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Anomalous (resonant) diffuse x-ray scattering measurements of local correlations in disordered solid-solution alloys

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With resonant (anomalous) x-ray scattering, the x-ray scattering contrast between elements can be controlled to highlight local correlations in solid-solution alloys. For some binary solid-solution alloys, three diffuse-scattering maps allow the scattering from short-ranged chemical correlations, and the three individual pair static atomic displacements to be separated from the thermal diffuse scattering (TDS). For elements A and B that are nearby in the periodic table, the scattering contrast, f_A-f_B can be made positive, negative or nearly zero by tuning the x-ray energy. This allows unprecedented sensitivity to static atomic displacements. Uncertainties in the static displacements < 0.0001 nm or better out to the 10th shell can be achieved. Measurements on Fe-Ni-Cr binary alloys and others show systematic trends not predicted by previous measurements or theories.

Key words: Diffuse x-ray scattering,; anomalous (resonant) x-ray scattering; short-range order; atomic size; static displacements.

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Introduction

Crystalline solid-solution alloys include a wide-range of materials critical to 20th century technology. Among the common Fe-Ni-Cr alloys are examples with many useful properties including, corrosion resistance, high-temperature strength, interesting magnetic properties and low thermal expansion coefficient. Yet our understanding of the origin and control of these properties has been limited by an immature theoretical understanding and experimental characterization of the local structure, especially the role of atomic size.

Early attempts to understand alloy phase stability recognized the importance of local atomic properties. In ionic materials Goldschmidt identified the ratio of components, the influence of polarization and the ratio of the atomic radii (atomic size) as contributing to phase stability.[1] In metals, Hume-Rothery identified the valence electron concentration, the electrochemical factor and again the ratio of the radii (atomic size) as contributing to phase stability.[2] Yet until recently, theoretical models have not included atomic size in calculations, and experimental measurements of atomic size have been difficult and limited.[3] For example, extended x-ray absorption fine structure (EXAFS) measurements can be used to measure first-neighbor static displacements to ~0.02 nm in dilute alloys. This uncertainty is marginal in many systems and depends on the assumption that all near-neighbor atoms are unlike. Powder diffraction can very accurately determine *average* lattice parameters, but cannot determine chemically distinct pair displacements.

Intense and tunable synchrotron x-ray sources have recently revolutionized our ability to characterize the local structure of materials.[4] By tuning near an absorption edge, it is now possible to vary the contrast between atoms and thereby highlight the local structure near particular atomic

species. In this paper we describe the use of resonant diffuse x-ray scattering to study the local-defect structure of crystalline solid-solution alloys. Resonant diffuse x-ray scattering can measure short-ranged chemical and displacement correlations with unprecedented precision and accuracy to provide new insights into the behavior of solid-solution alloys.[3]

Although resonant techniques have greatly extended our ability to study local correlations in solid-solution alloys, this work builds on earlier pioneering efforts. For example, Born and Von Karman recognized in the 1910's that the diffuse x-ray scattering from thermal motions could be understood in terms of lattice dynamics and plane waves.[5] Similarly Guiner was said to recognize order and atomic static displacement (size effect) scattering in x-ray photographs. Later, Huang,[6] Cowley[7]. Warren[8] and others quantitatively described the effects of chemical and displacement correlations on diffuse x-ray scattering. Of special note is the pioneering work of Krivoglaz[9] whose fluctuation description of chemical and displacement correlations is in a form amenable to modern theoretical interpretation.

Resonant diffuse X-ray Scattering by the 3λ method

The elastically scattered intensity from an ensemble of atoms is given by

$$I(\mathbf{h}) = \sum_m \sum_n f_m f_n e^{i\vec{\mathbf{h}}\bullet(\vec{\mathbf{R}}_m - \vec{\mathbf{R}}_n)} \quad . \qquad (1)$$

Here f_m and f_n denote the x-ray atomic scattering factor; m and n designate the sites and R_m and R_n the position vectors for those sites, and **h** is the scattering or reciprocal lattice vector[3]. 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 $\vec{\mathbf{R}} = \vec{\mathbf{r}} + \vec{\delta}$ where $\vec{\delta}$ is determined from the lattice constant and δ is the displacement of the atom from that average lattice. The exponential term can be expanded about real-space displacements as,

$$e^{i\vec{\mathbf{h}}\bullet(\vec{\mathbf{r}}_m - \vec{\mathbf{r}}_n) + (\vec{\delta}_m - \vec{\delta}_n)} \equiv e^{ix}$$
$$\approx 1 + ix - \frac{x^2}{2} - i\frac{x^3}{3!} + \ldots + \frac{i^n x^n}{n!} \cdot \qquad (2)$$

The first order (ix) term gives the displacements of the atoms from the sites of the average lattice.[10,11,12] 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 $<\vec{\delta}^{AA}>_{lmn}$ and $<\vec{\delta}^{BB}>_{lmn}$ 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,

$$\frac{I_{Diffuse}}{N} = c_A c_B |f_A - f_B|^2 \sum_{lmn} \alpha_{lmn} \cos 2\pi(h_1 l + h_2 m + h_3 n)$$
$$-\frac{2\pi}{a} c_A c_B \sum_{lmn} \left\{ \left(\frac{c_A}{c_B} + \alpha_{lmn} \right) \mathrm{Re}\left[f_A (f_A - f_B)^* \right] \left[h_1 \langle \delta_X \rangle_{lmn}^{AA} + h_2 \langle \delta_Y \rangle_{lmn}^{AA} + h_3 \langle \delta_Z \rangle_{lmn}^{AA} \right] \right.$$
$$+ \left(\frac{c_B}{c_A} + \alpha_{lmn} \right) \mathrm{Re}\left[f_B (f_B - f_A)^* \right] \left[h_1 \langle \delta_X \rangle_{lmn}^{BB} + h_2 \langle \delta_Y \rangle_{lmn}^{BB} + h_3 \langle \delta_Z \rangle_{lmn}^{BB} \right]$$
$$\mathrm{x} \sin 2\pi(h_1 l + h_2 m + h_3 n), \qquad (3)$$

where *lmn* denote the coordinates of the near neighbor shells and $\alpha_{lmn} \equiv 1 - P_{lmn}^{AB} / C_B$ is the Warren-Cowley[13] 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, then

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

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 $f_A(f_A\text{-}f_B)$ and $f_B(f_A\text{-}f_B)$ with choice of x-ray energies near to absorption edges[14-17]. For atoms nearby in the periodic table the contrast can actually be reversed, and since $f_A\text{-}f_B$ is small, then the displacement term containing $f_A(f_A\text{-}f_B)$ is large compared to the short-range order term containing $|f_A\text{-}f_B|^2$.

Although each shell may deviate from the average, the x-ray beam samples on the order of 10^{18} atoms so that only the average $<\delta>$ is recovered. From these displacements, the average bond distance $\vec{\mathbf{R}}_{lmn} = \vec{\mathbf{r}}_{lmn} + \vec{\delta}_{lmn}$ is determined for AA, AB, and BB pairs for several shells.

Deviation from the 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 $<\delta^2>$ 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. Typically, the Bragg reflections of crystalline solid solutions are sharp. 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 and broaden, split or produce new Bragg reflections. For such samples, the average lattice spacings become poorly defined and the diffraction is treated differently than discussed here.[13]

Near an absorption edge, the x-ray scattering factor of an atom changes by ~8 electron units for K edges and by ~20 electron units for L edges. The difference between the scattering factor of two atoms can therefore change by ~16 electron units as shown in Fig. 1. For atoms nearby in the periodic table, the contrast can therefore be made positve, negative or near zero (null Laue).

In the three λ method, two x-ray energies are selected to achieve the largest contrast , and a third energy is chosen with the minimum contast (null Laue condition). The null Laue measurement performs a key role in the measurement; it estimates the thermal-diffuse-scattering intensity. If $f_A \sim f_B$ or if the thermal motions of A and B atoms are similar, then the TDS and second order static displacement scattering scales like f_{av}^2 where f_{av} is the average scattering factor; $f_{av}=C_A f_A+C_B f_B$. The estimated TDS at different x-ray energies can then be subtracted from the diffuse x-ray scattering map by scaling acording to f_{av}^2.

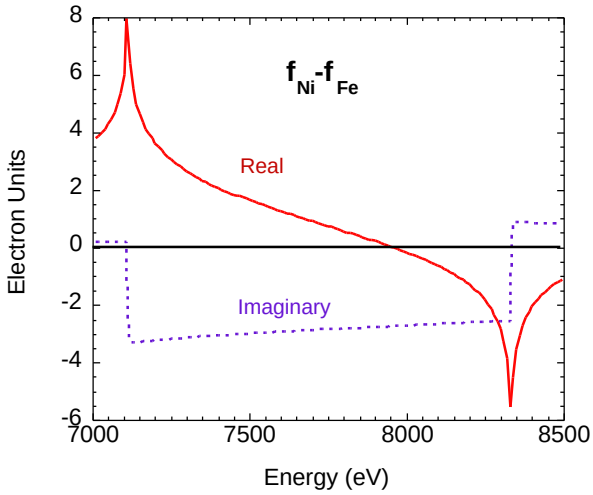

Fig. 1 The difference between the x-ray scattering factor for Ni and Fe has both real and imaginary components. Near the absorption edges the contrast can be varied by ~8 electron units for each atom kind.

The remaining diffuse scattering map contains only the first two terms of the expansion in Eq. 2 These two terms, given in Eq. 3, include the chemical short-ranged order diffuse scattering and the first-order static displacement scattering. Note that the static displacement scattering depends on $(f_A\text{-}f_B)$. Therefore changing the sign of the contrast between the scattering factors of a binary alloy changes the sign of this term. On the other hand the chemical short-ranged order term scales with $(f_A\text{-}f_B)^2$. This term is therefore insensitive to the sign of the contrast but depends sensitively on the magnitude of the contrast.

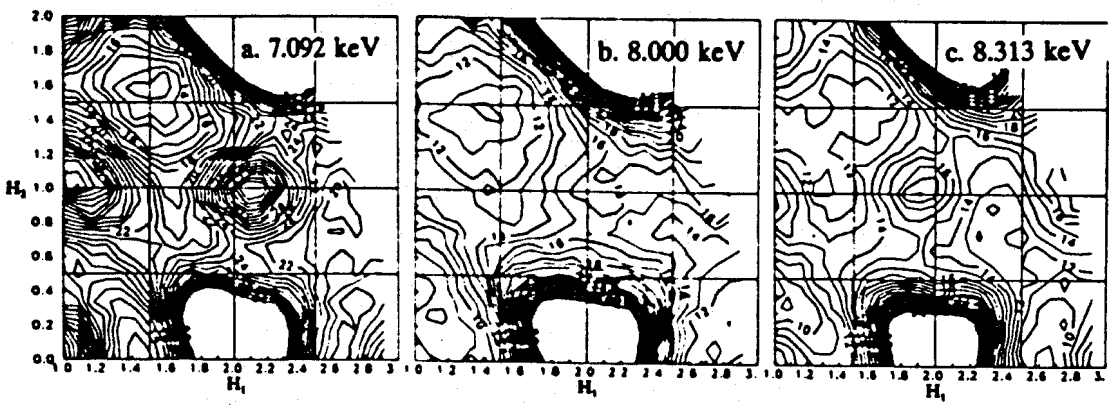

Fig. 2 Diffuse x-ray scattering from an $Ni_{77.5}Fe_{22.5}$ alloy at three different x-ray energies. The contrast is a maximum at 7.092. The broad peaks at the s 2,1,0 and 1,1,0 superlattice sites are due to short-ranged order and are moved to higher Q by the effect of static displacements. At 8.00keV there is very little contrast and the short-ranged-ordered superlattice lines are negligible. At 8.313 keV the contrast between Fe and Ni is reversed and the short-ranged ordered peaks are moved of the superlattice sites.