

Dale Sayers Festschrift

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Abstract. This Festschrift is in honor of Dale Sayers who passed away in November 2004. Dale played a pivotal role in initiating the modern era of X-ray Absorption Fine Structure (XAFS) 35 years ago. The prehistory of XAFS before the modern era consisted of 40 years of confusion caused by Kronig's two different theories of the extended XAFS (EXAFS), the Short-Range Order (SRO) and Long-Range Order (LRO) theories. Dale's PhD thesis on EXAFS led to the idea of a Fourier transform to definitely prove that SRO is the correct theory and then to the development of XAFS as a structure determination technique.

Keywords: Dale Sayers Festschrift, Prehistory, Modern Era, PhD thesis, History, XAFS

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INTRODUCTION

Thirty five years ago the modern era of XAFS was ushered in by the publication [1] of the PRL: D.E. Sayers, E.A. Stern, F.W. Lytle, "New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-ray Absorption Fine Structure", *Physical Review Letters* **27**, 1204-07 (1971). Dale Sayers, who was my graduate student at the time, had a crucial role in this development. Unfortunately Dale is not alive to celebrate this milestone since he died tragically at too early an age on November, 2004. In spite of his early departure he has left an exceptional legacy by his crucial pioneering role in ushering in the modern era of XAFS by developing it into a unique structure determination technique. This Festschrift is honoring Dale Sayers for his contribution to this development. It is most appropriate that Dale's Festschrift is being celebrated here since Dale had a major role in building the first XAFS synchrotron beamline in the world at SSRP, the predecessor to SSRL, and in obtaining the first XAFS spectrum with synchrotron radiation. I plan to give a history of the XAFS phenomenon explaining why it took 40 years after the first theory of EXAFS was presented to obtain **convincing** evidence for the correct theory and develop EXAFS into a structure determination technique. Dale's role in this development will be described and other speakers in this Festschrift will present their interactions with Dale and his influence on them.

CONFUSION

The 40 year delay in deciding the correct theory of the Extended XAFS (EXAFS) occurred because **two** different theories were presented by Kronig between 1931- 1932: (1) the long-range order (LRO) based on electron energy bands and gaps in solids[2,3]; and (2) the short-range order (SRO) based on scattering of the photoelectron by neighboring atoms [4]. Kronig proposed the LRO theory for periodic solids and the SRO theory for molecules. He did not address the case of the aperiodic condensed state. Although both theories, if properly done, would give similar answers for the periodic crystal state, we now know that his LRO theory had a fatal error, while his SRO theory was incomplete. It did not include Debye-Waller factors, and excited-state lifetime broadening. Moreover, because no powerful computers existed then, the photoelectron-atom interaction, such as phase shifts and scattering amplitudes, could not be accurately calculated to allow quantitative comparison with experiment.

Kronig's LRO theory argued on the basis of the recently developed Bloch theory of solids that the energy gaps would decrease the density-of-states causing minima in EXAFS and thus giving the fine structure (Fig. 1). As pointed out soon after the new era began [5] this change in density-of-states has a negligible effect in the extended spectrum because of lifetime broadening. Since the energy gaps are formed by redistributing energy levels in their

vicinity and the lifetime broadening is greater than the small energy gaps at the extended energies, this effect, after averaging over the broadening, will be cancelled. Only the scattering of the SRO theory remains to contribute to the fine structure.

Kronig never published an addendum to state that the SRO theory was correct for *both* molecules and solids, and the LRO theory was wrong, causing confusion for 40 years. Although in those years several theorists, notably Kostarev [6] who correctly concluded that the SRO theory should work for both solids and molecules, their correct conclusions were ignored since Kronig was so much more prestigious (Kramers-Kronig relations, Kronig-Penney model). In fact, what we now call EXAFS was called at that time the Kronig structure. Kostarev learned the hard fact that **it is not sufficient to be right in physics, one must also be convincing!** The right way to be convincing had not yet arrived.

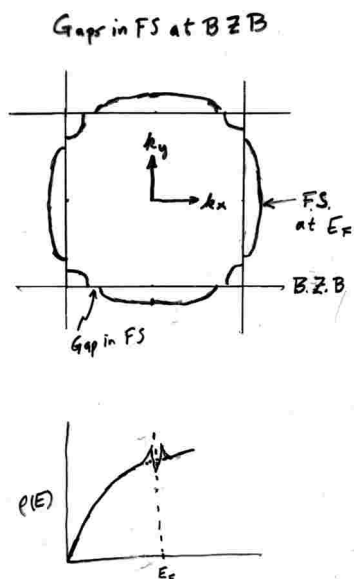


FIGURE 1. Top, sketch of the effect of a periodic potential in the nearly free electron model as the Fermi surface (FS) intersects a Brillouin zone plane boundary (BZB). Bottom, sketch of the effect on the density-of-states. The areas of the positive and negative deviation from the free electron value are equal and cancel when averaged by lifetime broadening of the excited photoelectron

No convincing evidence could be presented because both theories could not be calculated *quantitatively* and the experiments that could distinguish between them were not consistent because many were flawed. With no synchrotron sources available the measurements were tedious and were done manually over periods of the order of a

week per spectrum where stability of the setup was challenging, as was the graduate student's endurance. Near the latter part of the 40 year period of confusion some instruments added automation to the EXAFS data collection, decreasing the tedium of the measurements and improving their reliability, *e.g.*, Farrel Lytle's laboratory facility [7].

CLEVER EXPERIMENT

To overcome the lack of *quantitative* calculations an experiment was performed that appeared to have a clever way to distinguish the two theories *qualitatively* [8]. Their idea was to measure the XAFS on a series of perovskites (that have a composition ABO_3) with various A and B atoms and structures closely approximating cubic symmetry. The A atoms are at the eight corners of a cube, the B atoms are at the center of the cube and the oxygens are at the center of the faces of the cube. The A and B atoms have different local environments (SRO). They then argued, seemingly correctly, that if the SRO theory is correct the XAFS of all A atoms will be similar and different from those of all the B atoms who would also have similar XAFS among themselves. However, if the LRO theory is valid, then, since the band structure is common to both A and B atoms in a given perovskite they would have similar XAFS but somewhat different ones from the other perovskites which would be expected to have different band structures. **Surprisingly, and adding to the confusion, they concluded from their measurements that *neither* theory is supported by their data!**

WRONG ANSWER

The puzzle is what went wrong? To answer that we remeasured XAFS on the same series. Figure 2 compares the result and gives the answer. The 1970 measurements shown in the left compared to the later modern era measurements taken with synchrotron radiation shown in the right of Fig. 2 illustrate the experimental unreliability that contributed to the 40 year confusion. The center atom in (a)-(d) on both sides is the atom that is common, *e.g.*, Ti in (a) and Ca in (c). Note that three of the measurements in the 1970 data are incorrect. This unreliability, of course, is the reason why no conclusion could be made about the correct theory in ref. [8]. See reference [9] in these proceedings for more details.

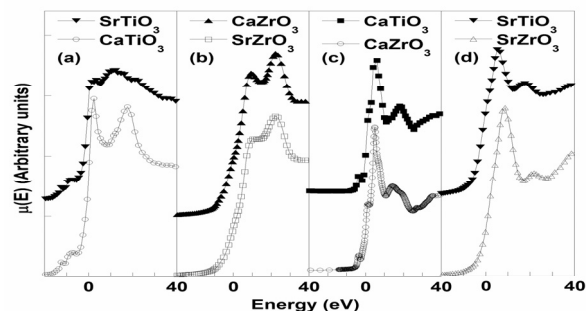
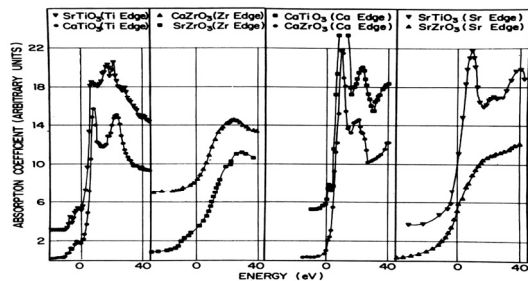


FIGURE 2. Left plots as measured by 1970 ref. [8]. Right plots as measured recently with synchrotron radiation.

CONVINCING ANSWER

One year later in 1971 the PRL [1] by D.E. Sayers, E.A. Stern, F.W. Lytle, showed by a Fourier transform (FT) that the SRO theory was the correct one for solids, both crystalline and aperiodic ones. Figure 3 shows the resulting phase shift corrected FT that clearly shows the SRO in Ge. This ushered in the modern era of XAFS.

It is worthwhile to expand on how the addition of the FT was the missing link necessary to prove **convincingly** the correctness of the SRO theory. There were 4 key steps that led to the PRL. They were:

1. Developing a theory, which we called the point scattering theory, that parameterized the quantities related to the atom-photoelectron interaction [10].
2. Realizing that the theory indicates that the natural variable to describe the EXAFS phenomenon is the photoelectron wave number k , not the energy variable in the experiment.
3. Reasonably reliable experimental EXAFS measurements.
4. Fourier transforming EXAFS measurements in k -space.

Dale was involved in all of these steps as part of his PhD thesis research during his tenure as my graduate student. The theory developments were supervised by me while the experiments were supervised by Farrel Lytle using his laboratory facilities. Initially, neither I nor Dale was aware of the previous history of the 40 year confusion. In hindsight items 1 - 3 were essentially available before my involvement. Kronig's SRO theory [4] contained the essential ideas of items 1. and 2., and among the experimental results there were many that

qualified for item 3 (but which ones!). The missing link was the FT of item 4.

We started this research that led to the PRL after I met Farrel Lytle soon after I moved from the University of Maryland in 1965 to the University of Washington in Seattle. At that time, during the golden age of physics, the Boeing Company had the Boeing Scientific Research Laboratories (BSRL), where basic research was being done. I became a consultant at BSRL and had the opportunity to talk to various researchers there. The meeting with Farrel Lytle was the one that had the biggest impact on me. He told me about his work on EXAFS. I had never heard about this phenomenon before and was struck by the fact that there was no understanding of the effect. I found out only later that I was indebted to Kronig for this. As I listened to Farrel, the physics of the phenomenon became self-evident. The photoelectron wave function would be scattered by surrounding atoms and the interference between the back-scattered and outgoing waves would modulate the absorption matrix element. Being ignorant of the previous history of the theoretical confusion about the Kronig structure, I was not encumbered by that legacy.

PhD THESIS

When I returned to my office I decided that this would be a good thesis project for one of my first graduate students at the University of Washington, Dale Sayers. Dale was interested, so we started developing the theory of EXAFS based on my physical picture and then planned to apply it to try to understand the EXAFS spectrum of an amorphous metallic alloy that he would measure under Lytle's supervision. Lytle had built one of the few remaining state-of-the-art facilities to measure EXAFS. This collaboration was cemented further when Dale spent the summer of 1968 working with

Farrel at his busy laboratory, measuring the EXAFS of various materials. However, a problem arose. Dale's wife was no longer willing to live frugally and insisted that Dale leave graduate school and take a job to support his family. Dale and his wife were later divorced and after some years Dale remarried Anne, his widow. Fortunately, a compromise ensued where Dale joined BSRL to help Farrel Lytle with his experimental measurements, while being able to pursue his thesis research under my supervision. The main parts of the theory were formulated by the summer of 1969 and the first presentation of the theory was given at the 18th Denver X-ray Conference [10]. The theory had the basic ideas of the modern theory, except for the phase shift contribution of the back-scattering atoms. (This and multiple scatterings (MS) were added to the theory by Patrick A. Lee, whom I was fortunately able to attract to join the UW for the 1973-74 academic year and to get interested in the theory of EXAFS [11]). Because of anticipated economic problems at Boeing, Dale was laid off and I placed him back on my grant to continue his thesis work at the University of Washington.

By the end of the 1969-70 academic year the basic parts of the theory were essentially fully formulated and I felt confident in Dale's mastery of it. In spite of the fact that our calculations of the photoelectron-atom interactions were crude, we had some success on materials with known structure to use the theory to fit their EXAFS, but it was clear that the real payoff would be to find a way to invert the process and apply EXAFS to determine the structure of unknown materials. Some details of the theory needed refinement and the experimental parts of the thesis needed completion, which Farrel Lytle was supervising. Dale was in the advanced stage where he could complete his thesis without my close supervision, so I left on sabbatical leave to Israel for the 1970-71 academic year with instructions to Dale to concentrate on how to invert the theory to obtain structural information from the EXAFS data. We maintained frequent contact through correspondence by postal mail, which typically took a month for an exchange (e-mail did not exist then).

FOURIER TRANSFORM

In late 1970 Dale sent me a letter giving the final equation he had obtained for EXAFS after simplification. I quickly wrote back to him suggesting that Fourier transforming XAFS data should show peaks at the position of atoms. Dale did such a transform on Ge data and, to our great excitement and satisfaction, the peaks appeared!

Later, Farrel told me that Dale had also independently come to the idea of Fourier transforming the EXAFS data a few days before my letter had arrived. With this exciting result, we wrote a Physical Review Letter and submitted it for publication. The referee reports were mixed. One referee, who had obviously been involved in x-ray spectroscopy, considered the idea of the Fourier transform (FT) as trivial and not warranting a Phys. Rev. Letter. Fortunately, our response together with other positive referee reports was sufficient to convince the editor to publish our Letter [1].

Not only did we have the correct theory for EXAFS, but we also had the convincing evidence to prove it and a way to invert the XAFS data to determine unknown structures! The Fourier transform was the key to this. The fact that EXAFS was an SRO phenomenon was obvious, since the FT showed that all of the EXAFS signal came from the near neighborhood of the center atom (Fig. 3). Similar data as in Fig. 4 are shown in a later investigation [12] showing improvements in both measuring capabilities using a synchrotron source and in analysis. Amorphous Ge with 4.9 at % H is shown in (a), while crystalline Ge is shown in (b). In both (a) and (b) the transform range was 3 to 14 \AA^{-1} and the XAFS were weighted by k^2 . Even though the data from Lytle's Lab facility and the analysis produced some spurious features in Fig. 3 the fact that only the SRO contributes is a robust result.

Dale officially completed his PhD thesis on Dec. 9, 1971 and his PhD degree was conferred in March 1972.. Figure 5 shows Dale lecturing on XAFS in 1971.

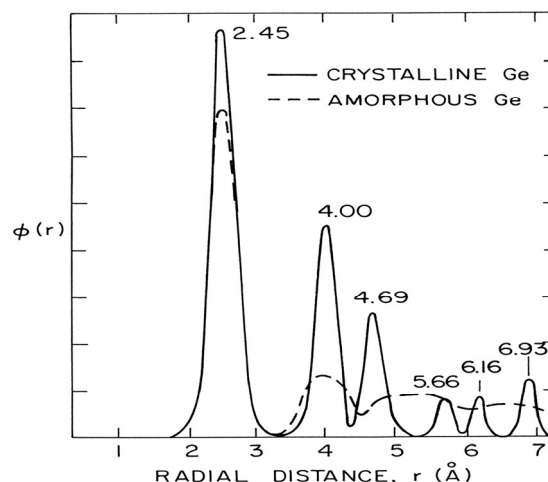


FIGURE 3. Magnitude of Fourier transforms of the EXAFS of crystalline (solid) and amorphous (dash), as given in Sayers et al. (1971) using Lytle's lab x-ray spectrometer. The distance of the neighboring shells of atoms in crystalline Ge are given in Angstroms.

The FT suggested how to overcome the major remaining theoretical obstacle to calculate correctly the photoelectron interaction with atoms. One did not have to do such a calculation! Known structures can be used to obtain the information by measuring their EXAFS spectrum and then using the FT to isolate the signal from a given absorbing atom and its surrounding neighbor. This use of experimental standards was quite effective in the beginning to determine the structure of many materials and to prove its utility. The birth of the modern era of EXAFS as a quantitative structure determination technique had arrived. A set of three papers summarized the theoretical [5], experimental [7] and analysis status [13] of our development of EXAFS up to 1974. A discussion of the development of XAFS including beyond 1974 is given in ref. [14]. In recognition of his pioneering work on XAFS, Dale joined Farrel and me in receiving the 1979 Bertram E. Warren Diffraction Physics Award of the American Crystallography Association (Fig. 6).

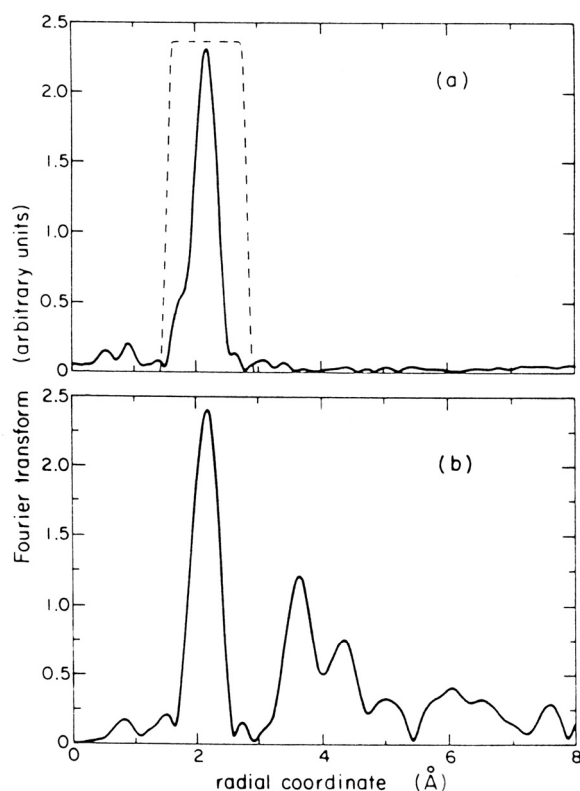


FIGURE 4. Similar data as in Fig. 3 are shown in a later investigation [12], showing improvements in both measuring capabilities using a synchrotron source and in analysis. (a) Amorphous Ge with 4.9 at % H. (b) crystalline Ge. In both (a) and (b) the transform range was 3 to 14 \AA^{-1} and the XAFS were weighted by k^2

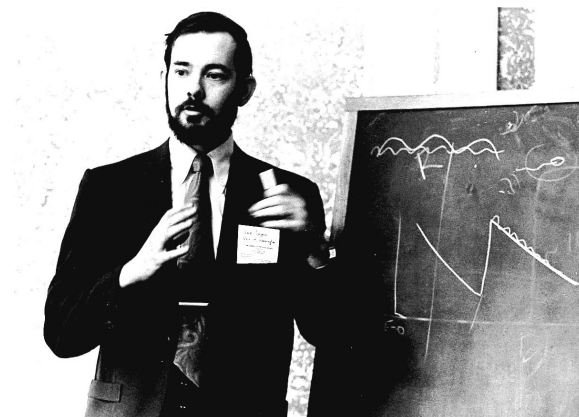


FIGURE 5. Dale Sayers lecturing in 1971.



FIGURE 6. Dale E. Sayers (middle) with Edward A. Stern (left) and Farrel W. Lytle (right) receiving the 1979 Bertram E. Warren Diffraction Physics Award of the American Crystallography Association

SYNCHROTRON RADIATION

It should be noted that initially all EXAFS analysis of materials we made was based on measurements using Farrel's laboratory apparatus, thus the modern era of XAFS predated the introduction of synchrotron radiation XAFS beamlines. On the contrary, synchrotron XAFS beamlines were built because the modern era introduced a new technique for structure determination. Synchrotron radiation (SR) came on the scene during a visit of Artie Bienenstock to the University of Washington to give a seminar. Artie told me about the exciting possibilities of using

SPEAR, the Stanford University electron-positron collider at SLAC, for generation of x-rays from the synchrotron radiation that was a nuisance to the high-energy particle experimentalists. He convinced me to use this source of high-intensity x-rays to measure EXAFS. I subsequently testified at Artie's invitation to an NSF committee visiting SPEAR to evaluate the proposal from Stanford University to develop SPEAR as a high-intensity source of hard x-rays. The committee strongly encouraged me to go ahead and develop an XAFS beamline at SPEAR and Dale took the initial major responsibility to build it. The world's first SR spectrum on Cr in stainless steel was obtained by Dale using a strip recorder is shown in Fig. 7. Together with Peter Eisenberger, Brian Kincaid and Sally Hunter (the latter two being Artie's students), Dale, Farrel and I put together the first operating beamline and the world's first XAFS beamline on the SPEAR machine at SSRP, the predecessor to SSRL [15].

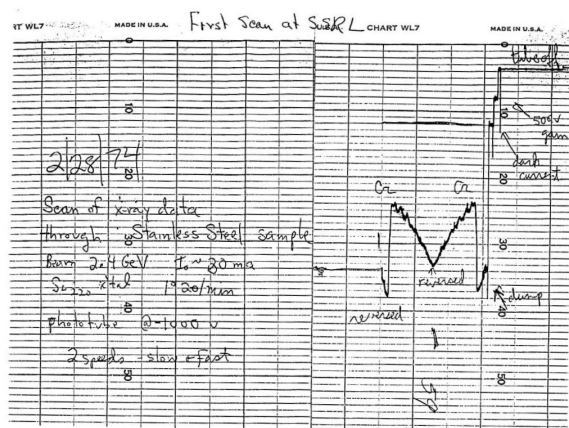


FIGURE 7. A strip recorder plot at the Cr K-edge by Dale Sayers of the first XAFS scan ever made at a synchrotron source taken at SSRP on 2/28/74.

As you all know, synchrotron radiation revolutionized the experimental side of EXAFS, making it accessible to non-experts and attracting the largest numbers of users at synchrotron sources. The revolution is best summarized by quoting from Lytle's article [16]: "In one trip to the synchrotron we collected more and better data in three days than in the previous ten years (with three laboratory x-ray spectrometers)."

POSTSCRIPT

Afterwards Dale continued to make his mark on the development and applications of XAFS and at North Carolina State University. The following speakers will describe some of these aspects of his

career. Figure 8 shows Dale as he received the 2003 International XAFS Society Outstanding Achievement Award in recognition of his contributions.

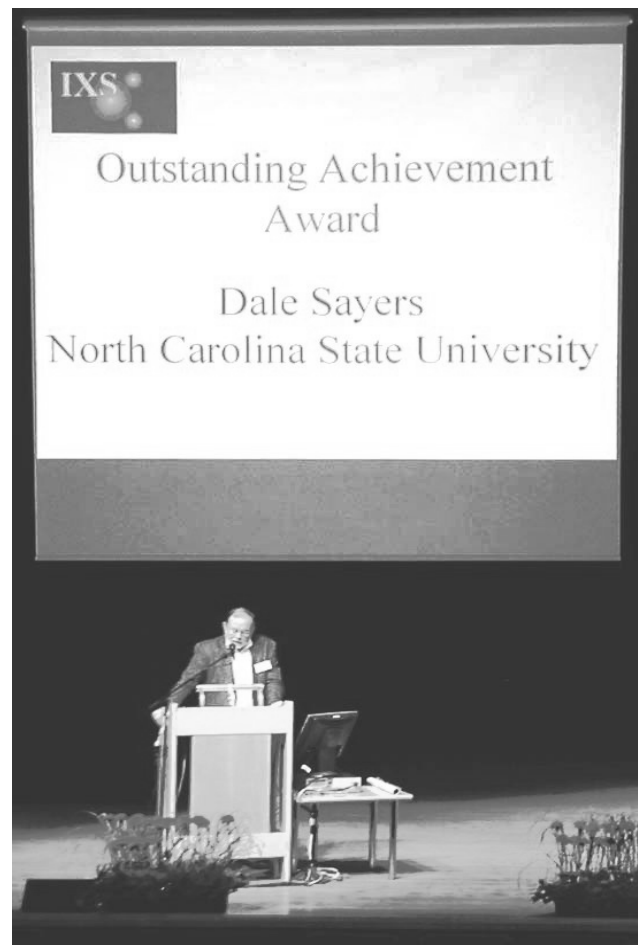


FIGURE 8. Dale Sayers giving his presentation on receiving his 2003 IXS Outstanding Award.

SUMMARY

Kronig started the 40 year confusion about the correct theory of XAFS which was compounded by the unreliability of experiments during that period. The introduction of Fourier transforms in XAFS showed directly, robustly, and unequivocally the correctness of the SRO theory without relying on any theoretical analysis, ushering in the modern era of XAFS as a structure determination technique. Dale Sayers had a pivotal role in this during his thesis research and beyond.

ACKNOWLEDGMENTS

I am indebted to Dale Sayers and Farrel Lytle who accompanied me on the exciting ride initiating the Modern XAFS Era, and to my numerous graduate students, postdocs, colleagues and all of you who helped make XAFS the important structure

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determination technique it is today. We are honoring two of them here with the 2006 IXS Stern Award for their lifetime outstanding achievements! I am also indebted to NSF and especially DOE for funding support. Thanks are due Farrel Lytle for supplying Figs. 5, 7 and 8.