

Local Structure in Solid Solutions Revealed by Combined XAFS/Neutron PD Refinement, using the Multiple-Scattering RMC Method

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Abstract. The classical model of oxide solid solutions is one in which cations randomly occupy distinct sites of fixed geometry, where lattice constants are in proportion to the mean cationic radius (Vegard's Law), or with small departures from this due to factors such as local ordering or local distortions of the lattice. By means of our Multiple-Scattering Reverse Monte-Carlo (RMC) technique, using both XAFS and neutron powder diffraction (PD) datasets, we show that departures from this model may be large, with cations occupying a site close to optimum in terms of its preferred coordination geometry and bond valence requirements. In particular, for a series of ternary and quaternary spinel solid solutions, we show that Ti has a unique 5-fold coordinated site over a range of compositions.

Keywords: RMC, Spinel, XAFS, Neutron Powder Diffraction, Combined Refinement, Oxide Solid Solution, Local Lattice Distortion.

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INTRODUCTION

Oxide Solid Solutions

Classically, oxide solutions have been described in terms of a rigid oxygen framework, with fixed cation sites. If the cation distribution is entirely random, then the cell volume may be proportional to the mean cation radius, giving a linear relationship between fractional occupancy of a cation site and cell volume [1]. Such solids are said to obey Vegard's law. Where significant positive deviations from Vegard's law occur, they are almost invariably associated with a tendency to unmixing resulting from clustering. This behaviour is often associated with phases formed above a sub-solidus dome, or quenched phases occurring metastably within a two-phase region. Conversely, negative departures are associated with ordering or incipient intermediate compound formation. The rigid framework model is reinforced by powder diffraction (PD) results, which record a temporal and spatial average of the structure. Local techniques such as NMR may allow cation order to be detected. Structures conforming to this model certainly do exist. Solid solutions $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ show only a very small positive departure from Vegard's law, and a

combined refinement yields an excellent fit to both X-ray PD and Mo K-edge XAFS [2]. This case is however far from typical. The last 25 years have seen a re-evaluation of solid structures, largely resulting from an interest in non-stoichiometric materials (Fe_{1-x}O , cuprate superconductors ...). This has resulted in a realisation that cation sites in solid solutions may show a strong chemical dependence resulting from distortions of the oxygen lattice. XAFS has played a major role in this, and there are many published examples which highlight the discrepancy between XAFS and PD results in oxide solid solutions (e.g. [3]). The result of such studies, using a combination of PD and XAFS techniques, is all too often, however, a crystal structure plus an incompatible first shell distance derived from XAFS. Such results do not do much to aid the understanding of the 3-dimensional structure of the solid. Here we show not only that massive departures from the rigid lattice model of solid solutions may occur, but that we have a reliable way of analysing and describing them.

RMC Method

Given the difficulty in constructing local models of lattice distortion which allow interpretation of the XAFS data [4], the only realistic solution to such problems is to allow distortion of the lattice over a

model space consisting of many unit cells. The obvious approach to this is to use the Reverse Monte-Carlo (RMC) method. A description of an implementation of this method appropriate to combined XAFS/PD refinements has been previously published [5]. That paper discusses the importance of using multi-shell contributions including multiple-scattering, and the method used to allow such multiple scattering (MS) simulations to be undertaken on a reasonable time scale. The references therein also acknowledge the major contribution to the field by R. McGreevy. Here, we describe new features in the simulation and in the presentation of its results, and describe the application of the method to complex spinels, with reference to other oxide solid solutions.

Spinel

Spinel is a cubic oxide phase crystallising in $Fd-3m$ containing 8 tetrahedral four-fold [T_d] sites and 16 trigonal bipyramidal (quasi-octahedral) six-fold [D_{3d}] sites per unit cell (Figure 1). The presence of an additional unoccupied set of tetrahedral sites, leads to a low activation energy of formation of defects, and effective inter-site communication at the high temperatures of synthesis. The consequent high cation mobility leads to site mixing and spinel solid solutions may thus be more complicated than at first appears. Previously we have described site mixing and local lattice distortions in $Co_xAl_{1-x}O_4$ spinels [6]. Here we concentrate on spinels in the system $CoO-MgO-ZnO-TiO_2$.

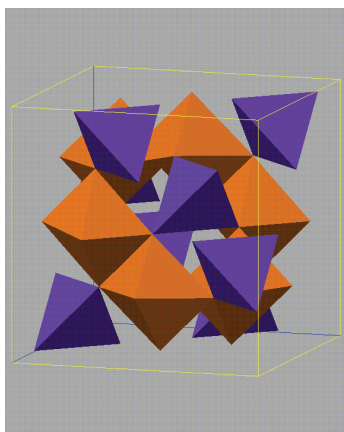


FIGURE 1. Spinel structure.

METHOD

Four spinel phases with compositions in the system $CoO-MgO-ZnO-TiO_2$ were selected for study by combined neutron powder diffraction/XAFS refinement using the MS RMC method with the

program P [7]. A number of other compositions were analysed using conventional combined refinement techniques [7], to determine site occupancies and to identify sites showing local distortions. Their synthesis and characterization, and details of XAFS and neutron PD experiments have been described by Owens [6]. Simulation boxes consisting of 27 unit cells or 1512 atoms were used. This is much too small a number to ensure that special positions in the lattice do not generate extra PD peaks, but the program imposes crystallographic symmetry on the box in order to avoid this problem. This effectively results in the superposition of 192 boxes in the orientations specified by the space group symmetry operations. Assignment of site occupancies was not straightforward. For binary compositions, neutron PD refinements were adequate, for other compositions combined refinements could be performed provided Ti was excluded. Occupancy of the Co sites was also correlated with subtle changes in the pre-edge feature, and for both Co and Zn, small amounts of site mixing also produced shoulders on some FT peaks. In conclusion, we found Zn to be largely associated with the T_d site, but with around 5% in the D_{3d} site in some compounds. In order to simplify the calculation and reduce the memory required for MS tables however, we assumed it to be entirely tetrahedral. Co showed a preference for T_d and Mg for D_{3d} , but some mixing occurred in all cases. Ti was clearly almost all in the D_{3d} site in the binary and ternary compounds, and mostly so in the others. It was assumed to be entirely D_{3d} . Sites were initially populated randomly using the site occupancies determined above. The program can also model clustering and ordering, by swapping atoms and then further relaxing the structure. This process was attempted for some compounds, but took too long for us to attempt to establish equilibrium, or even to determine whether different configurations are distinguishable. We conclude by saying that there was no direct evidence of non-random distributions, and that this proved a satisfactory model. The initial coordinates of the atoms were taken from neutron PD refinement. Steps in the refinement included not only random moves of single atoms, but the addition of random vectors to move all the atoms, and movement of bonded MO clusters. We have also added an option to randomly rotate clusters. This was particularly effective in early stages of the refinement of La_2GaCoO_6 , and played some role in spinel simulations. Refinement criteria were as for a conventional combined refinement [7]. The structure was assumed to have reached an equilibrium configuration when no further improvements took place, and XAFS R-factors were similar to those obtained for simple end-member compounds – typically around 25%.

RESULTS

The initial fit to the XAFS spectra, using coordinates derived from neutron PD refinements, adjusted DW factors, and refined Ef was always poor. For Co and Zn small discrepancies in first shell distances were noted. For Ti however, the fit was extremely poor, especially in the low- k region. An example is given in Figure 2.

Results of all the refinements are shown in Table 1. The results include the first three cumulants of the interatomic bondlengths for each metal in each site. The first being the interatomic distance in Å, the second the Gaussian width parameter σ^2 in Å², and the third the skewness in Å³. The second cumulant is directly comparable with the XAFS DW factor, but note that P uses $2\sigma^2$.

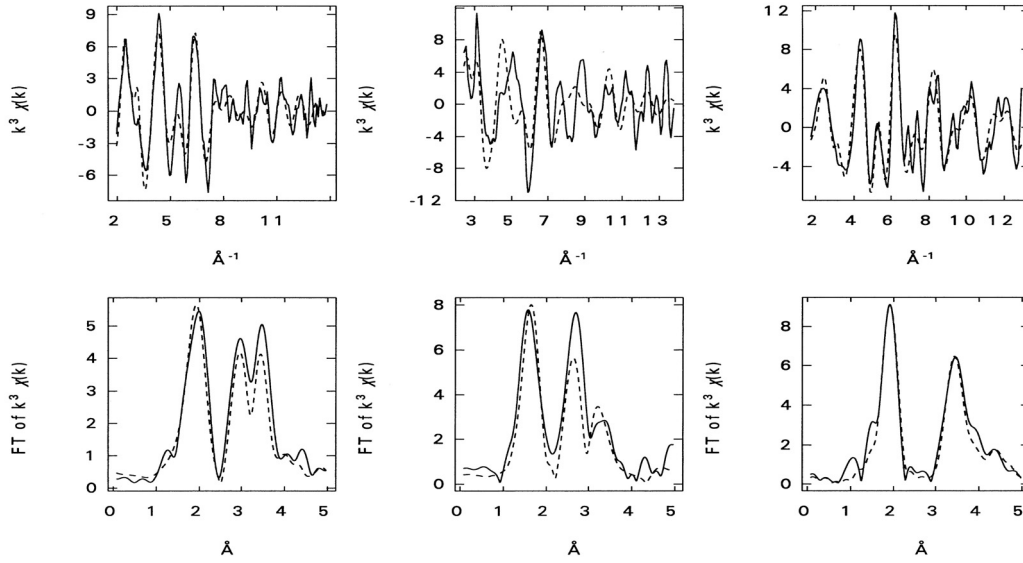


FIGURE 2. Fit to XAFS of $\text{Co}_{0.8}\text{Mg}_{0.6}\text{Zn}_{0.6}\text{TiO}_4$ using coordinates derived from neutron diffraction only, for (left to right), Co, Ti and Zn.

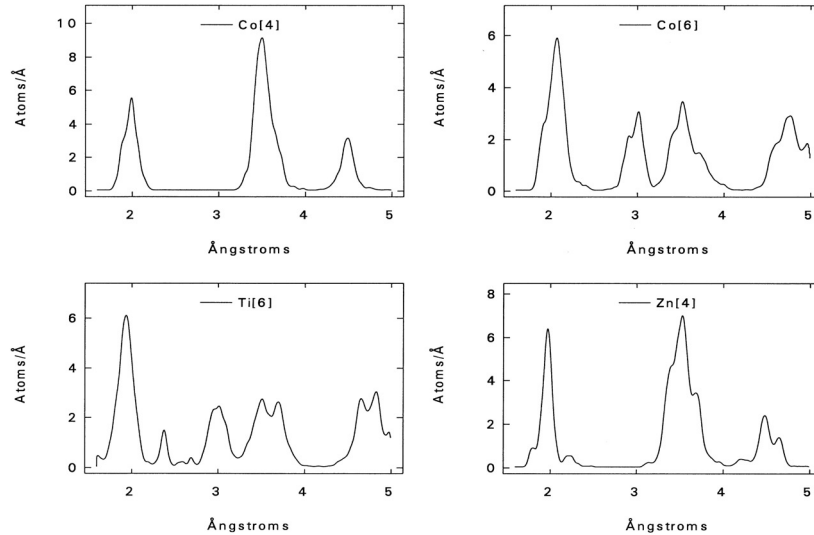


FIGURE 3. Gaussian broadened histograms for $\text{Co}_{0.8}\text{Mg}_{0.6}\text{Zn}_{0.6}\text{TiO}_4$, for (left to right), Co[4], Co[6], Ti[6] and Zn[4].

The table also shows the effective atomic coordinates (x,y,z) after the simulation, and the calculated net displacement in Å (δ). The second cumulant of the displacement is comparable to the neutron PD DW factor u^2 . Finally the bond valence values for each metal are shown (uncorrected for

temperature effects). These are always within 10% of the actual valence and show the physical reasonableness of the results. In most cases they represent an improvement on the starting position. The distances for Co and Zn are unremarkable, being typical for these metals.

TABLE 1. Results of RMC Simulation – for Explanation, See Text.

	$\text{Co}_{0.8}\text{Mg}_{0.6}\text{Zn}_{0.6}\text{TiO}_4$	$\text{CoMg}_{0.4}\text{Zn}_{0.6}\text{TiO}_4$	CoZnTiO_4	Co_2TiO_4
a Å	8.4508	8.4509	8.4508	8.4479
	First three cumulants	of bonds		
Co[4]-O	1.9903 .0059 .0000	1.9906 .0090 -.0010		1.9837 .0124 .0004
Co[6]-O	2.0701 .0016 .0005	2.0688 .0200 -.0008	2.0662 .0185 -.0016	2.0811 .0091 .0004
Ti[6]-O	1.9984 .0315 .0055	2.0196 .0294 .0053	2.0266 .0314 .0057	1.9928 .0298 .0061
Zn[4]-O	1.9948 .0125 .0017	1.9867 .0114 .0015	1.9806 .0136 .0006	
	First two cumulants	of displacement from	starting position	
Co[6]x	.5001 .0043	.4989 .0124	.5009 .0121	.4998 .0057
Co[6]y	.4998 .0043	.5000 .0119	.5001 .0037	.5006 .0054
Co[6]z	.4991 .0051	.5013 .0105	.4998 .0021	.5006 .0057
Delta Co[6] Å	.0076	.0144	.0076	.0076
Co[4]x	.1241 .0023	.1256 .0027		.1251 .0042
Co[4]y	.1254 .0013	.1241 .0032		.1253 .0044
Co[4]z	.1254 .0021	.1254 .0018		.1240 .0060
Delta Co[4] Å	.0090	.0097		.0084
Ti[6]x	.5004 .0072	.4993 .0141	.5004 .0074	.5012 .0074
Ti[6]y	.5011 .0064	.4991 .0149	.5004 .0065	.4991 .0065
Ti[6]z	.4978 .0084	.4996 .0163	.4998 .0043	.4996 .0078
Delta Ti[4] Å	.0211	.0102	.0051	.0135
Zn[4]x	.1245 .0071	.1258 .0083	.1240 .0094	
Zn[4]y	.1245 .0073	.1252 .0092	.1258 .0117	
Zn[4]z	.1250 .0081	.1256 .0060	.1247 .0022	
Delta Zn[4] Å	.0059	.0086	.0110	
Mg[4]x	.1208 .0098	.1268 .0241		
Mg[4]y	.1245 .0118	.1194 .0216		
Mg[4]z	.1243 .0071	.1208 .0193		
Delta Zn[4] Å	.0363	.0611		
Mg[6]x	.5001 .0096	.4988 .0436		
Mg[6]y	.5002 .0072	.5009 .0273		
Mg[6]z	.4978 .0071	.5007 .0285		
Delta Mg[6] Å	.0186	.0139		
Ox	.2610 .0098	.2613 .0099	.2578 .0292	.2599 .0112
Oy	.2600 .0098	.2617 .0102	.2592 .0254	.2597 .0094
Oz	.2608 .0118	.2582 .0091	.2604 .0145	.2608 .0018
Delta O Å	.0067	.0198	.0211	.0076
Co bond val.	2.137	2.185	2.336	2.034
Ti bond val.	4.035	3.783	3.713	4.064
Zn bond val.	1.899	1.934	2..003	

The DW factors are also only a little higher than to be expected from thermal factors. Net displacements from initial positions are largest for Mg, but these results should be treated with caution as the absence of Mg XAFS data means that there are few constraints on the Mg positions. The other displacements are small. The most remarkable result is the set of cumulants for Ti, the second and third cumulant being very high in each case. The reason

for this is shown in Figure 3, which shows a Gaussian broadened histogram for each metal in each site. Ti here shows a peak at a typical distance, about 1.95 Å, but with a significant short distance contribution (around 1.88 Å). Moreover, there is another peak at around 2.36 Å, which is essentially non-bonding. Essentially the same result is found for each composition, although the position of the non-bonding peak varies somewhat. The integral of the

atom density between 0 and 2.3 Å is always very close to 5 (e.g. 5.033 for CoZnTiO₄), demonstrating that although occupying a 6-fold site, Ti has effective 5-fold coordination. This type of site, a highly contorted 5- or 6-fold coordination including one very short distance, is actually typical of Ti in silicate minerals and other mixed oxide phases.

Overall an improvement in fit was obtained for all the spectra in comparison with the starting configuration. For the Ti K-edge XAFS this was very large, but for the neutron PD pattern it was small, illustrating the insensitivity of the Bragg component of PD patterns to local lattice distortions. A final fit to Co_{0.8}Mg_{0.6}Zn_{0.6}TiO₄ is shown in Figure 4.

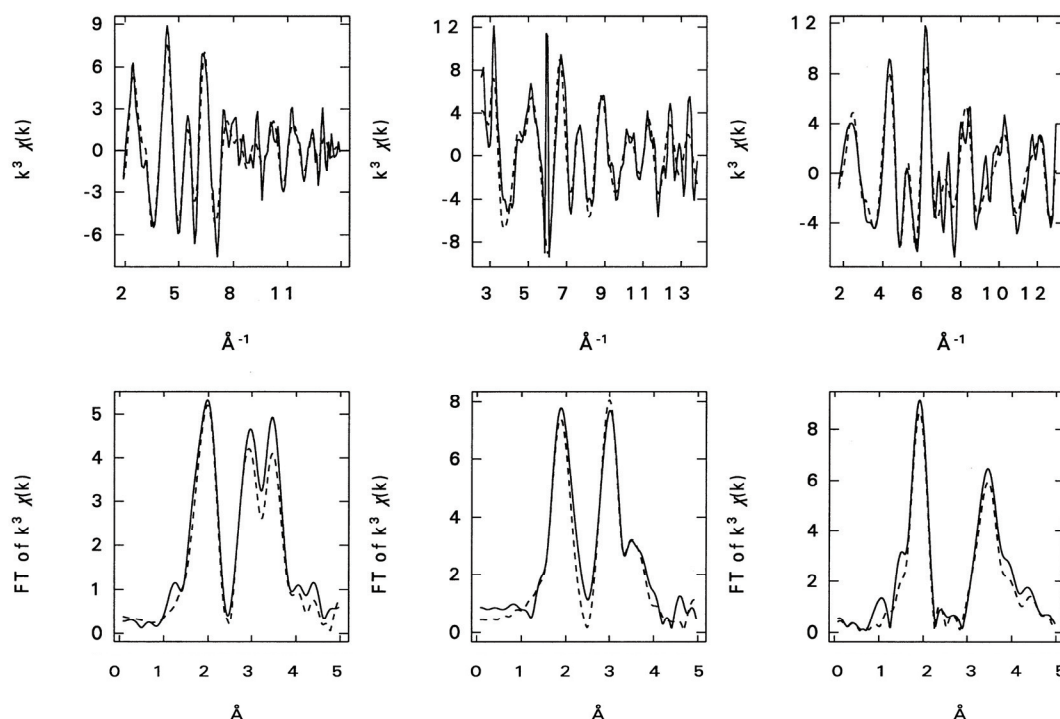


FIGURE 4. Final fit to the XAFS of Co_{0.8}Mg_{0.6}Zn_{0.6}TiO₄, for (left to right), Co, Ti and Zn.

CONCLUSIONS

We have demonstrated that the MS RMC method is capable of analysing multiple datasets derived from complex solid solutions. We also show that a rigid lattice model is in general inappropriate in such cases, and a better model is one in which each site is assumed to have its optimum coordination for bonding. This is likely to produce large distortions for the more covalent metals. In particular we show that Ti in a wide range of spinels, including near end-member inverse spinels, has a unique 5-fold environment resulting from extreme distortion of the D_{3d} site.

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