

MODERN RESONANT X-RAY STUDIES OF ALLOYS: Local Order and Displacements

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KEY WORDS: local correlations, x-ray diffuse scattering, atomic size, static displacements, short-range order.

Shortened Title: X-RAY STUDIES OF ALLOY CORRELATIONS

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ABSTRACT

The recent availability of intense synchrotron sources with selectable x-ray energies permits high-precision measurements of chemically specific atomic-pair correlations in solid-solution alloys. Short-range chemical order can be accurately measured to identify one atom in a 100 for 10 or more shells even in alloys with elements nearby in the periodic table, and chemically specific static displacements can be measured with 0.0001 nm resolution. This new information tests theoretical models of alloy phase stability and structure and gives new insights into the physical properties of alloys.

INTRODUCTION

General Perspective

One of the great triumphs of materials science is the success of periodic electron wavefunctions to describe the properties of crystalline materials. Yet increasingly sophisticated calculations within the perfect periodic lattice approximation cannot account for the influence of local correlations within real crystalline alloys or even elemental crystals. For example, both thermal (dynamic) displacements and chemically specific static displacements from the average lattice sites result in local strain which influences the energetics of phase stability (1,2). In fact, atomic size disparity between the constituents of alloys has long been known to be a major factor controlling the ability to form solid solutions as discussed by Hume-Rothery (3). He included atomic size differences with electronegativity (measure of an atoms ability to attract electrons) and valence electron concentration in his empirical rules for the formulation of substitutions solid solutions; >15% size difference results in limited solubility and $L1_2$ ordering is not observed for size differences > 12%. Though the influence of electronegativity and

valence electron concentration are included within a perfect periodic array model, alloy theorists have only recently turned their attention to atomic size (1,2,4-6).

Movements of the atoms off the sites of the average lattice because of thermal or static displacements has long been of interest to x-ray crystallographers as discussed by Kuhs (7). In general, crystalline solid solution alloys have unit cell dimensions which are nearly linear with concentration. This is referred to as Vegard's Law (8) and has been generally assumed to imply that atomic volumes of the constituent elements are independent of the alloy concentration. As discussed here, recent research has shown this not to be the case.

The influence of local correlations on alloy phase stability and properties is a challenge not only to theory, but also to experiment. Diffuse x-ray scattering due to local fluctuations is relatively weak in comparison to Bragg diffraction, and diffuse scattering experiments are often count-rate limited and very time consuming. For alloys with elements nearby in the periodic table, x-ray scattering contrast is too small for accurate measurements of local order by traditional x-ray diffraction methods. Even when count-rate and contrast are sufficient for precision measurements of local correlations, local chemical order and atomic size (static displacements) can be coupled in alloys by geometrical factors and by chemical bonding effects. For example, in long-range ordered alloys, tendencies to form different bond distances between unlike atom pairs can be suppressed by the symmetry of the neighboring atoms. Hence in many cases, short-ranged tendencies must be inferred from average lattice trends. In short-range ordered alloys, measurements of local correlations are also complicated by the multitude of possible local environments. In a face-centered cubic, fcc, alloy where each atom has

twelve nearest neighbors, there are 144 distinct chemical combinations in just the first shell. Thus the influence of atomic size on phase stability and physical properties has been traditionally very difficult to access except by rather indirect means.

Local correlations are not only important in terms of their energetic contribution to phase stability, but also represent precursors to stable phases which may be difficult or impossible to obtain experimentally because of slow kinetics (9, 10). For example, when electronegativity between two elements exceeds a certain limit, there is a tendency to form intermetallic phases at specific electron-to-atom ratios (3). This tendency may be frustrated because the equilibrium ordering temperature is so low that slow diffusion prevents ordering for years, decades, millennia or longer. Yet the tendency to locally deviate from a random solid solution can indicate a stable lower temperature phase.

The presence of local chemical order can also have a major effect on the physical and chemical properties of alloys. Even though equilibrium phase diagrams exist for binary metals, many of their properties are not known nor are they predictable from the properties of their pure element constituents. The pure elements may be ductile, but their intermetallic combinations can be very brittle as in the case for Al_3Ti (11).

Effect of local order on alloy properties

Although the properties of pure elements are determined by nature, man has long known that by mixing elements, we can create alloys with properties tailored to specific needs. Although such alloying is critically important to materials science, often the observed property changes remain unexplained, particularly for solid solutions where there is a lack of information about local atomic arrangements. A review with a useful list

of references on the effect of local structure on the properties of crystallographically ordered compounds and solid solutions has been given by Cahn (12). Electrical resistivity, corrosion resistance, plasticity, strength, superconductivity, magnetic properties, and diffusion are among the properties affected by the local order.

Solid solution strengthening is one example where local atomic size disparity and local atomic arrangements between solute and solvent atoms play an important role. Shown in Figure 1 is a strong correlation between the solute content and solid solution hardening as discussed by Predmore, et al. (13). The alloys Ta-Mo, Ta-W and Nb-Mo have about a 5% difference in their atomic sizes and exhibit substitutional solid-solution hardening. Nb and Ta differ in size by less than 0.1% as measured from the lattice parameters of the pure elements and show little solid solution strengthening (13). In addition, the local chemical orders can affect the strength of a solid solution where an affinity for like neighbors (clustering) seems to have the larger strengthening effect as discussed by Patu and Arsenault (14). Measurements of the local atomic arrangements in terms of the local chemical order and displacements from the sites of the average lattice provide modeling information for calculations of property changes.

FIGURE 1

Figure 1. Strengthening of crystalline solid solutions is strongly correlated with the mismatch in atomic size (13).

Comparison with alternative methods for the study of local correlations

Although the importance of chemical order and static displacements (size effect) on phase stability and materials properties has long been acknowledged, direct measurements of chemical order and particularly measurements of chemically specific displacements in alloys are rare. Present interpretation of local alloy structure is based primarily on average lattice parameter measurements and first neighbor correlations. As a result, models of local strain often do a good job of fitting observed average lattice parameters, but disagree with recent experimental measurements of local strain.

Local chemical order and displacements can be studied experimentally with diffuse neutron (17,18), electron (19) and x-ray scattering(20,21,22), by Mössbauer measurements (23), field ion microscopy (24), and by extended x-ray absorption fine structure, EXAFS, measurements (25). Diffuse neutron scattering is an especially powerful tool for the measurement of local chemical correlations but is restricted by difficulties in obtaining large samples with the correct isotopic compositions and by relatively weak neutron sources (18). Electron diffuse scattering is limited by the difficulty of measuring the intensity in absolute unit. Diffraction measurements most sensitive to the displacements are those where the scattering amplitudes of the constituent atoms is large compared with their difference as discussed by Jiang (26). Mössbauer measurements can be sensitive to local environment, but they are difficult to interpret and are limited to only a few isotopes.

EXAFS measurements are the most common method for determining chemically-specific bond distances and first neighbor chemical correlations. This technique also profits from the availability of intense and tunable synchrotron X radiation and has been

applied to the study of near-neighbor distances in alloys. The most precise measurements are done on very dilute alloys (< 2% solute) where the solute near-neighbor atoms are all solvent atoms (25). For these measurements however only A-B type near-neighbor bond distances can be recovered. EXAFS measurements on concentrated Au-Ni alloys were used to recover the interatomic distances for the individual pairs as a function of concentration. The large 14% difference in size between Au and Ni atoms made this a favorable case for EXAFS (27). In addition, with EXAFS, the reliability of the measured bond distances falls off quickly with each shell. Thus in bcc, body-centered cubic, and other alloys where 2nd or higher shell neighbor distances may be important, EXAFS methods are inadequate. The uncertainty in the first neighbor bond distance for the best EXAFS measurements is believed to be as low as ~0.001-0.002 nm. For many alloys, however, this precision is inadequate to test theoretical models. In contrast, diffuse x-ray scattering can measure bond distances to better than 0.0001 nm in both random and locally ordered or clustered systems. However, whenever EXAFS measurements can be made with sufficient precision, the ease and simplicity of EXAFS experiments compared with three dimensional diffuse scattering measurements makes EXAFS attractive.

Theoretical insights into local structure in crystalline alloys

Although a clear picture of the role of local disorder in crystalline alloys is still emerging, theoretical models can give important insights into the mechanisms by which local disorder affects phase stability and alloy properties.

PHENOMENOLOGICAL TREATMENT OF ATOMIC SIZE The simplest model of atomic size in solid solution alloys assumes that the average lattice constant of an alloy

results from close packing of hard sphere atoms. With this assumption the average lattice parameter is predicted to have a linear dependence on concentration: Vegard's law (8),

$$r_{av} = c_A r_A + c_B r_B . \quad 1.$$

Here the atomic radii r_A and r_B refer to the pure elements A and B at a concentration of C_A and C_B respectively. Deviations from the linear (Vegard's law) dependence of lattice parameter versus concentration are often associated with tendencies towards ordering (unlike near-neighbors) or clustering (like near-neighbors). This observation can be explained by a simple phenomenological extension of Vegard's model where A-A and B-B near-neighbor bond distances do not change from their pure element values on mixing. If atomic volume is conserved, then the A-B distance is given by,

$$r_{AB} = \frac{r_A + r_B}{2} . \quad 2.$$

Any deviation of the lattice parameter from the linear relationship with concentration is assumed to be due to bonding (28). If the A-B near-neighbor distance, $2r_{AB}$ is less than $(r_A + r_B)$ then there is an attraction between A-B pairs and a tendency to order. If, however, $2r_{AB}$ is greater than $(r_A + r_B)$ then there is a repulsion between A-B pairs and a tendency for like pairs to cluster. This model is usually but not always consistent with the observed tendency for negative or positive deviations from Vegard's law to predict ordering or clustering respectively. With this phenomenological "distorted ball" model the average near-neighbor distance for non-random alloys is given by Hartley (29) as

$$r_{av} = c_A^2 r_A + c_B^2 r_B + 2c_A c_B r_{AB} - c_A c_B \alpha_1 (2r_{AB} - r_A - r_B) . \quad 3.$$

Here α_1 is the nearest-neighbor Warren-Cowley (30) short-range-order parameter, which depends on elemental concentration, C_A , and the conditional probability, P^{AF} , of finding an A atom around a B atom (tendency to order or cluster).

$$\alpha_1 = 1 - P_1^{AB} / c_A . \quad 4.$$

Although this model can often do a good job of fitting the observed average lattice constant, recent resonant x-ray measurements find that the actual A-A, B-B and A-B bond distances change with atomic concentration, Jiang et al (26).

CONTINUUM ELASTICITY APPROACH Further insight into the strain energy introduced by atoms of varying size can be gained from a simple elastic model. This model was first proposed by Friedel (31) and extended by Eshelby (32). It assumes that an oversized solute atom introduced into a vacant solvent host site exerts a pressure on the surrounding atoms. This pressure distorts the host lattice and results in a back pressure on the solute atom. With this model, the stress in the host lattice is found to be pure shear (volume conserved as there is no change in the average lattice dimensions of the host atoms), but the radius of the solute atom is modified from the stress-free value. In addition, within this elastic model, differences in atomic size result in a positive term to the free energy and to the enthalpy. Because a positive enthalpy of mixing leads to a miscibility gap, the conclusion is that large differences in atomic volume limit solubility, in agreement with the rules of Hume-Rothery (3). This simple model, however, does not account for local bonding effects which can dramatically alter atomic volumes for specific local chemical environments.

ISING MODEL Elasticity can also be included in an Ising model of pair displacements. For example, Froyen & Herring (33) have included elasticity in a simple alloy model with a first order treatment of size and atomic interactions. They find that within this model, the predicted AB distance is always intermediate between AA and BB distances. This apparently reasonable result actually is contrary to modern resonant measurements which find AB distances less than AA or BB in short-ranged ordering alloys and AB distances greater than AA or BB distances in clustering alloys. To address this inherent limitation of the model, Chakraborty (4) has included a displacement dependence to the Ising interaction. This expresses the fact that the interaction between different types of atoms, whether attractive or repulsive depends on the distance between them. With this extension, the observed correlation between ordering and displacements is found to be a natural feature of alloy structure. Although this Ising model can account for the observed displacement behavior of ordering and clustering, systems, first principles models are required to understand the mechanisms which lead to the distance dependence of the atomic interactions.

FIRST-PRINCIPLES MODELS In addition to bulk first-principles methods for treating atomic relaxations in alloys as discussed by Laks et al (34), it has proved useful to apply first-principles atomic cluster models. These accurately account for the charge redistribution which is important to our understanding of the bonding preference as discussed by Averill and Painter (35). Analysis of cluster results identify the role of local-chemical near-neighbors bonding and provide trends from which we can infer the mechanisms for the local structural arrangements.

An example of cluster calculations on Fe-Ni solid solutions by Ice et al (36) provides insight into the charge redistribution responsible for the interatomic distances

between nearest neighbor pairs. Bond distances between the Fe-Fe, Fe-Ni, and Ni-Ni near-neighbor, NN, were calculated for a model consisting of fourteen atoms which occupy the corner and face centered sites of a fcc unit cell with various concentrations of Fe and Ni atoms (36). An appreciable charge buildup occurred between Fe and Ni first neighbor pairs with a corresponding decrease between Fe-Fe and Ni-Ni pairs. This charge redistribution can explain the observed large increase in lattice parameter with the addition of Fe to Ni. The formation of strong localized bonds between Fe-Ni NN allows them to come closer together while the depletion of charge between the Ni-Ni pairs increases their separation. In addition to the charge decrease between Fe-Fe NN pairs, ferromagnetic spin alignment also contributes to their larger distance as observed by Jiang et al (26) from diffuse x-ray measurements. These theoretical calculations (36) also revealed that the Fe-Fe NN interatomic distance was not sensitive to the presence of Ni in the lattice. This agrees with experimental observations shown in Figure 2. These data taken from the work of Jiang et al (26) show that the average Fe-Fe NN distances are much larger than for the average lattice which is attributed to the large ferromagnetic coupling between the Fe-Fe NNpairs. This magnetic coupling aligns the unpaired electron spins which pushes the Fe pairs apart since these paired electrons avoid occupying the same space according to Pauli's exclusion principle. Part of the larger Fe-Fe first neighbor distance arises because the Fe atom is larger than the Ni atom. Several estimations are given for the spacings between Fe-Fe NN at room temperature if fcc Fe were to exist. These estimates are obtained from the Goldschmidt (37) ratio of 1.03 times the bcc lattice, the volume change associated with the α - γ transformation at 912°C and applied at room temperature, and an extrapolation of the fcc lattice parameters for antiferromagnetic, Fe-Mn alloys at room temperature to pure Fe (38,39a). We estimate that from 1/3 to 1/2 the lattice expansion caused by the addition of Fe to Ni arises from

the magnetic interaction. More indepth discussion is given in Jiang et al (26). New insight to phase stability will come about with the symbiotic interaction between experiment and theory so that we can test and refine our understanding of local structures.

Figure 2. Average interatomic distances between nearest nighbor pairs relative to the average from lattice parameters measurements for two Fe-Ni alloys containing 46.5 and 22.5 at. % Fe as given by Jiang et al (26). The very large interatomic distance between Fe-Fe nearest neighbors is from both magnetic spin alignment and charge redistribution as discussed in the text. The nonmagnetic contribution to the lattice expansion estimated in three different ways are indicated by left pointing arrows.

BRIEF REVIEW OF DIFFUSE DIFFRACTION THEORY AND EXPERIMENT

X-ray averages

The variables recovered from measurements of diffuse x-ray scattering from binary substitutional alloys provide the pair correlation probabilities of finding chemically specific atom pairs (e.g. Fe-Ni or A-B) and their average interatomic distances. Since a mm-diam x-ray beam intercepts $\sim 10^{20}$ atoms, the average A-B probabilities and interatomic distance is the mean for $\sim 10^{21}$ pairs of atoms since each atom has typically eight to 12 first neighbors. This information can be recovered for many shells with high precision. Because diffuse x-ray scattering intensities normally do not include phase information, only pair correlation information can be recovered. With coherent x-ray sources it may be possible in the future to image small atom clusters to recover three body and higher order correlations. At present however the most detailed information

about local atomic structure comes from resonant x-ray scattering with extremely intense but incoherent x-ray beams from synchrotrons. Below we review briefly the basic diffraction theory of scattering from locally disordered alloys.

Basic Diffraction Theory

For an ensemble of atoms with complex x-ray atomic scattering factors f_p at the site p and the complex-conjugate f_q^* at the site q , the elastically scattered x-ray intensity is given by,

$$I(\vec{\mathbf{H}})_{TOTAL} = \left| \sum_p f_p \exp(2\pi i \vec{\mathbf{H}} \cdot \vec{\mathbf{r}}_p) \right|^2 = \sum_p \sum_q f_p f_q^* \exp[2\pi i \vec{\mathbf{H}} \cdot (\vec{\mathbf{r}}_p - \vec{\mathbf{r}}_q)]. \quad 5.$$

The sums over the lattice sites run from 0 to $N-1$ for N atoms, where $\vec{\mathbf{r}}_p$ and $\vec{\mathbf{r}}_q$ are the atomic position vectors for those sites, and $\vec{\mathbf{H}}$ is the momentum transfer or reciprocal lattice vector $|\vec{\mathbf{H}}| = (2 \sin \theta)/\lambda$, as shown in Figure 3. For crystalline solid solutions with a well-defined average lattice (sharp Bragg reflections) the atom positions can be represented by $\vec{\mathbf{r}} = \vec{\mathbf{R}} + \vec{\delta}$ where $\vec{\mathbf{R}}$ is determined from the lattice constants measured from positions of the Bragg reflections. $\vec{\delta}$ is the displacement both thermal and static of the atom from that average lattice. Equation (5) can be separated into terms of the average lattice $\vec{\mathbf{R}}$ and the local fluctuations $\vec{\delta}$,

$$I(\vec{\mathbf{H}})_{TOTAL} = \sum_p \sum_q f_p f_q^* \exp[2\pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q)] \exp[2\pi i \vec{\mathbf{H}} \cdot (\vec{\mathbf{R}}_p - \vec{\mathbf{R}}_q)]. \quad 6.$$

Figure 3. A cubic structure is used to illustrate the notation for the atom positions in a real space lattice with unit cell dimensions of $\vec{\mathbf{a}} = \vec{\mathbf{b}} = \vec{\mathbf{c}}$. The corresponding reciprocal space lattice is $\vec{\mathbf{a}}^*, \vec{\mathbf{b}}^*, \vec{\mathbf{c}}^*$. The position in reciprocal space $h_1 h_2 h_3$ at which the scattered intensity, $I(\vec{\mathbf{H}})$, is measured for an incoming x-ray in the direction of $\vec{\mathbf{S}}_0$ of wavelength λ

and detected in the outgoing direction of $\bar{\mathbf{S}}$ is $\bar{\mathbf{H}} = (\bar{\mathbf{S}} - \bar{\mathbf{S}}_0) / \lambda = h_1 \bar{\mathbf{a}}^* + h_2 \bar{\mathbf{b}}^* + h_3 \bar{\mathbf{c}}^*$. At Bragg reflections $h_1 h_2 h_3$ are integers and are usually designated hkl , the Miller indices of the reflection. This notation follows that used in the International Tables for Crystallography.

Our discussion of the diffraction theory is limited to crystalline binary alloys of A and B atoms with atomic concentration C_A and C_B respectively. The sums over all the atoms are a statistical description which includes all possible atom pairs that can be formed, i.e., A-A, A-B, B-A, B-B as described by Warren (20). A preference for like or unlike neighboring pairs is introduced by the conditional probability term P_{pq}^{AB} defined as the probability for finding a B atom at site q after having found an A atom at site p as given by Cowley, (30). The probability for A-B pairs is $C_A P_{pq}^{AB}$ which must equal $C_B P_{pq}^{BA}$ the number of B-A pairs. Also, $P_{pq}^{BB} = 1 - P_{pq}^{BA}$, $P_{pq}^{AA} = 1 - P_{pq}^{AB}$ and $C_A + C_B = 1$. We include all possible pairs and write the average value as ,

$$\begin{aligned} \left\langle f_p f_p^* \exp\left[2\pi i \bar{\mathbf{H}} \cdot (\bar{\delta}_p - \bar{\delta}_q)\right] \right\rangle &= C_A P_{pq}^{AA} f_A f_A^* \left\langle \exp\left[2\pi i \bar{\mathbf{H}} \cdot (\bar{\delta}_p^A - \bar{\delta}_q^A)\right] \right\rangle \\ &+ C_A P_{pq}^{BA} f_A f_B^* \left\langle \exp\left[2\pi i \bar{\mathbf{H}} \cdot (\bar{\delta}_p^B - \bar{\delta}_q^A)\right] \right\rangle + C_B P_{pq}^{AB} f_A f_A^* \left\langle \exp\left[2\pi i \bar{\mathbf{H}} \cdot (\bar{\delta}_p^A - \bar{\delta}_q^B)\right] \right\rangle \quad 7. \\ &+ C_B P_{pq}^{BB} f_B f_B^* \left\langle \exp\left[2\pi i \bar{\mathbf{H}} \cdot (\bar{\delta}_p^B - \bar{\delta}_q^B)\right] \right\rangle . \end{aligned}$$

Spatial and time averages are indicated for the chemically distinct A-A, A-B or B-B pairs with relative atom positions p-q. The Warren-Cowley short-range-order parameter is defined by Cowley (30) as $\alpha_{pq} \equiv 1 - P_{pq}^{AB} / C_B$ (Equation 4). With the substitution of Eq. (7) into Eq. (6), the total elastically and quasi-elastic (thermal) scattered intensity in electron units for a crystalline solid solution of two components is given as,

$$\begin{aligned}
I(\vec{\mathbf{H}})_{TOTAL} = & \sum_p \sum_q \left[(C_A^2 + C_A C_B \alpha_{pq}) |f_A|^2 \langle \exp 2\pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q) \rangle^{AA} \right. \\
& + C_A C_B (1 - \alpha_{pq}) f_A f_B^* \left(\langle \exp 2\pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q) \rangle^{BA} + \langle \exp \pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q) \rangle^{AB} \right) \\
& \left. + (C_B^2 + C_A C_B \alpha_{pq}) |f_B|^2 \langle \exp 2\pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q) \rangle^{BB} \right] \exp \pi i \vec{\mathbf{H}} \cdot (\vec{\mathbf{R}}_p - \vec{\mathbf{R}}_q), \quad 8.
\end{aligned}$$

where $|f_A|$ and $|f_B|$ denote the absolute value or moduli of the complex amplitudes.

The spatial and time average of the j^{th} order Taylor series expansion of the exponential displacement term is

$$\langle \exp \pi i \vec{\mathbf{H}} \cdot (\vec{\delta}_p - \vec{\delta}_q) \rangle \equiv \langle \exp i X_{pq} \rangle = 1 + i \langle X_{pq} \rangle - \frac{\langle X_{pq}^2 \rangle}{2} - \frac{i \langle X_{pq}^3 \rangle}{3!} + \dots + \frac{i^j \langle X_{pq}^j \rangle}{j!}. \quad 9.$$

Our interest is in the diffusely distributed intensity associated with the short-ranged correlations. We remove the long-ranged correlations which give rise to the sharply peaked (Bragg) reflections. With the definition $\langle X_{pq} \rangle = \langle X_p - X_q \rangle$ so that $\langle (X_p - X_q)^2 \rangle = \langle X_p^2 \rangle + \langle X_q^2 \rangle - 2 \langle X_p X_q \rangle$, and for sharply peaked Bragg reflections where $p - q \rightarrow \infty$ the displacements become uncorrelated so that $\langle X_p X_q \rangle = 0$. Therefore,

$$\langle X_{pq}^2 \rangle_{p-q \rightarrow \infty} = \langle X_p^2 \rangle + \langle X_q^2 \rangle, \text{ and with the harmonic approximation which relates the}$$

higher moment terms to the second moment, we can write the sharply peaked

intensity, $I(\vec{\mathbf{H}})_{Fund}$ as

$$I(\vec{\mathbf{H}})_{FUND} = \left[C_A f_A e^{-M_A} + C_B f_B e^{-M_B} \right]^2 \sum_p \sum_q \exp 2\pi i \vec{\mathbf{H}} \cdot (\vec{\mathbf{R}}_p - \vec{\mathbf{R}}_q). \quad 10.$$

Here M_A and M_B are the usual designation for the Debye-Waller factors including both dynamic and static displacements. This expression accounts for the reduced intensity of the fundamental Bragg reflections due to thermal motion and static displacements of the

atoms. Fundamental reflections scale as the average scattering factor and are insensitive to how the chemical composition is distributed on the lattice sites. When the alloy has long-range order among the kinds of atoms, the α_{pq} 's do not converge rapidly with larger p, q and account for the superstructure Bragg reflections that depend on how the atoms are distributed among the sites. To recover the diffuse intensity, we subtract $\mathbf{I}(\vec{\mathbf{H}})_{FUND}$ from $\mathbf{I}(\vec{\mathbf{H}})_{TOTAL}$ Eq. (8) without making the harmonic approximation used in Eq. (10).

To second order in the Taylor series expansion of the static and thermal displacements, we have that,

$$\begin{aligned}
\mathbf{I}(\vec{\mathbf{H}})_{DIFFUSE} = & \sum_p \sum_q \left\{ (C_A^2 + C_A C_B \alpha_{pq}) |f_A|^2 \left(1 + i \langle X_p^A - X_q^A \rangle - \frac{1}{2} \langle (X_p^A - X_q^A)^2 \rangle \right) \right. \\
& - C_A^2 |f_A|^2 \left(1 - \langle X^2 \rangle^A \right) + C_A C_B (1 - \alpha_{pq}) f_A f_B^* \left(1 + i \langle X_p^B - X_q^B \rangle - \frac{1}{2} \langle (X_p^B - X_q^B)^2 \rangle \right) \\
& - 2 C_A C_B f_A f_B^* \left(1 - \frac{1}{2} \langle X^2 \rangle^A - \frac{1}{2} \langle X^2 \rangle^B \right) \\
& + C_A C_B (1 - \alpha_{pq}) f_A f_B^* \left(1 + i \langle X_p^A - X_q^B \rangle - \frac{1}{2} \langle (X_p^A - X_q^B)^2 \rangle \right) \\
& + (C_B^2 + C_A C_B \alpha_{pq}) |f_B|^2 \left(1 + i \langle X_p^B - X_q^B \rangle - \frac{1}{2} \langle (X_p^B - X_q^B)^2 \rangle \right) \\
& \left. - C_B^2 |f_B|^2 \left(1 - \langle X^2 \rangle^B \right) \right\} \exp \left[i \vec{\mathbf{H}} \cdot (\vec{\mathbf{R}}_p - \vec{\mathbf{R}}_q) \right].
\end{aligned} \tag{11}$$

For an alloy which is on average statistically cubic such as that shown in Figure 3, we define

$$\vec{\mathbf{R}}_p - \vec{\mathbf{R}}_q \equiv \vec{\mathbf{R}}_0 - \vec{\mathbf{R}}_{lmn} = \frac{l}{2} \vec{\mathbf{a}} + \frac{m}{2} \vec{\mathbf{b}} + \frac{n}{2} \vec{\mathbf{c}} \quad ; \quad \vec{\mathbf{H}} \equiv h_1 \vec{\mathbf{a}}^* + h_2 \vec{\mathbf{b}}^* + h_3 \vec{\mathbf{c}}^*, \tag{12}$$

so that

$$2\pi \vec{\mathbf{H}} \cdot (\vec{\mathbf{R}}_0 - \vec{\mathbf{R}}_{lmn}) = \pi (h_1 l + h_2 m + h_3 n). \tag{13}$$

In addition,

$$\vec{\delta}_{lmn} \equiv \Delta X_{lmn} \vec{a} + \Delta Y_{lmn} \vec{b} + \Delta Z_{lmn} \vec{c}, \quad 14.$$

so that

$$\begin{aligned} X_0 - X_{lmn} &\equiv 2\pi \vec{H} \cdot (\vec{\delta}_0 - \vec{\delta}_{lmn}) \equiv 2\pi [h_1(\Delta X_0 - \Delta X_{lmn}) \\ &+ h_2(\Delta Y_0 - \Delta Y_{lmn}) + h_3(\Delta Z_0 - \Delta Z_{lmn})]. \end{aligned} \quad 15.$$

This definition of $\vec{R}_0 - \vec{R}_{lmn}$ causes the continuous variables h_1, h_2, h_3 in reciprocal space to have the integer values of the Miller indices at reciprocal lattice points. We further specify that the site symmetry is cubic such as for the bcc Fe structure and fcc Cu structure. With these definitions the various diffuse x-ray scattering terms through the second moment contained in Eq. (11) can be written, starting with the local chemical order term as,

$$\frac{I(\vec{H})_{Diffuse}}{N} = \frac{I(\vec{H})_{SRO}}{N} + \frac{I(\vec{H})_{j=1}}{N} + \frac{I(\vec{H})_{j=2}}{N} \quad 16a.$$

where

$$\frac{I(\vec{H})_{SRO}}{N} = \sum_{lmn} C_A C_B |f_A - f_B|^2 \alpha_{lmn} \cos\pi(h_1 l + h_2 m + h_3 n) \quad , \quad 16b.$$

which describes the diffuse scattering arising from local chemical order among the atoms as first given by Cowley (30),

$$\begin{aligned} \frac{I(\vec{H})_{j=1}}{N} &= -\text{Re}\left(f_A (f_A^* - f_B^*)\right) \left[h_1 Q_x^{AA} + h_2 Q_y^{AA} + h_3 Q_z^{AA} \right] \\ &+ \text{Re}\left(f_B (f_A^* - f_B^*)\right) \left[h_1 Q_x^{BB} + h_2 Q_y^{BB} + h_3 Q_z^{BB} \right] \quad , \end{aligned} \quad 16c.$$

This first moment of the static displacements is the term with which we are most concerned when recovering interatomic distances. The second moment of the displacements is written as,

$$\begin{aligned}
\frac{I(\vec{H})_{j=2}}{N} &= |f_A|^2 (h_1^2 R_X^{AA} + h_2^2 R_Y^{AA} + h_3^2 R_Z^{AA}) \\
&+ f_A f_B^* (h_1^2 R_X^{AB} + h_2^2 R_Y^{AB} + h_3^2 R_Z^{AB}) + |f_B|^2 (h_1^2 R_X^{BB} + h_2^2 R_Y^{BB} + h_3^2 R_Z^{BB}) \\
&+ |f_A|^2 (h_1 h_2 S_{XY}^{AA} + h_1 h_3 S_{XZ}^{AA} + h_2 h_3 S_{YZ}^{AA}) + f_A f_B^* (h_1 h_2 S_{XY}^{AB} + h_1 h_3 S_{XZ}^{AB} \\
&+ h_2 h_3 S_{YZ}^{AB}) + |f_B|^2 (h_1 h_2 S_{XY}^{BB} + h_1 h_3 S_{XZ}^{BB} + h_2 h_3 S_{YZ}^{BB}),
\end{aligned} \tag{16d}$$

which describes the diffuse intensity distribution associated with the second moment of the displacements (both static and thermal). The terms contained in Eq. 16c are given by,

$$Q_X^{AA} = 2\pi \sum_{lmn} (C_A^2 + C_A C_B \alpha_{lmn}) \left\langle \Delta X_{lmn}^A \right\rangle_0^A \sin \pi h_1 l \cos \pi h_2 m \cos \pi h_3 n$$

and

$$Q_X^{BB} = 2\pi \sum_{lmn} (C_B^2 + C_A C_B \alpha_{lmn}) \left\langle \Delta X_{lmn}^B \right\rangle_0^B \sin \pi h_1 l \cos \pi h_2 m \cos \pi h_3 n ,$$

and similarly for the y and z terms as first given by Warren et al (40) and later by Borie & Sparks (41) without their earlier assumption of radial displacements. The displacement terms are written as $\left\langle \Delta X_{lmn}^A \right\rangle_0^A = \left\langle \Delta X_0^A - \Delta X_{lmn}^A \right\rangle$, and schematically shown in Figure 4.

Figure 4. Rectangular cube of solid lines is the average lattice about which the atom centers + are displaced by the amount $\vec{\delta}_{pq}$. Shown in the small box on the right are the rectangular components of the displacement, ΔX , ΔY , and ΔZ .

Equations (16b,c,d) are derived from the terms first given by Borie & Sparks (42), but with notation similar to that used by Georgopoulos & Cohen (43). There are twenty-five Fourier series in Eqs. (16b-16d). For a cubic system with centrosymmetric sites if we know Q_X^{AA} , then we know Q_Y^{AA} and Q_Z^{AA} . Similarly if we know Q_X^{BB} , R_X^{AA} , R_X^{BB} ,

R_X^{AB} , S_{XY}^{AA} , S_{XY}^{BB} , and S_{XY}^{AB} then we know all the Q's, R's and S's. Thus with the addition of the α series, there are nine independent Fourier series for cubic diffuse scattering to second order.

From the definition of an average lattice, the weighted average of the displacements for all the kinds of pairs formed for any coordination shell was shown by Warren et al (40) to be zero. Thus

$$2(\alpha_{pq} - 1) \langle \bar{\delta}_p^A - \bar{\delta}_q^B \rangle = \left(\frac{C_A}{C_B} + \alpha_{pq} \right) \langle \bar{\delta}_p^A - \bar{\delta}_q^A \rangle + \left(\frac{C_B}{C_A} + \alpha_{pq} \right) \langle \bar{\delta}_p^B - \bar{\delta}_q^B \rangle. \quad 17.$$

If a crystal structure has more than one kind of sublattice with different site symmetries, then Eq. (17) may be true for only that sublattice with all the same site symmetries. This conservation of volume is why there are but two of the three possible pair terms in Eq. (16c). Details of the individual terms of Eq. (16d) are given by Borie & Sparks (42) and Georgopoulos & Cohen (43). As it is difficult to separate second-moment static from second-moment thermal displacements, we will address attempts for their separation from the diffraction pattern so that we can recover $I(\vec{\mathbf{H}})_{SRO}$ and $I(\vec{\mathbf{H}})_{j=1}$.

Recovery of local order and displacement parameters

BORIE-SPARKS METHOD As illustrated above in Eq. (16b), local chemical order (Warren-Cowley α 's) can be recovered from a crystalline binary alloy with a single measurement of the diffuse scattering distribution provided $f_A - f_B \neq 0$, and the displacement contributions are negligible. This was the early practice until a series of papers used the symmetry relationships among the various terms to isolate their contributions to the diffuse x-ray scattering. First, Borie & Sparks (41) showed how symmetry could be used to remove the $I(\vec{\mathbf{H}})_{j=1}$ term in two dimensions. Sparks & Borie (44) extended the technique to three dimensions then Borie and Sparks (42), henceforth referred to as BS, developed a separation of the diffuse scattering through the second moment into all three components in three dimensions: $I(\vec{\mathbf{H}})_{\text{SRO}}$, $I(\vec{\mathbf{H}})_{j=1}$, $I(\vec{\mathbf{H}})_{j=2}$. The major assumption of the BS method is that the x-ray atomic scattering factor terms $|f_A - f_B|^2$, $\text{Re}(f_A(f_A^* - f_B^*))$, $\text{Re}(f_B(f_A^* - f_B^*))$, $|f_A|^2$, $|f_B|^2$, and $f_A f_B^*$ of Eq. (16) have a similar $\vec{\mathbf{H}}$ dependence so that a single divisor renders them independent of $\vec{\mathbf{H}}$.

The periodicity of the terms of Eqs. (16b-d) and the assumption that the scattering factor terms can be made independent of $\vec{\mathbf{H}}$ permits us to write them as a sum of periodic functions;

$$\begin{aligned} \frac{I(\vec{\mathbf{H}})_{\text{DIFFUSE}}}{N|f(\vec{\mathbf{H}})|^2} &= A(h_1 h_2 h_3) + h_1 B(h_1 h_2 h_3) + h_2 B(h_2 h_3 h_1) \\ &+ h_3 B(h_3 h_1 h_2) + h_1^2 C(h_1 h_2 h_3) + h_2^2 C(h_2 h_3 h_1) + h_3^2 C(h_3 h_1 h_2) \\ &+ h_1 h_2 D(h_1 h_2 h_3) + h_1 h_3 D(h_2 h_3 h_1) + h_2 h_3 D(h_3 h_1 h_2), \end{aligned} \quad 18.$$

where $A(h_1, h_2, h_3)$ is given by Eq. (16b) $\div |f(\vec{\mathbf{H}})|^2$, and $B(h_1 h_2 h_3)$ contains the two terms $-f_A \Delta f^* Q_X^{AA} + f_B \Delta f^* Q_X^{BB}$ given by Eq. (16c) $\div |f(\vec{\mathbf{H}})|^2$ and likewise for the other terms.

For neutron nuclear scattering, the assumption that the scattering cross sections are independent of $\vec{\mathbf{H}}$ is valid. In addition, thermal scattering of neutrons results in a sufficient shift in energy that the phonon contribution to terms C and D of Eq. (18) can be filtered out. A neutron scattering experiment by Müller et al (17) on Al+1.7 at. % Cu single crystals was used to study the structure of Guinier-Preston zones. Two different isotopes were used to separate the A-A and B-B displacements in the $j=1$ term. This technique removes the large thermal diffuse scattering contribution and for small displacements, where the second moment is negligible, is an excellent method. The major uncertainties are the ability to produce two single crystals identical in every way except for the kind of isotope, and restrictions from limited data and statistics because of low flux levels of neutron sources. The BS procedure has been applied for example to studies of compositions between 9 and 13 at. % Al in Cu by Epperson et al (45). Shown in Figure 5 are the x-ray atomic scattering factor terms which appear in Eq. (16) for the composition $\text{Al}_{14}\text{Cu}_{86}$ with a lattice parameter of $a=3.654 \text{ \AA}$. Data in $\vec{\mathbf{H}}$ space coordinates typically includes $|\vec{\mathbf{H}}| = 1$ to 4 which is sufficient for the BS separation through the second moment of the displacements. The minimum volume of data has been described by Gragg et al (46). With a proper choice of the divisor, the $\vec{\mathbf{H}}$ dependence of the scattering factor terms can be minimized. We chose $\langle f \rangle^2$ for the divisor in Figure 5. Various divisors could be chosen which would cause the curves in Figure 5 to have various slopes and in this way bracket the values of the recovered α 's and displacement parameters. This would allow an estimate of the errors associated with the assumption of linearity for

the various scattering factor terms contained in Eq. (16) and plotted in Figure 5. Since the terms Q_X^{AA} and Q_X^{BB} have the same symmetry and $\bar{\mathbf{H}}$ dependence, the BS method does not allow for their separation with one measurement of the diffuse scattering.

Figure 5. Variation of the x-ray atomic scattering factor terms divided by $\langle f \rangle^2$ as a function of the magnitude of the momentum transfer $|\mathbf{H}|$. Division by other terms could be used to reduce and/or change their $|\mathbf{H}|$ dependence.

GEORGOPOULOS-COHEN METHOD To overcome this limitation, Georgopoulos and Cohen (3), following a suggestion by Tibballs (47), used the difference in the variation of the x-ray scattering factors with $\bar{\mathbf{H}}$ to separate the A-A and B-B pair displacements. This procedure by Georgopoulos and Cohen (43), henceforth GC, was widely applied.

Though in principle the GC method used the symmetries of the BS separation, the GC method recovered the Fourier coefficients α 's, Q's, R's, and S's of Eq. (16b,c) in a large least squares program. A Householder transformation was used to avoid matrix inversion with ridge-regression techniques for stabilization. This still resulted in unacceptable large errors for the individual A-A, A-B, and B-B values of the R's and S's as discussed by Wu et al (48). However, the symmetry of the various terms was preserved, and their separation allowed for the recovery of the α 's with report uncertainties of 10% or less of their value (48). Smallest uncertainties occur when there is a preference for unlike first neighbors which places the diffuse maxima in the scattering away from the intense Bragg peaks. When there is a preference for clustering (like nearest neighbors), errors increase (Gragg 46). Wu et al (48) reports smaller uncertainties with the GC method compared with the BS method for clustering systems. Experience and more systematically correct

data from intense synchrotron sources will permit further reduction in the measurement uncertainties.

MODERN RESONANT METHODS When the difference in the atomic numbers of the constituent elements is small such as for Fe-Ni, the Laue scattering term proportional to $|f_{Fe} - f_{Ni}|^2$ is small. This is the basis for a methodology by Ice et al (49) to recover the pair correlation parameters with selectable x-ray energies. Of most practical interest are the α 's and the first moment of the static displacements as given in Eqs. (16b,c,d). The scattering factor term $f_A - f_B$ can be made to be nearly zero by proper choice of x-ray energy nearby to an x-ray absorption edge. In this way, the intensities expressed in Eqs. (16b-c) are made nearly zero, and only that intensity associated with Eq. (16d) remains. Thus, the term $I(\vec{\mathbf{H}})_{j=2}$ can be measured without the terms of equations (16b-c), then scaled to diffuse scattering measurements made at other x-ray energies (which emphasize the contrast between the A and B atoms) and subtracted off. This leaves only the $I(\vec{\mathbf{H}})_{SRO}$ term Eq. (16b) and the first moment of the static displacements $I(\vec{\mathbf{H}})_{j=1}$, Eq. (16c). Recovery of these individual static displacements for the A-A and B-B pairs requires that the ratio $\text{Re } f_A(f_A - f_B)^* / \text{Re } f_B(f_A - f_B)^*$ be changed by an appropriate choice of x-ray energies, as shown in Figure 6. The variation or contrast obtained by changing the x-ray energy especially near the Fe K and Ni K absorption edges shown in Figure 6a is much larger than obtained by changing the scattering angle or momentum transfer as shown in Figure 6b. Near the Ni K edge one can actually reverse the ratio (contrast) as shown in Figure 6a, which produces notable changes in the diffraction pattern as shown in Figure 7. This sensitivity of the diffuse scattering to changes in the x-ray atomic

scattering factor of one or more of the constituent atoms permits the separation and recovery of the A-A and B-B pair contributions as originally proposed by Ramesh and Rameshan (50) and implemented by Ice et al (49).

Figure 6. (a) Separation of the contribution of the two kinds of pairs A-A and B-B to the diffuse scattering depends on how large a difference can be affected by changing x-ray energy near absorption edges. (b) Reliance on the much smaller change in ratio obtained by changes in scattering angle does not produce as robust a solution.

FIGURE 7

Figure 7. The change in the diffuse intensity at the Fe K edge O and Ni K edge permits the separation of the Fe-Fe and Ni-Ni pair displacements. The near null Laue energy of 8000 eV allows removal of thermal diffuse scattering from the data taken at the other two energies.

The major assumption in this null Laue or 3λ method (49) is that the $I(\vec{\mathbf{H}})_{j \geq 2}$ which includes the higher moment terms scale with x-ray energy as $|C_A f_A + C_B f_B|^2$. This implies that the A and B atoms have the same second and higher moment displacements or that the different elements have the same x-ray atomic scattering factors. This assumption is most valid for alloys of elements with similar atomic numbers which have similar masses (similar thermal motion), similar atom sizes (small static displacement), and similar numbers of electrons (similar x-ray scattering factors). This 3λ method has

been used to analyze four different alloys, Fe_{22.5}Ni_{77.5} (40) Cr₄₇Fe₅₃ (51), Cr₂₀Ni₈₀ (52), and Fe_{46.5}Ni_{53.5} and recalculated Fe_{22.5}Ni_{77.5} (26). An improvement in the null-Laue method by Jiang et al (26) removed the iteration procedure to account for the residuals left by the fact that $f_A - f_B$ was not strictly zero over the measured volume.

Estimation of the statistical and systematic errors of this null Laue method has been given by Jiang et al (26) and by Ice et al (22). The statistical uncertainties of the recovered parameters can be estimated by propagating the standard deviation $\pm\sqrt{n}$ of the total number of counts n for each data point through the non-linear least squares processing of the data. Systematic errors can be determined by changing the values of input variables such as the x-ray atomic scattering factors, backgrounds, and composition. The data is then reprocessed and the recovered parameters compared.

Since the procedure calls for the subtraction of the large thermal scattering contribution represented by the 8000 eV data of Figure 7, the measured pair correlation coefficients are very sensitive to the relative and to a lesser degree the absolute intensity calibration of the data sets. The addition of constraints on the intensity calibrations of the three (or more) energy data sets, greatly increases reliability and reduces uncertainties. Scaling factors of the measured scattering intensities are varied as input parameters. The intensities are adjusted until $\alpha_{000}=1$, and the I_{SRO} values are everywhere positive and match values at the origin of reciprocal space measured by small-angle scattering. These constraints eliminate most of the systematic errors associated with converting the raw intensities into absolute units as discussed by Sparks et al., (53). The intensities measured at three different energies are adjusted to within ~1% on a relative scale and the intensity at the origin is matched to measured values. With adequate statistics, the systematic errors for α_{000} are estimated at ~1%. Estimated uncertainties on the other α 's are less than 1%, and the first moment of the displacements can be recovered to ± 0.003

Å or less for the first five shells, as discussed by Jiang (26). Experimental details have been given by Ice et al (54).

The use of resonant scattering to separate the A-A and B-B local correlations has proven to be a robust method which unambiguously identifies the atom pairs which have the larger and smaller displacements. Butler and Cohen (55) in earlier work used the GC method of analysis to recover the static displacements from a single x-ray wavelength measurement of disordered AuCu₃ and concluded that the Au-Au pair first neighbor distance was shorter than that for Cu-Cu. This result is puzzling in light of the experimental observation that ordering of AuCu₃ reduces the lattice constant (more first neighbor Au-Cu pairs are formed at the expense of Cu-Cu and Au-Au pairs) and the experimental finding that the addition of the ~14% larger Au atoms to Cu increases the lattice constant. The dilation of the lattice constant is evidence that either the Au-Au bond and/or the Au-Cu bond distance is larger than that of Cu-Cu. EXAFS measurements also show that Au-Au first neighbor distances are the largest of the three pairs for all Au-Cu alloys (56). Theoretical considerations by Charkraborty (4); Horiuchi et al.(57) and Ozolins et al (58) have all concluded that the Au-Au bond distance is the largest of the three kinds. Apparently, the \vec{H} variation of $f_{Au} \Delta f^*$ and $f_{Cu} \Delta f^*$ is not adequately different to provide for a meaningful separation of the Au-Au and Cu-Cu bond distances with the GC method. In a direct comparison with the 3λ technique by Schönfeld et al (52) on an alloy of Ni₈₀Cr₂₀, the GC result gave a Cr-Cr bond distance which was smaller than the average lattice, an opposite conclusion to the 3λ result. Since the addition of Cr to Ni increases the lattice parameter, there is reason to suspect that Cr is the larger atom and that Cr-Cr NN distances should be larger than the average lattice. This was the result given by the 3λ method (52). A full

accounting of the possible errors introduced by the assumption of similar second and higher order moments of the displacements for the different atom constituents for the 3λ method has not been made. Surely the assumption would become less valid for atoms with increasing different masses like Au and Cu. However, there is also a concern about calculating the thermal diffuse scattering from the force constants and subtracting it off. The Born-Von Karman approach as discussed by Warren (20) assumes that Au and Cu have similar thermal amplitudes. Iterative techniques which force known symmetries on the measured diffuse scattering are being considered by the present authors as a way to remove any assumptions in recovering the parameters which describe the local structure.

OBSERVATIONS OF LOCAL ATOMIC ARRANGEMENTS

Chemical order

There have been but few diffuse scattering studies where anomalous x-ray scattering (or isotopic substitution with neutrons) has been used to recover local order and atomic displacements. The earliest reported work was a recovery of the local order among atoms in ternary solid solutions. For a ternary alloy of A, B and C type atoms, there are three independent pair probabilities: A-B, A-C and B-C. These pair probabilities are related such that $P^{AA} = 1 - P^{AB} - P^{AC}$. A neutron study of the local atomic chemical order in a $\text{Cr}_{21}\text{Fe}_{56}\text{Ni}_{23}$ stainless steel separated the three pair probabilities by using three isotopically different compositions as reported by Cenedese et al (59). Thermal contributions were filtered out by the energy shift and static displacements through first order, $I_{j=1}$, were removed by the BS symmetry arguments. Magnetic scattering was considered to be insignificant. An analysis of the results showed that the individual pair probabilities were significant and known to about ± 0.01 with even smaller uncertainties for the Fe-Ni pairs. Shown in Figure 8 in the left-hand column is a plot of the Warren-Cowley short-range

order parameters recovered for the $\text{Cr}_{21}\text{Fe}_{56}\text{Ni}_{23}$ (59) ternary alloy. Under the reasonable assumption that the second order and higher moments of the static displacements are small. For comparison the α 's recovered from binary alloys (51, 52, and Robertson JL et al submitted) are plotted in the right-hand. Though the binary concentrations are not in the same ratio as those for the ternary, this comparison, nevertheless, provides an insight into how the addition of a third element can affect the probability for specific pair formation. The preference for Fe-Ni near-neighbor pairs in the binary alloy (from Robertson JL et al submitted) is reduced by the addition of Cr. Chromium seems to have a greater affinity for Ni nearest neighbors than does Fe, thus Cr replaces the Fe-Ni NN pairs with Ni-Cr NN pairs. Though the bcc binary $\text{Fe}_{53}\text{Cr}_{47}$ has a miscibility gap and was shown to have a preference for Fe-Fe as NN (51), in the fcc stainless steel alloy this tendency for phase separation has been replaced with a nearly equal affinity to form either Fe-Cr NN or Fe-Fe NN pairs.

Figure 8. The Warren-Cowley short-range order parameters α_{lmn}^{AB} in the left-hand column for a ternary alloy $\text{Fe}_{56}\text{Cr}_{21}\text{Ni}_{23}$ obtained by Cenedese et al (59) is compared with those from binary alloys in the right-hand column (51,52, Robertson JL et al submitted). The bonding preference of an atom pair can be affected by the addition of a third element.

A $\text{Cu}_{47}\text{Ni}_{29}\text{Zn}_{24}$ ternary alloy is a case in which resonant diffuse scattering at three x-ray energies provided the contrast to measure the three independent chemical pair correlations. This study with tunable synchrotron radiation by Hashimoto et al (60)

assumed that the static displacements were small and recovered the α 's for Ni-Zn, Cu-Zn and Cu-Ni pairs out to four shells. They found that Zn had a preference for unlike NN of Cu and Ni while Cu-Ni pairs preferred not to be NN. From a study of the binary phase diagrams, we find that there is a tendency for Ni-Zn and Cu-Zn to bond and form compounds, whereas Cu-Ni has a tendency to phase separate. Thus the presence of a third constituent in this case does not seem to qualitatively alter the bonding preference of the remaining pairs. This seems reasonable if there is no strong preference for forming one kind of near neighbor bond over another. Information of the kind illustrated above, will provide important tests for theoretical modeling of phase stability. We can now measure local chemical preferences among atomic neighbors which would be very difficult if not impossible to measure by any other means.

Local atomic displacements and chemical order

An early neutron scattering experiment in one dimension by Müller et al (17) on two isotopically different single crystals of $\text{Al}_{98.5}\text{Cu}_{1.75}$ recovered the displacements perpendicular to the Cu rich {100} planes of atoms known as Guinier-Preston zones. A planer model was used to interpret the results. The large displacement of the Al atoms towards the smaller Cu rich planes was sufficient to make a significant contribution to the measured intensity especially for $|H| \geq 2$. These measurements have added valuable information to the understanding of the local displacements in the early stages of precipitation.

In the series of papers in which the 3λ or null Laue method Ice et al (50) was applied to the study of $\text{Fe}_{22.5}\text{Ni}_{77.5}$, $\text{Fe}_{53}\text{Cr}_{47}$ by Reinhard et al (51), $\text{Ni}_{80}\text{Cr}_{20}$ by Schonfeld et al (52), and then on $\text{Fe}_{46.5}\text{Ni}_{53.5}$ by Jiang et al (26), both the local order coefficients and the atomic displacements were recovered for the individual pairs. Most recently the

composition $\text{Fe}_{63.2}\text{Ni}_{36.8}$ has been studied with the 3λ x-ray method by J.L. Robertson et al submitted. Information on local chemical order for $\text{Ni}_{80}\text{Cr}_{20}$ and $\text{Fe}_{53}\text{Cr}_{49}$ was shown in Figure 8. Recovered displacements are shown schematically in Figure 9. Both the Fe-Ni and Cr-Ni alloys show a preference for unlike nearest neighbors pairs and have the smallest average separation. A clustering alloy such as Cr-Fe with a preference for like nearest neighbors have the unlike nearest neighbors furthest apart as shown in Figure 9c. Other than the earlier mentioned cluster calculation on Fe-Ni compositions which gave qualitative insight into the interatomic distances with charge redistribution between the atom pairs (36), most theoretical effort has avoided the magnetic transition metals.

Figure 9. Schematic representation of the average first neighbor displacements of the three kinds of pairs from the average lattice by a square of solid lines. The atom centers + are on average closest for those pairs with a preference as nearest neighbors. Data from references 26,51, 52.

SUMMARY AND FUTURE DIRECTIONS

Resonant x-ray measurements of diffuse scattering from solid-solution alloys is an emerging technique made possible by intense and tunable 2nd generation synchrotron sources. The use of three wavelengths to vary the scattering contrast of elements within a binary alloy can already yield high precision measurements of local chemical order and chemically specific displacements for binary alloys with elements nearby in the periodic table. Efforts are now underway to extend resonance techniques to alloys with elements further apart in the periodic table. A better treatment of second moment and higher order

displacement scattering is central to extending resonance techniques to most alloys systems.

Present theoretical calculations of atomic displacements have concentrated on the non-transition and non-ferromagnetic metal alloys due to theoretical simplifications. Since resonance experiments to date have surveyed only the Fe-Ni system at different elemental concentrations, comparisons to theoretical models is controversial. There is therefore an urgent need in the immediate future to apply resonance techniques to study local correlations on a classical system such as Au-Cu. Here for example, diffuse scattering measurements of displacements in three or more compositions across the phase diagram are needed to provide an unambiguous test of theoretical insights into local correlations in alloys.

With the new 3rd generation synchrotron sources now coming on line, experimental uncertainties will be further reduced due to the ~20 fold increase in flux and smaller focus size which improves the scattered-beam energy resolution for separation of the elastic and quasi-elastic scattering from the inelastic scattering. These sources also make available high-energy K and L edges which will extend resonance techniques to new alloys systems. Most helpful would be a way to recover the second and even higher moments of the static displacements from which distributions of the displacements could possibly be deduced. Neutron diffuse scattering measurements can resolve thermal diffuse scattering, but are impractical for full three-dimensional studies on alloys due to their limited flux. However, a combination of both x-ray and neutron scattering could help resolve thermal from static displacements. Thus careful calibration of the absolute intensities, attention to experimental detail and new methodologies will result in local

correlations with sufficient precise to challenge theoretical models for virtually any alloy combination.

ACKNOWLEDGMENTS Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05 96OR22464 with Lockheed Martin Energy Research Corporation.

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