RECOVERY OF SRO PARAMETERS AND PAIRWISE ATOMIC DISPLACEMENTS IN A Fe$_{46.5}$Ni$_{53.5}$ ALLOY

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ABSTRACT

Resonant (anomalous) x-ray scattering is used to alter the contrast between atoms nearby in the periodic table to recover local pair correlations. Both Warren-Cowley short-range order parameters and chemically specific interatomic distances are recovered from diffusely scattered x-ray intensities measured at three different x-ray energies ($3\lambda$ method). Analysis of the statistical and systematic errors shows that the average values for the number and kinds of first nearest neighbors are recovered to about one atom in one hundred and their interatomic distances to about $\pm 0.002 \text{Å}$.

INTRODUCTION

Although the influence of atomic size on the structure of alloys has been recognized since the first attempts to understand alloy phases, the exact role of size has remained elusive due to the difficulty of measuring atomic size in alloys. Recent experiments are beginning to measure atomic size within an alloy. Such measurements include extended x-ray absorption fine structure measurements (EXAFS) on dilute alloys, diffuse neutron scattering on isotopically tailored samples, and diffuse x-ray scattering.

The diffuse x-ray scattering measurements on single crystals provide the most detailed information of local structure, chemical ordering, and pairwise atomic displacements, but have been limited until recently by weak sources and by low contrast between elements nearby in the periodic table. The recent availability of synchrotron radiation allows the measurement of chemical and displacement correlation in alloys even with elements nearby in the periodic table; with an intense and tunable x-ray source, the x-ray energy can be selected to lie below an absorption edge of the low Z-element. Here resonant (anomalous) x-ray scattering factors reduce the x-ray scattering from the low Z element and enhance the contrast, $\Delta f = f_a - f_b$, between unlike neighbor atoms. The recovery of chemical correlation, although previously difficult for alloys with atoms nearby in the periodic table, is now robust and uncontroversial.

Measurement of chemically specific displacement correlation, however, remains sensitive to the recovery technique and to uncertainties in the relative calibration between x-ray scattering at different energies. We describe a new formulation of the diffuse x-ray scattering equations which is optimized for the recovery of chemical and displacive correlation with anomalous x-ray scattering methods. The new method explicitly avoids the need for a null or near null contrast...
measurement as was previously required. This allows the $3\lambda$ resonant scattering method to be applied to a wider range of binary alloys with greater stability in the recovered coefficients.

**THEORY**

The total elastic scattering intensity of x rays from a crystalline binary alloy is given by

$$I_T = I_{\text{fund}} + I_{\text{Laue}}.$$  \hspace{1cm} (1)

Here $I_{\text{fund}}$ is the so called fundamental scattering component, which scales as the square of the average scattering factor $<f>_2^2$, and $I_{\text{Laue}}$ is the Laue component, which depends on the x-ray scattering contrast between unlike atoms. With a first order expansion in displacements from an ideal lattice, $I_{\text{Laue}} = I_{\text{sko}} + I_{\text{size}}$, where the chemical short-range order scattering, $I_{\text{sko}}$, and the first order size effect scattering, $I_{\text{size}}$, are given by $^{1,2}$:

$$I_{\text{sko}} = \sum_{i,m,n} c_A (1 - c_A) f_A - f_B |^2 \alpha(\text{lmn}) \cos[2\pi(h_1 + h_2 + h_3 + h_4)],$$  \hspace{1cm} (2)

and

$$I_{\text{size}} = -\sum_{i,m,n} \frac{2\pi}{a} c_A (1 - c_A) \sin[2\pi(h_1 + h_2 + h_3 + h_4)]
\times \left[ \left[ \frac{c_A}{1 - c_A} + \alpha(\text{lmn}) \right] \times \text{Re}\\left[ f_A (f_A - f_B) \right] \right]
\times \left[ \delta_{\text{AA}}^+ (\text{lmn}) > h_1 + \delta_{\text{BB}}^+ (\text{lmn}) > h_2 + \delta_{\text{AB}}^+ (\text{lmn}) > h_3 \right]
+ \left[ \frac{1 - c_A}{c_A} + \alpha(\text{lmn}) \right] \text{Re}\\left[ f_B (f_B - f_A) \right] \right]
\times \left[ \delta_{\text{BB}}^+ (\text{lmn}) > h_1 + \delta_{\text{BB}}^- (\text{lmn}) > h_2 + \delta_{\text{BB}}^- (\text{lmn}) > h_3 \right].$$  \hspace{1cm} (3)

Here $c_A$ is the atom concentration, $f_A$ and $f_B$ are the respective atomic scattering factors, $a$ is the lattice parameter of a cubic system, and $h_1$, $h_2$, and $h_3$ are the coordinates of the momentum transfer vector $h$ in reciprocal lattice units. The average pair displacements for AA and BB pairs with relative coordinates 1, $m$, and $n$ are given by $\delta_{\text{AA}}^+$ and $\delta_{\text{BB}}^+$, respectively. The average displacements $\delta_{\text{AB}}^+$ can be derived from the AA and BB displacements.

Several authors$^{3,4}$ have recently applied resonant x-ray scattering to studies of local structure in binary alloys. In this $3\lambda$ method, two measurements are made near the absorption edges of each element and another measurement is made at the energy where the contrast of atomic scattering factors $\Delta f = f_A - f_B$ is a minimum. This method is ideal for binary alloys with elements nearby in the periodic table. It has been shown that the $3\lambda$ method can successfully recover both pairwise displacements and short-range order parameters.
To extend this method to crystals with elements no longer nearby in the periodic table and simplify data analysis procedure, we introduce a “normalized intensity difference”, $\Delta S$, which is defined as:

$$\Delta S = \frac{I_1(E_1)}{< f(E_1) >^2} - \frac{I_1(E_2)}{< f(E_2) >^2}.$$  

Here, $I_1(E_1)$ and $I_1(E_2)$ are the total intensities with the incident photon energy $E_1$ and $E_2$, respectively. $\Delta S$ has only two components: short-range order term $\Delta S_{\text{short}}$ and size-effect term $\Delta S_{\text{size}}$, since $I_{\text{ref}}(E)/< f(E) >^2$ is independent of incident photon energy. An expression of $\Delta S_{\text{short}}$ can be easily obtained by substituting $|f_A - f_B|^2$ in Eq.(2) with $|f(A) - f(B)|^2/|f(E)| >^2$. Similarly, one can obtain the expression of $\Delta S_{\text{size}}$ by replacing $f(A) - f(B)$ with $f(A) - f(B)$ and $f(E)$ with $f(E)$. With measurements at three different energies, two sets of the normalized intensity difference can be constructed, and thus both short-range order parameters and pairwise displacements may be recovered by applying the least-square fit on $\Delta S$.

The application of the normalized intensity difference analysis to the 3A method simplifies the analysis procedure by eliminating iterations, and reduces the time for data processing by a factor of three or more. It also remains valid for crystals where no null contrast measurement is possible, and hence extends the 3A method to a wider range of materials.

**EXPERIMENT**

The diffuse scattering experiments were carried out on the beam line X-14 at the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL). The sample was mounted on a Huber four-circle diffractometer and enclosed in a hemispherical Be dome. The Be dome was evacuated to minimize parasitic scattering and the x-ray beam path was filled with He to minimize absorption and air scattering. X-ray energies were selected to enhance the contrast $f(A) - f(B)$ and the differences of $\text{Re}(f(A) - f(B))$ among three energies. The absolute values of $\text{Re}(f(A) - f(B))$ reach a maxima at the Fe absorption edge (7112 eV) and Ni absorption edge (8333 eV). Near an absorption edge, however, small fluctuations in incident photon energy can cause large uncertainties in the resonant scattering factors. The intensity of resonant Raman scattering also increase as the incident photon energy approaches an absorption edge. As a compromise, the incident energies were chosen to be 7092 eV, 8313 eV, and 8000 eV. A mosaic curved-graphite (002) crystal spectrometer was used to resolve the energy spectrum near the elastic scattering peak. The resolution of the spectrum was limited by the spot size of the incident beam on the sample. As a result of limited resolution, the elastic scattering partially overlaps with the RRS and Compton scattering. To remove the Compton and RRS scattering, the following procedure was employed: raw data were converted into electron units, the Compton scattering intensity in electron units was computed via the Impulse approximation and subtracted from the data, and each data point was then least-square fitted to the energy spectrum with one Gaussian function for the elastic component and two split Pearson-7 functions for the RRS component. The conversion factors
into electron units were obtained by measuring the integrated intensity of five Bragg reflections from a standard Ni powder sample at each incident photon energy. The absolute scale conversion factor can then be calculated for each energy. The data were collected in a volume defined by $4.0 > h_i > h_0 > h_3 > 0.0$. Intervals of $\Delta h = 0.1$ were used in general with $\Delta h = 0.05$ near the fundamental (200) reflection.

DATA ANALYSIS

With the techniques described in previous section, the inelastic scattering, Resonant Raman scattering and Compton scattering, were removed from the measured intensities at all three energies. Points near fundamental reflections were eliminated because of low signal to background ratios in these regions. Two sets of the normalized intensity difference were constructed with

$$\Delta S_i = \frac{I(E_i = 7092\text{eV})}{<f(E_i)>, 2} - \frac{I(E_i = 8000\text{eV})}{<f(E_i)>, 2}$$

and

$$\Delta S_2 = \frac{I(E_i = 8313\text{eV})}{<f(E_i)>, 2} - \frac{I(E_i = 8000\text{eV})}{<f(E_i)>, 2}.$$

The SRO parameters and pairwise displacements recovered by the least-square fitting are listed in Table 1. In these tables the recovered parameters for $\text{Ni}_{77.5}\text{Fe}_{22.5}$, similar to a previous study but corrected for the thermal vibration effects on the short-range order parameters are also listed for comparison.

<table>
<thead>
<tr>
<th>lmn</th>
<th>Ni$<em>{77.5}$Fe$</em>{22.5}$</th>
<th>Ni$<em>{77.5}$Fe$</em>{22.5}$</th>
<th>Ni$<em>{77.5}$Fe$</em>{22.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\delta_{Fe-Fe}$</td>
<td>$\delta_{Fe-Ni}$</td>
</tr>
<tr>
<td>000</td>
<td>1.000(83)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$XX0$</td>
<td>-0.076(18)</td>
<td>0.022(4)</td>
<td>-0.008(1)</td>
</tr>
<tr>
<td>100</td>
<td>0.062(9)</td>
<td>-0.023(5)</td>
<td>0.015(1)</td>
</tr>
<tr>
<td>$XX$</td>
<td>-0.003(3)</td>
<td>0.000(6)</td>
<td>0.000(4)</td>
</tr>
<tr>
<td>$1X$</td>
<td>-0.003(3)</td>
<td>0.000(3)</td>
<td>-0.000(7)</td>
</tr>
<tr>
<td>110</td>
<td>0.004(3)</td>
<td>0.003(1)</td>
<td>-0.001(3)</td>
</tr>
<tr>
<td>$XX0$</td>
<td>-0.011(4)</td>
<td>0.002(1)</td>
<td>-0.002(4)</td>
</tr>
<tr>
<td>$1X0$</td>
<td>-0.011(4)</td>
<td>0.000(3)</td>
<td>-0.001(9)</td>
</tr>
</tbody>
</table>

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Table 2. Estimates of both statistical error \( \sigma \) and various systematic errors (Å) in the recovered parameters in Ni\(_{46.4}\)Fe\(_{46.4}\): errors due to atomic scattering factor, errors due to the uncertainty in conversion factors, errors due to RRS, and errors due to Compton scattering.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \sigma )</th>
<th>( \Delta(\mathbf{f}, \mathbf{f}') )</th>
<th>( \Delta(\mathbf{f}_d) )</th>
<th>( \Delta(\text{RRS}) )</th>
<th>( \Delta(\text{Compton}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha(000) )</td>
<td>0.006</td>
<td>0.078</td>
<td>0.029</td>
<td>0.005</td>
<td>0.007</td>
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<tr>
<td>( \alpha(\mathbf{K}, \mathbf{K}) )</td>
<td>0.002</td>
<td>0.017</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>( \alpha(100) )</td>
<td>0.002</td>
<td>0.007</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>( \delta_{\mathbf{Fe}-\mathbf{Fe}}(\mathbf{K}, \mathbf{K}) )</td>
<td>0.001</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( \delta_{\mathbf{Fe}-\mathbf{Fe}}(100) )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( \delta_{\mathbf{Ni}-\mathbf{Ni}}(\mathbf{K}, \mathbf{K}) )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( \delta_{\mathbf{Ni}-\mathbf{Ni}}(100) )</td>
<td>0.001</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
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Both systematic and statistical errors in the recovered parameters due to various factors were estimated, and they are listed in Table 2. As shown in Table 2, the uncertainties in short-range order parameters are largely introduced from the uncertainties in resonant scattering factors and conversion factors to electron units. These errors are about an order of magnitude larger than the other errors. The uncertainties in pairwise displacements, up to 0.001 Å, are mainly due to the errors in subtracting the RRS and the Compton scattering intensities. With more accurate subtraction of the RRS and the Compton scattering from increased spectrum resolution, we may improve the accuracy of pairwise displacements to about 0.001 Å.

Chemical ordering decreases as the Fe concentration increases from the stoichiometric concentration Ni\(_{51.5}\)Fe toward the Invar region of Ni\(_{46.4}\)Fe, as seen in Table 1. This trend is expected, since the ordering to disordering phase transition temperature reaches a maximum around Ni\(_{46.4}\)Fe with \( T_c = 503 \)°C, and drops to 345°C near the Invar concentration.

Table 1 shows that the Fe-Fe pairwise displacement from the average atomic distance is positive for the first nearest neighbor, compatible with the observed increase of the average atomic distance with increasing Fe concentration. It is curious that the displacement of Ni-Ni is negligible, reflecting that the size of a Ni atom increases with the increasing Fe concentration. The Ni-Fe pairwise displacement is negative, derived from the measured Ni-Ni and Fe-Fe pairwise displacements. These results are consistent with the study on Ni\(_{71.7}\)Fe\(_{28.3}\).

The pairwise atomic distances in both Ni\(_{51.5}\)Fe\(_{46.4}\) and Ni\(_{46.4}\)Fe\(_{51.5}\), the sum of the measured pairwise displacement and the average atomic distance calculated from lattice constant taken from ref.[9, 10] are listed in Table 3. The fcc Fe-Fe distance is taken for pure Fe and adjusted by the coefficient of thermal expansion to room temperature.\(^9\) The Ni-Ni and Ni-Fe \([\mathbf{4+0}]\) distances increase from Ni\(_{51.5}\)Fe\(_{46.4}\) to Ni\(_{46.4}\)Fe\(_{51.5}\), while the Fe-Fe \([\mathbf{4+0}]\) distances are nearly independent on the Fe concentration. We compare our direct measurements with the hard-sphere model, which is sometimes adopted to extract chemically specific pair displacements from a single x-ray or neutron diffuse scattering measurement. The hard-sphere approximation assumes atoms are in contact along their close-packed direction and predicts that pairwise distances are independent of concentration. Our results, however, show that both Ni-Ni and Ni-Fe distances are functions of Fe or Ni concentration: Ni-Ni distance increases by 0.024 Å and Ni-Fe distance increases by 0.014 Å from 22.5 to 46.5 percent Fe concentration. Although Fe-Fe \([\mathbf{4+0}]\) distances are nearly constant at both concentrations, their values are larger by about 0.03 Å than
predicted from the hard-sphere model. We also notice that the unlike Ni-Fe atomic distance is the
shortest among three pairs, Ni-Ni, Fe-Fe and Ni-Fe, in the ordering Ni-Fe system, contradictory
to the intermediate distance for the unlike atomic pair predicted by the hard-sphere model. In a
clustering FeCr system, the unlike atomic distance was found to be the longest. More alloys
must be examined in order to find out whether it is a general rule that in binary alloy the unlike
atomic pair has the shortest distance in ordering system and the longest distance in clustering
system, as suggested from this and other studies.

Table 3. Average pairwise atomic distances of nearest neighbor in fcc NiFe alloys. The distances
are the summation of the measured pairwise displacements and the lattice constant. The fcc Fe-
Fe distance in the hard-sphere approximation is taken for pure Fe and adjusted by the

<table>
<thead>
<tr>
<th></th>
<th>Fe-Fe (Å)</th>
<th>Ni-Fe (Å)</th>
<th>Ni-Ni (Å)</th>
<th>Average d(XX0) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;13&lt;/sub&gt;Fe&lt;sub&gt;46&lt;/sub&gt;</td>
<td>2.563</td>
<td>2.521</td>
<td>2.533</td>
<td>2.532</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;77&lt;/sub&gt;Fe&lt;sub&gt;22&lt;/sub&gt;</td>
<td>2.565</td>
<td>2.508</td>
<td>2.511</td>
<td>2.511</td>
</tr>
<tr>
<td>Hard-sphere</td>
<td>2.530</td>
<td>2.511</td>
<td>2.492</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSIONS

We have introduced a normalized intensity difference in order to remove both the Bragg
scattering and thermal diffuse scattering from the measured intensity within the 3λ method. This
new method allowed a reliable recovery of the pairwise atomic displacements as well as the
short-range order parameters in a Ni<sub>33</sub>Fe<sub>46</sub> crystalline solid solution. The computation time
of the program is reduced with the use of this new technique, because it avoids the need to
iteratively remove the TDS and Bragg backgrounds. Compared to the result of a Ni<sub>77</sub>Fe<sub>22</sub>
measurement, the extracted short-range order parameters reveal that chemical ordering decreases
with increasing Fe concentration in the region from Ni<sub>Fe</sub> to Invar concentration in fcc NiFe
systems. This is consistent with the behavior anticipated from the phase diagram of NiFe. In this
study, we found that Ni-Ni and Ni-Fe distances expanded with increasing Fe concentration,
while Fe-Fe distance is nearly independent on Fe concentration. This study also finds that the
[Ni<sub>13</sub>Fe<sub>46</sub>] Ni-Fe pair in fcc NiFe system has the shortest distance among three pairs, which is the
same as for the Ni<sub>77</sub>Fe<sub>22</sub> measurement.

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REFERENCES

8. F. Biggs, L.B. Mendelsohn, and J.B. Hann, At. Data Nucl. Data Tables 16