}} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega}_{ans4} + \underbrace{\int_{a_{o}}^{b_{o}} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega}_{ans4} + \underbrace{\int_{a}^{b_{o}} \frac{f''(\omega)}{\omega - \omega} d\omega}_{ans4} + \underbrace{\int_{a}^{b$$

The quantities ans1, ans2, ans3, ans5 and ans6 are all numerically integrable. The integrals ans5 and ans6 are carried out using a numerical integration built-in Matlab function using theoretical values of f'' in the regions from b to $50 \times K$ -edge energy and from the L_{III} -edge to a. The integral ans4 contains the singularity. We will first address *ans3* which contains no singularities: $\int_x^y \frac{f''(\omega)}{\omega+\omega_o} d\omega$. Carrying out a Taylor Series expansion of $f''(\omega)$ about ω_o and inserting it into the integral, we obtain

$$\int_{x}^{y} \frac{f''(\omega)}{\omega + \omega_{o}} d\omega = f''(\omega_{o}) \int_{x}^{y} \frac{d\omega}{\omega + \omega_{o}} d\omega + \frac{df''}{d\omega}(\omega_{o}) \int_{x}^{y} \frac{\omega - \omega_{o}}{\omega + \omega_{o}} d\omega$$
(A.6)
$$+ \frac{1}{2} \frac{d^{2} f''}{dw^{2}}(\omega_{o}) \int_{x}^{y} \frac{(\omega - \omega_{o})^{2}}{\omega + \omega_{o}} d\omega + \cdots$$
$$\int_{x}^{y} \frac{f''(\omega)}{\omega + \omega_{o}} d\omega \approx f''(\omega_{o}) \left[\ln |y + \omega_{o}| - \ln |x + \omega_{o}| \right]$$
(A.7)
$$+ \frac{df''}{d\omega}(\omega_{o}) \left[(y - x) - 2\omega_{o} \left(\ln |y + \omega_{o}| - \ln |x + \omega_{o}| \right) \right]$$
$$+ \frac{1}{2} \frac{d^{2} f''}{d\omega^{2}}(\omega_{o}) \left[\frac{(y + \omega_{o})^{2} - (x + \omega_{o})^{2}}{2} - 4\omega_{o}(y - x) \right]$$
$$+ 4\omega_{o}^{2} \left(\ln |y + \omega_{o}| - \ln |x + \omega_{o}| \right) \right]$$

The integrals ans1 and ans2 are carried out using the following integral: $\int_x^y \frac{f''(\omega)}{\omega - \omega_o} d\omega$. In the same manner as Equation A.6, a Taylor Series expansion is substituted in the integral to yield

$$\int_{x}^{y} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega = f''(\omega_{o}) \int_{x}^{y} \frac{d\omega}{\omega - \omega_{o}} d\omega + \frac{df''}{d\omega}(\omega_{o}) \int_{x}^{y} d\omega + \frac{1}{2} \frac{d^{2} f''}{dw^{2}}(\omega_{o}) \int_{x}^{y} \omega - \omega_{o} d\omega + \cdots \int_{x}^{y} \frac{f''(\omega)}{\omega - \omega_{o}} d\omega \approx f''(\omega_{o}) \left[\ln |y - \omega_{o}| - \ln |x - \omega_{o}| \right] + \frac{df''}{d\omega}(\omega_{o})(y - x) + \frac{1}{2} \frac{d^{2} f''}{d\omega^{2}}(\omega_{o}) \left[\frac{(y - \omega_{o})^{2} - (x - \omega_{o})^{2}}{2} \right]$$
(A.8)

The integral ans₄ is the integral about the singularity and is carried out by again

Taylor Series expanding $f''(\omega)$ about ω_o and recognizing that

$$\oint_{x}^{y} \frac{d\omega}{\omega - \omega_{o}} = \ln |y - \omega_{o}| - \ln |x - \omega_{o}|.$$

This leads to

$$\oint_{a_o}^{b_o} \frac{f''(\omega)}{\omega - \omega_o} d\omega = f''(\omega_o) \left[\ln |b_o - \omega_o| - \ln |a_o - \omega_o| \right] + \frac{df''}{d\omega} (\omega_o) (b_o - a_o) \\
+ \sum_{n=2}^{\infty} \frac{1}{n \cdot n!} \frac{d^n f''}{d\omega^n} (\omega_o) \left[(b_o - \omega_o)^n - (a_o - \omega_o)^n) \right] \quad (A.9)$$

This integral is carried out numerically by fitting a 5th order polynomial to the $f''(\omega)$ data. Again using the matrix form described in the previous section, the following equation is solved for the coefficients C_n :

$$\Delta f'' = \sum_{n=1}^{4} C_n \ \Delta \omega^n \tag{A.10}$$

This is a clever way to fit the *derivative* of f'': The Taylor Series expansion of $\frac{df''(\omega)}{d\omega}$ expanded about ω_o is

$$\frac{df''}{d\omega}(\omega) = \frac{df''}{d\omega}(\omega_o) + \frac{d^2 f''}{d\omega^2}(\omega_o)(\omega - \omega_o) + \frac{1}{2!}\frac{d^3 f''}{d\omega^3}(\omega_o)(\omega - \omega_o)^2 + \frac{1}{3!}\frac{d^4 f''}{d\omega^4}(\omega_o)(\omega - \omega_o)^3 + \cdots$$
(A.11)

So, dividing both sides of Equation A.10 by $\Delta \omega$, the fitting coefficients are given by

$$C_1 = \frac{df''}{d\omega}(\omega_o)$$
$$C_2 = \frac{d^2f''}{d\omega^2}(\omega_o)$$

$$C_{3} = \frac{1}{2} \frac{d^{3} f''}{d\omega^{3}} (\omega_{o})$$

$$C_{4} = \frac{1}{6} \frac{d^{4} f''}{d\omega^{4}} (\omega_{o})$$
(A.12)

These coefficients are substituted back into Equation A.9 to calculate the value of the integral.

For each energy, the total Kramers-Krönig integral is calculated according to Equation A.5.

A.2.3 Output

• E vs. $f_{exp}^{\prime\alpha}$ – experimental values of the real part of the ASF as a function of energy for the α atom in the sample [eV, electrons]

Appendix B

Data Analysis Code

This appendix provides the filename and primary purpose of some of the major components (macros) of the Matlab data analysis code. Figure B.1 contains a flowchart describing the data analysis. Macros in shaded boxes are called independently by the user.



Figure B.1: Flowchart for Matlab data analysis code to obtain radial, differential and partial pair distribution functions.

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