STATIC DISPLACEMENTS OF ATOMS IN CRYSTALLINE
METALLIC SOLID SOLUTIONS

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CULLIE SPARKS,* GENE ICE,* XIAOGANG JIANG,** AND PAUL ZSCHACK,***

*Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6118

**Sandia Livermore National Laboratory, P. O. Box 969, Livermore, CA 94550

***Oak Ridge Institute of Science and Education, Oak Ridge, TN 37831

ABSTRACT

Measurement of diffuse x-ray scattering from binary crystalline solid solutions at more than one x-ray energy is a sensitive probe of the average interatomic distance between neighboring pairs of atoms. Deviations of these bond distances by as little as $0.001\text{\AA}$ are easily detected in the diffuse scattering from binary alloys consisting of atoms nearby in the periodic table and/or where x-ray energies chosen near their absorption edges can change the scattering contrast. Individual bond distances (AA, AB and BB) are recovered out to several near neighbor shells by combining three scattering measurements at x-ray energies chosen for maximum and minimum contrast. Average bond distances recovered from four metal alloys $\text{Fe}_{77.5}\text{Ni}_{22.5}$, $\text{Fe}_{46.5}\text{Ni}_{53.5}$, $\text{Cr}_{47}\text{Fe}_{53}$ and $\text{Cr}_{20}\text{Ni}_{80}$ are discussed. We find that the interatomic distances measured for these alloys give interesting insights to atomic displacements in solid solutions. Nearest neighbor bond distances are not well represented by phenomenological models based on pure element atomic size and concentration dependence of the lattice constants. Radial and non-radial displacements are recovered from these measurements of diffuse scattering.

INTRODUCTION

The effect of atomic size disparity between solvent and solute on solubility and mechanical properties of crystalline solid solutions is well-known. Laves¹ in his discussion of atomic size in alloys shows that the ratio of the atomic radii of the components is important to their crystal symmetry. The effects of atomic size difference on solid solution strengthening or hardening have been discussed by Fleischer². Except in a few recent cases the magnitude of the atomic size difference in crystalline solid solutions has not been obtained from actual measurements of bond distances. Instead, bond distances have been deduced from like atom pair distances in pure elements and compounds with various coordinations. Vegard's law³ is based on atoms being hard spheres with radii of the pure elements. In this case the changes in lattice parameter with concentration should follow a straight line. Negative deviations from this straight line are observed to occur most often when atoms prefer unlike first neighbors, a tendency towards order. A positive deviation from the straight line is most often observed when atoms prefer like neighbors, a tendency to cluster. Changes in lattice constant with composition have also been treated in terms of compressibility of the atoms⁴ and continuum elasticity theory.⁵ Hartley⁶ and Moreen et al.⁷ have treated the concentration dependence of the lattice parameter for alloys in terms of the number of different first neighbor pairs and their average first neighbor bond distances. They use like-neighbor bond distances taken from pure elements and unlike bond distances taken from intermetallic compounds and lattice parameter versus concentration curves for low concentrations. The change in lattice parameter at low concentrations is assumed to be related to the bond distance between the solute atom and the solvent (unlike) nearest neighbors.

Validation of these approaches has mainly been by comparison with lattice parameter versus concentration curves. Though these phenomenological approaches have had limited success for some alloys, they are not universal in their application. Reinhard et al.⁸ and Ice et al.⁹ have recently discussed the failure of these approaches when compared with actual measurements of bond distances in Cr-Fe ⁸ and Fe-Ni ¹⁰ alloys recovered from diffuse scattering

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measurements. The details of these measurements of weak diffuse x-ray scattering to recover bond distances are treated by Jiang et al. in this proceedings. There he will show that displacements from the average lattice which is defined by the lattice constants determined from the Bragg reflections can be detected when as small as 0.001 Å and even less. Comparison of methods to extract the bond distances from measurements of diffuse scattering has been given by Schönfeld et al.¹¹ for the 3λ method^{8,10} and the Georgopoulos-Cohen¹² procedure. Extended x-ray absorption fine structure (EXAFS) measurements of the oscillations in the absorption edge extending 1 kV or so above threshold gives bond distances between first, second and perhaps third nearest neighbors with descending sensitivity. Scheuer and Lengeler¹³ have measured 61 binary metal alloys with 1 to 2 at. % solute concentration and derived the average distance between the solute atom and the first shell assumed to consist of all solvent atoms. They recover only the unlike atom pair bond distance to an accuracy of about 0.5% or typically 0.01 to 0.02 Å. This precision is on the borderline for testing theoretical calculations such as those by Mousseau and Thorpe¹⁴, Zunger et al.¹⁵, and Bozzolo et al.¹⁶ where variations in bond distances from that of the average lattice are typically 0.005 to 0.05 Å. Displacements recovered from diffuse scattering measurements such as presented here will provide more stringent tests of theoretical developments.

DIFFUSE SCATTERING MEASUREMENTS OF BOND DISTANCES

Brief Overview of the Theory

The elastically scattered intensity in electron units, eu, per atom from an ensemble of atoms is given by

$$I(\mathbf{h}) = \sum_m \sum_n f_m f_n e^{i\mathbf{h} \cdot (\mathbf{R}_m - \mathbf{R}_n)} \quad , \quad (1)$$

where f_m and f_n denote the x-ray atomic scattering factor (or neutron scattering lengths); m and n designate the sites and $\mathbf{R}_m$ and $\mathbf{R}_n$ the position vectors for those sites, and $\mathbf{h}$ is the scattering or reciprocal lattice vector¹⁷. For crystalline solid solutions in which the Bragg reflections are sharp and the average lattice is well-defined, the atom positions can be represented by $\mathbf{R} = \mathbf{r} + \boldsymbol{\delta}$ where $\mathbf{r}$ is determined from the lattice constant and $\boldsymbol{\delta}$ is the displacement of the atom from that average lattice. The exponential term is written

$$e^{i\mathbf{h} \cdot (\mathbf{r}_m - \mathbf{r}_n) + (\boldsymbol{\delta}_m - \boldsymbol{\delta}_n)} \equiv e^{i\mathbf{x}} = 1 + i\mathbf{x} - \frac{\mathbf{x}^2}{2} - i\frac{\mathbf{x}^3}{3!} + \dots + \frac{i^n \mathbf{x}^n}{n!} \quad . \quad (2)$$

We recover the $i\mathbf{x}$ term which gives us the displacements of the atoms from the sites of the average lattice. Methods for this recovery and the approximations made are given in references 8, 10, 11 and Jiang et al. in this proceedings. For a binary alloy of A and B atoms of atom fractions C_A and C_B , complex atomic scattering factors f_A and f_B and average static displacements $\langle \boldsymbol{\delta}^{AA} \rangle_{lmn}$ and $\langle \boldsymbol{\delta}^{BB} \rangle_{lmn}$ for like neighbor atoms the recovered diffusely scattered intensity per atom from the first two terms of the series expansion in Eq.(2) is given by

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$$\begin{aligned}
\frac{I_{\text{Diffuse}}}{N} &= c_A c_B |f_A - f_B|^2 \sum_{lmn} \alpha_{lmn} \cos 2\pi(h_1 l + h_2 m + h_3 n) \\
&- \frac{2\pi}{a} c_A c_B \sum_{lmn} \left\{ \left(\frac{c_A}{c_B} + \alpha_{lmn} \right) \text{Re} \left[f_A (f_A - f_B)^* \right] \left[h_1 \langle \delta_x \rangle_{lmn}^{AA} + h_2 \langle \delta_y \rangle_{lmn}^{AA} + h_3 \langle \delta_z \rangle_{lmn}^{AA} \right] \right. \\
&+ \left. \left(\frac{c_B}{c_A} + \alpha_{lmn} \right) \text{Re} \left[f_B (f_B - f_A)^* \right] \left[h_1 \langle \delta_x \rangle_{lmn}^{BB} + h_2 \langle \delta_y \rangle_{lmn}^{BB} + h_3 \langle \delta_z \rangle_{lmn}^{BB} \right] \right. \\
&\times \sin 2\pi(h_1 l + h_2 m + h_3 n),
\end{aligned} \quad (3)$$

where lmn denote the coordinates of the near neighbor shells and $\alpha_{lmn} \equiv 1 - P_{lmn}^{AB} / C_B$ is the Warren-Cowley¹⁷ short-range order coefficient and where P_{lmn}^{AB} is the conditional probability that after finding an A atom at lmn there is a B atom at the origin. Since the displacements of the atoms averaged over all the pairs (AA, AB and BB) that can be formed for any coordination shell lmn must equal zero to match the "d" spacing for that shell defined from the average lattice constant "a", then

$$2(1 - \alpha_{lmn}) \langle \delta^{AB} \rangle_{lmn} + \left(\frac{c_A}{c_B} + \alpha_{lmn} \right) \langle \delta^{AA} \rangle_{lmn} + \left(\frac{c_B}{c_A} + \alpha_{lmn} \right) \langle \delta^{BB} \rangle_{lmn} \equiv 0. \quad (4)$$

Shown in Fig. 1 is a schematic of the displacements that are recovered by this technique.

Fig. 1. Displacements of atoms off the sites of an average lattice in a crystalline solid solution. The average lattice is defined by the square. Atom pairs are separated by $(\mathbf{R}_m - \mathbf{R}_n) = (\mathbf{r}_m - \mathbf{r}_n) + \delta_{mn}$ which defines the average bond distance.

The precision with which the displacements can be recovered depends on how significant the second term is relative to the first term of Eq. (3) and on how large a contrast change can be effected in $f_A(f_A - f_B)$ and $f_B(f_A - f_B)$ with choice of x-ray energies near to absorption edges^{8,10,11}. For atoms nearby in the periodic table the contrast can actually be reversed, and since $f_A - f_B$ is small, then the displacement term containing $f_A(f_A - f_B)$ is large compared to the short-range order term containing $|f_A - f_B|^2$. Each shell may deviate from this average, but the x-ray beam samples on the order of 10^{18} atoms so that only the average $\langle \delta \rangle$ is recovered. From

these displacements, the average bond distance $R_{lmn} = r_{lmn} + \delta_{lmn}$ is determined for AA, AB, and BB pairs for several shells. Deviation from this average bond distance are contained in the higher order terms of the series expansion of Eq. (2). A recovery of the static displacement components of the $\langle \delta^2 \rangle$ terms depends on a reliable separation of the large thermal contribution.

As defined in Eq. (3), the diffusely distributed intensity is a measure of both the short-range chemical pair correlations and displacements of the atoms from the sites of the average lattice. We define the average lattice as shown in Fig. 2 where atoms displaced out of the planes still define planes with constant "d" spacings. As the Bragg reflections of the crystalline solid solutions are very sharp, as illustrated in Fig. 2b, this means that the "d" spacing between the crystallographic planes is constant over distances of several hundred plane spacings. In materials where faulting or displacive transformations are possible, then large and correlated changes in "d" spacings can occur over hundreds of planes which broaden, split or produce new Bragg reflections. In this case, the average lattice spacings become poorly defined and the diffraction is treated differently than discussed here.¹⁷

Fig. 2(a). Displacements about the average lattice preserve the regular spacing between atomic planes, and that average lattice is obtained from (b) the positions of the sharp Bragg reflections. Information about short-range correlations among the atoms is contained in the diffusely distributed intensity between the Bragg peaks.

Fig. 3. Two-dimensional diagram showing that the displacements δ_{lmn} must be parallel to the interatomic vector r_{lmn} for directions such as $\langle 110 \rangle$ with multiplicities less than 24 to conserve cubic symmetry. For multiplicities of 24 or more, such as $\langle 310 \rangle$, δ_{lmn} need not be parallel to r_{lmn} to conserve cubic symmetry.

Discussion of the Displacements

Average displacements may or may not be along the interatomic vector connecting the atom pair. This depends on the multiplicity of lmn which defines the number of atoms in that coordination shell¹⁸. For example in a face-center cubic alloy for those coordination shells with multiplicities less than 24, the displacements must on the average be parallel to the interatomic vector to conserve cubic symmetry. This is illustrated in Fig. 3 for the (100) plane of the crystal. If the displacements are not on the average along the $[110]$ interatomic vector, the square lattice representative of the cubic (100) plane becomes distorted into a rectangle as illustrated by the dashed lines. For interatomic vectors with multiplicities of 24 or greater, such as the $\langle 310 \rangle$, the displacements are not required to be parallel to that vector. As shown in Fig. 3, the displacements δ_{310} can be drawn to preserve cubic symmetry and not be parallel to the interatomic vector.

Displacements for four metal alloys are given in Tables I and II along with the Warren-Cowley short-range order coefficients α . The statistical and systematic error given in Table I were added in quadrature. All but the bcc $\text{Cr}_{47}\text{Fe}_{53}$ alloys have preference for unlike first neighbors. The three fcc alloys of Fe-Ni and $\text{Cr}_{20}\text{Ni}_{80}$ in which the unlike atoms have a chemical preference for each other also have shorter first-neighbor bond distances than like neighbors. At temperatures lower than the heat treatment of this Cr-Fe alloy, phase separation will occur. This preference for like neighboring atoms is reflected in the positive sign of the first neighbor α_{111} . This chemical preference for like atom first neighbors is reflected in the displacements which show Cr-Cr and Fe-Fe first neighbor pairs closer together than the unlike Cr-Fe pairs. As shown by Ice et al.⁹, these displacements do not fit models based on concepts of hard spheres, compressibility or continuum elasticity theory. First principle calculations have yet to be made on these alloys so that theory and experiment can be compared.

Table I. Short-range order coefficients and pairwise displacements (Å) recovered for Fe_{46.5}Ni_{53.5} and Fe_{22.5}Ni_{77.5} for the various coordination shells with estimates of both statistical and systematic errors

Fe _{46.5} Ni _{53.5}						Fe _{22.5} Ni _{77.5}			
xyz	lmn	$\alpha(lmn)$	δ_x^{Fe-Fe}	δ_x^{Ni-Ni}	δ_x^{Ni-Fe}	$\alpha(lmn)$	δ_x^{Fe-Fe}	δ_x^{Ni-Ni}	δ_x^{Ni-Fe}
0 0 0	000	1.0000(830)	0	0	0	1.0012(910)	0	0	0
1/2 1/2 0	110	-0.0763(178)	0.0216(39)	0.0008(4)	-0.0084(11)	-0.1082(200)	0.0381(44)	-0.0004(5)	-0.0024(15)
1 0 0	200	0.0615(85)	-0.0229(46)	-0.0049(11)	0.0145(14)	0.1194(120)	-0.0225(50)	-0.0000(15)	0.0052(18)
1 1/2 1/2	211	-0.0027(27)	0.0004(11)	-0.0002(4)	-0.0001(4)	-0.0047(30)	-0.0022(14)	0.0005(6)	-0.0006(5)
1/2 1 1/2	121	-0.0027(27)	0.0016(27)	-0.0007(3)	-0.0003(7)	-0.0047(30)	-0.0072(32)	-0.0005(4)	0.0018(8)
1 1 0	220	0.0041(25)	0.0034(8)	-0.0013(4)	-0.0007(3)	0.0307(48)	0.0058(12)	-0.0016(6)	0.0021(4)
3/2 1/2 0	310	-0.0107(35)	0.0018(11)	0.0018(6)	-0.0018(4)	-0.0179(45)	0.0057(14)	0.0005(4)	-0.0016(5)
1/2 3/2 0	130	-0.0107(35)	0.0008(31)	0.0010(5)	-0.0009(9)	-0.0179(45)	-0.0055(38)	-0.0001(2)	0.0009(11)

Table II. Short-range order coefficients and pairwise displacements (Å) recovered for fcc Cr₂₀Ni₈₀ and bcc Cr₄₇Fe₅₃ with estimate of statistical errors only

Cr ₂₀ Ni ₈₀						Cr ₄₇ Fe ₅₃					
xyz	lmn	$\alpha(lmn)$	δ_x^{Cr-Cr}	δ_x^{Ni-Ni}	δ_x^{Cr-Ni}	xyz	lmn	$\alpha(lmn)$	δ_x^{Cr-Cr}	δ_x^{Fe-Fe}	δ_x^{Cr-Fe}
0 0 0	0	1.258(7)	0	0	0	0 0 0	000	1.181(2)	0	0	0
1/2 1/2 0	110	-0.112(2)	0.010(2)	0.0000(1)	-0.0007(1)	1/2 1/2 1/2	111	0.160(1)	-0.0019(1)	-0.0007(1)	0.0017(1)
1 0 0	200	0.064(3)	0.003(2)	0.0001(1)	-0.0007(1)	1 0 0	200	0.069(1)	0.0027(1)	-0.0003(1)	-0.0012(1)
1 1/2 1/2	211	0.036(2)	-0.002(1)	0.0001(5)	0.0000(1)	1 1 0	220	0.046(1)	-0.0005(1)	-0.0002(5)	0.0004(5)
1/2 1 1/2	121	0.036(2)	0.001(1)	0.0000(1)	-0.0001(1)	3/2 1/2 1/2	311	0.027(1)	0.0001(1)	0.0002(5)	-0.0001(5)
1 1 0	220	-0.045(2)	0.010(1)	-0.0003(1)	-0.0003(1)	1/2 3/2 1/2	131	0.027(1)	0.0001(1)	-0.0002(5)	0.0001(5)
3/2 1/2 0	310	-0.022(2)	-0.000(1)	0.0001(5)	-0.0002(1)	1 1 1	222	0.025(1)	0.0004(1)	-0.0005(1)	0.0001(5)
1/2 3/2 0	130	-0.022(2)	-0.000(1)	0.0001(5)	-0.0001(1)	2 0 0	400	0.004(1)	-0.0006(1)	0.0001(1)	-0.0003(1)

CONCLUSION

This work gives us an insight as to the details of the displacements of atoms from the sites of the average lattice which are available from diffuse scattering measurements of crystalline solid solutions. Though these measurements and data analysis are few and still under development, precisions to 0.001 Å are already possible. Sensitivity to such small displacements will give new information on solid solutions and provide tests of theoretical calculations which allow for relaxation of the atoms. This will help us to understand the contribution of strain to the energy of alloy systems and the effects of strain on phase equilibria.

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