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Determination of the Static Displacement of Atoms in a Binary Alloy System using Anomalous Scattering

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It is shown that the anomalous scattering of either X-rays or thermal neutrons provides a method of separating the individual static displacements due to *AA* and *BB* pairs of atoms in a solid solution.

Introduction

It is well known that the static displacement of the atoms from the nodes of the average lattice causes diffuse scattering of X-radiation. The effect of the root mean square of the static displacements is to reduce the intensity of the Bragg reflexions in a manner similar to thermal diffuse scattering. The intensity lost in the Bragg reflexions is conserved by the resultant Huang (1947) diffuse scattering which is distributed close to the reciprocal-lattice points. The presence of short-range order (SRO) in a solid solution manifests itself as modulations in intensity of the Laue monotonic diffuse scattering with broad peaks at positions

close to the super lattice reflexions of an ordered solution. The difference in the effective size of the two types of atoms in the solid solution results in the static displacement of atoms which predominates in the region where local order exists. The diffuse scattering arising due to these distortions modulates the SRO diffuse intensity in such a manner as to render it aperiodic in reciprocal space. The static displacement coefficients which enter the expression for diffuse scattering involve the atomic displacements of both the *AA* and *BB* pairs of atoms in an *AB* alloy system (Borie & Sparks, 1964). However, no method of separating these two has been reported in the literature. It is the object of this paper to suggest a method of separating these two contributions and which enables one to obtain maximum information regarding the atomic displacements in a binary alloy system.

The use of anomalous scattering of X-rays in solving complex crystal structures is well known. The resonant elastic scattering of thermal neutrons by some nuclides like ^{7}Li, ^{10}B, ^{113}Cd, ^{149}Sm, ^{157}Gd *etc.* results in a more-pronounced imaginary component of the scattering length than for X-rays. The importance of this in crystallographic work has been noted by Peterson & Smith (1961, 1962), Ramaseshan (1966) and Singh & Ramaseshan (1968). Recently Ramaseshan & Viswanathan (1970) and Ramesh & Ramaseshan (1971) have shown that a measurement of the intensity of the coherent one-phonon process in a two-atom structure when one of the atoms is an anomalous neutron scatterer can, in principle, be utilized to determine the polarization vectors of the lattice waves propagating along a general direction in the crystal. We now propose that a measurement, at two wavelengths, of the diffuse intensity associated with short-range order and static displacement of atoms, when one of the species of atoms in the binary alloy system are anomalous scatterers, leads to a separation of the atomic displacements due to *AA* and *BB* pairs of atoms for a given coordination shell. Unlike thermal diffuse scattering, both short-range order and static distortion diffuse scattering are elastic so that the method is of general validity as regards both X-ray and neutron anomalous scattering.

Static displacement modulated diffuse scattering

Consider a binary alloy system consisting of *A*- and *B*-type atoms whose atomic fractions in the solid solution are X_A and X_B respectively. Let the species of atoms of the *A* type scatter either X-rays or thermal neutrons anomalously so that the scattering factor of an *A* atom can be represented as

$$f_A = f_{A0} + f'_A + i f''_A . \qquad (1)$$

f_{A0} represents the normal scattering factor while f'_A and f''_A correspond to dispersion corrections. For thermal neutrons f_{A0} represents the potential scattering length whereas f'_A and f''_A arise owing to resonant elastic scattering. The variation of f'_A and f''_A with wavelength is very significant in the resonant region and their dispersion behaviour, different from that in X-rays, can be noted in the measurements on ^{113}Cd resonance by Brockhouse (1953). The typical values of f'_A and f''_A close to the resonant wavelength are as large as 100 to 150% of f_{A0}, the normal scattering length.

The intensity of radiation expressed in electron units in a direction defined by **K** is given by

$$I_{\text{e.u.}} = \sum_m \sum_n f_m f_n^* \exp\{i\mathbf{K} \cdot \mathbf{R}_{mn}\} . \qquad (2)$$

$\mathbf{R}_{mn}$ is the interatomic vector connecting the atoms m and n. Allowing for the static displacement of atoms from the nodes of an average lattice, one can write

$$\mathbf{R}_{mn} = \mathbf{R}^0_{mn} + \boldsymbol{\delta}_{mn}$$

where $\mathbf{R}^0_{mn}$ represents the average interatomic vector and $\boldsymbol{\delta}_{mn}$, the static displacement vector for the pair of atoms m and n. Thus for a given coordination shell, there can be three different displacement vectors $\boldsymbol{\delta}_{mn}$ *i.e.* $\boldsymbol{\delta}^{AA}_{mn}$, $\boldsymbol{\delta}^{AB}_{mn}$ and $\boldsymbol{\delta}^{BB}_{mn}$ corresponding to *AA*, *AB* and *BB* pairs of atoms respectively. Making use of the fact that $\exp\{i\mathbf{K} \cdot \boldsymbol{\delta}_{mn}\} \simeq 1 + i\mathbf{K} \cdot \boldsymbol{\delta}_{mn}$ when the static displacements are small, equation (2) can be written as

$$\begin{aligned} I_{\text{e.u.}} = & \sum_m \sum_n \langle f_m f_n^* \rangle \exp\{i\mathbf{K} \cdot \mathbf{R}^0_{mn}\} \\ & + \sum_m \sum_n \{f_m f_n^* - \langle f_m f_n^* \rangle\} \exp\{i\mathbf{K} \cdot \mathbf{R}^0_{mn}\} \\ & + \sum_m \sum_n f_m f_n^* \, i\mathbf{K} \cdot \boldsymbol{\delta}_{mn} \exp\{i\mathbf{K} \cdot \mathbf{R}^0_{mn}\} . \end{aligned} \qquad (3)$$

The first term on the right-hand side of (3) represents the Bragg reflexions for the average crystal, whereas the second and the third terms correspond to diffuse scattering due to SRO and static displacement respectively.

Now

$$\langle f_m f_n^* \rangle = f f^* = (X_A f_A + X_B f_B)(X_A f_A^* + X_B f_B) .$$

Introducing the conditional probability P^{AB}_{mn} which represents the probability of finding an *A* atom at m and a *B* atom at n, we can write

$$\begin{aligned} f_m f_n^* = & X_A f_A (1 - P^{AB}_{mn}) f_A^* + X_B (1 - P^{BA}_{mn}) f_B^2 \\ & + X_A f_A P^{AB}_{mn} f_B + X_B f_B P^{BA}_{mn} f_A^* . \end{aligned}$$

Since

$$X_A P^{AB}_{mn} = X_B P^{BA}_{mn} ,$$

we have

$$\begin{aligned} f_m f_n^* = & X_A (1 - P^{AB}_{mn}) \{(f_{A0} + f'_A)^2 + (f''_A)^2\} \\ & + X_B \left(1 - \frac{X_A}{X_B} P^{AB}_{mn}\right) f_B^2 + 2 X_A P^{AB}_{mn} f_B (f_{A0} + f'_A) . \end{aligned}$$

Therefore

$$\begin{aligned} f_m f_n^* - \langle f_m f_n^* \rangle = & X_A X_B \left(1 - \frac{P^{AB}_{mn}}{X_B}\right) \\ & \times \{(f_A + f'_A - f_B)^2 + (f''_A)^2\} . \end{aligned} \qquad (4)$$

Thus

$$I_{\mathrm{SRO}}=X_AX_B[(f_{A_0}+f'_A-f_B)^2+(f''_A)^2] \times \sum_{mn}\left(1-\frac{P^{AB}_{mn}}{X_B}\right)\exp\{i\mathbf{K}\,.\,\mathbf{R}^0_{mn}\}. \quad (5)$$

Since $\alpha_{mn}=1-P^{AB}_{mn}/X_B$, the Warren short-range order parameter approaches zero for large values of $|R^0_{mn}|$, the double summation in (5) can be replaced by N times a single sum taken over the neighbouring atoms of coordinates l,m,n.

$$I_{\mathrm{SRO}}=NX_AX_B[(f_{A_0}+f'_A-f_B)^2+(f''_A)^2] \times \sum_{lmn}\alpha_{lmn}\exp\{i\mathbf{K}\,.\,\mathbf{R}^0_{mn}\}. \quad (6)$$

Since α_{lmn} are statistically averaged quantities for every site lmn, there is an equivalent site $\bar{l}\bar{m}\bar{n}$ characterized by the same value of α_{lmn}. This leads to

$$I_{\mathrm{SRO}}=NX_AX_B[(f_{A_0}+f'_A-f_B)^2+(f''_A)^2] \times \sum_{lmn}\alpha_{lmn}\cos\mathbf{K}\,.\,\mathbf{R}^0_{mn}. \quad (7)$$

It may be worth emphasizing that, in neutron scattering, $(f_{A_0}+f'_A)$ can be made negative by choosing an appropriate wavelength for thermal neutrons so that the short-range order diffuse intensity can be considerably enchanged while the intensity of the Bragg reflexions are correspondingly reduced. The intensity of the static displacement modulated diffuse scattering is given by

$$I_{\mathrm{SD}}=\sum_m\sum_n f_mf^*_n\,i\mathbf{K}\,.\,\boldsymbol{\delta}_{mn}\exp\{i\mathbf{K}\,.\,\mathbf{R}^0_{mn}\}\quad(m\neq n) \quad (8)$$

where

$$f_mf^*_n\,i\mathbf{K}\,.\,\boldsymbol{\delta}_{mn}=X_A(1-P^{AB}_{mn})f_Af^*_A\,i\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{mn} + X_B\left(1-\frac{X_A}{X_B}P^{AB}_{mn}\right)f_B^2\,i\mathbf{K}\,.\,\boldsymbol{\delta}^{BB}_{mn} + 2X_AP^{AB}_{mn}f_B(f_{A_0}+f'_A)i\mathbf{K}\,.\,\boldsymbol{\delta}^{AB}_{mn}. \quad (9)$$

Since, on the average, the interatomic vector $\mathbf{R}_{mn}$ should tend to $\mathbf{R}^0_{mn}$, the weighted average of the deviations from the average lattice should vanish. This approximation which is of greater validity for the immediate coordination shell leads to a relationship between $\boldsymbol{\delta}^{AB}_{mn}$, $\boldsymbol{\delta}^{BB}_{mn}$ and $\boldsymbol{\delta}^{AB}_{mn}$, given by

$$X_AP^{AA}_{mn}\,\boldsymbol{\delta}^{AA}_{mn}+X_B\,P^{BB}_{mn}\,\boldsymbol{\delta}^{BB}_{mn}+2X_AP^{AB}_{mn}\,\boldsymbol{\delta}^{AB}_{mn}=0$$

i.e.

$$2X_A\,P^{AB}_{mn}\,\boldsymbol{\delta}^{AB}_{mn}=-X_AP^{AA}_{mn}\,\boldsymbol{\delta}^{AA}_{mn}-X_BP^{BB}_{mn}\,\boldsymbol{\delta}^{BB}_{mn}. \quad (10)$$

Substituting (10) in expression (9) and introducing the Warren short-range order parameter, we get

$$f_mf^*_n\,i\mathbf{K}\,.\,\boldsymbol{\delta}_{mn}=X_AX_B\{f_{A_0}+f'_A-f_B\}\left[\left\{\frac{X_A}{X_B}+\alpha_{lmn}\right\}\times(f_{A_0}+f'_A)i\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{mn}-\left\{\frac{X_B}{X_A}+\alpha_{lmn}\right\}\times f_Bi\mathbf{K}\,.\,\boldsymbol{\delta}^{BB}_{mn}+X_AX_B\left\{\frac{X_A}{X_B}+\alpha_{lmn}\right\}\times(f''_A)^2\,i\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{mn}. \quad (11)$$

The first term on the right-hand side of (11) is similar to the expression found under normal conditions, whereas the second term which contains only the static displacement of AA pairs, arises owing to anomalous scattering.

For cubic solid solutions, the expression for the diffuse intensity can be considerably simplified since for each site defined by l,m,n, there is an equivalent site $\bar{l},\bar{m},\bar{n}$. Thus $i\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{lmn}=-i\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{\bar{l}\bar{m}\bar{n}}$ and $i\mathbf{K}\,.\,\boldsymbol{\delta}^{BB}_{lmn}=-i\mathbf{K}\,.\,\boldsymbol{\delta}^{BB}_{\bar{l}\bar{m}\bar{n}}$. On substituting these relations and replacing the double summation by N times a single sum over l,m,n, we finally get

$$I_{\mathrm{SD}}=-NX_AX_B[f_{A_0}+f'_A-f_B]\sum_{lmn}\left\{\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)\times(f_{A_0}+f'_A)\,\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{lmn}-\left(\frac{X_B}{X_A}+\alpha_{lmn}\right)f_B\,\mathbf{K}\,.\,\boldsymbol{\delta}^{BB}_{lmn}\right\}\times\sin\mathbf{K}\,.\,\mathbf{R}^0_{mn}-NX_AX_B(f''_A)^2\sum_{lmn}\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)\times\mathbf{K}\,.\,\boldsymbol{\delta}^{AA}_{lmn}\sin\mathbf{K}\,.\,\mathbf{R}^0_{mn}. \quad (12)$$

The static displacement vectors $\boldsymbol{\delta}^{AA}_{mn}$ and $\boldsymbol{\delta}^{BB}_{mn}$ can be expressed in terms of their components along the cube axes so that

$$\left.\begin{aligned}\boldsymbol{\delta}^{AA}_{lmn}&=L^{AA}_{lmn}\,\mathbf{a}_1+M^{AA}_{lmn}\,\mathbf{a}_2+N^{AA}_{lmn}\,\mathbf{a}_3\\ \text{and}\quad\boldsymbol{\delta}^{BB}_{lmn}&=L^{BB}_{lmn}\,\mathbf{a}_1+M^{BB}_{lmn}\,\mathbf{a}_2+N^{BB}_{lmn}\,\mathbf{a}_3\,.\end{aligned}\right\} \quad (13)$$

Further $\mathbf{K}\,.\,\mathbf{R}^0_{mn}=2\pi(h_1l+h_2m+h_3n)$ where h_1,h_2,h_3 are continuous variables in reciprocal space.

$$I_{\mathrm{SD}}=-NX_AX_B[f_{A_0}+f'_A-f_B]\sum_{lmn}2\pi(h_1\gamma^l_{lmn}+h_2\gamma^m_{lmn}+h_3\gamma^n_{lmn})\times\sin2\pi(h_1l+h_2m+h_3n)-NX_AX_B(f''_A)^2\times\sum_{lmn}\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)2\pi(h_1L^{AA}_{lmn}+h_2M^{AA}_{lmn}+h_3N^{AA}_{lmn})\times\sin2\pi(h_1l+h_2m+h_3n) \quad (14)$$

where

$$\gamma^l_{lmn}=\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)(f_{A_0}+f'_A)\,L^{AA}_{lmn}-\left(\frac{X_B}{X_A}+\alpha_{lmn}\right)f_B\,L^{BB}_{lmn}.$$

There are similar expressions for γ^m_{lmn} and γ^n_{lmn}.

Method of separation of the components of $\boldsymbol{\delta}^{AA}_{lmn}$ and $\boldsymbol{\delta}^{BB}_{lmn}$

The procedure for separating the static displacement diffuse scattering from that of short-range order has been worked out by Borie (1961). The method essentially consists of measuring the total diffuse intensity at points in reciprocal space separated by a reciprocal

lattice vector. Since the short-range order diffuse scattering is periodic with the period of a reciprocal-lattice vector, the formulation of a function, which expresses the difference in the intensity at two points separated by a reciprocal-lattice vector, contains only the static displacement-modulated diffuse scattering. Further, if the points in reciprocal space are chosen so that only one variable, h_2 say, is changed by unity, the function contains only the contributions of the static displacements of AA and BB pairs of atoms along the a_2 axis.

$$\begin{aligned} Q_2(h_1,h_2,h_3) &= I(h_1,h_2,h_3) - I(h_1,h_2-1,h_3) \\ &= -NX_AX_B[f_{A0}+f'_A-f_B]\sum_{lmn} 2\pi\,\gamma^m_{lmn} \\ &\times \sin 2\pi(h_1l+h_2m+h_3n) \\ &-NX_AX_B(f''_A)^2\sum_{lmn} 2\pi\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)M^{AA}_{lmn} \\ &\times \sin 2\pi(h_1l+h_2m+h_3n)\,. \end{aligned} \tag{15}$$

Two-wavelength method

The scattering factor terms f'_A and f''_A in (1) are wavelength dependent so that they can be varied by choosing a different wavelength for the incident X-ray or thermal neutron beam. We write

$$\left.\begin{aligned} \{f_A\}_{\lambda_1} &= f_{A0}+f'_{A1}+if''_{A1} \\ \text{and} \qquad \{f_A\}_{\lambda_2} &= f_{A0}+f'_{A2}+if''_{A2}\,. \end{aligned}\right\} \tag{16}$$

Thus the functions $Q_2(h_1,h_2,h_3)$ become wavelength dependent through the scattering factor of A-type atoms. It can be easily shown from (15) and (16) that by constructing a new function

$$\begin{aligned} \Psi_2(h_1,h_2,h_3) &= \{Q_2(h_1,h_2,h_3)\}_{\lambda_1}\{f_{A0}+f'_{A2}-f_B\} \\ &-\{Q_2(h_1,h_2,h_3)\}_{\lambda_2}\{f_{A0}+f'_{A1}-f_B\}\,, \end{aligned} \tag{17}$$

the term M^{BB}_{lmn} of the BB pair of atoms gets eliminated leaving only M^{AA}_{lmn}, the component of the static displacement of the anomalously scattering AA pair of atoms.

$$\begin{aligned} \Psi_2(h_1,h_2,h_3) &= -NX_AX_B\sum_{lmn} 2\pi\left(\frac{X_A}{X_B}+\alpha_{lmn}\right)M^{AA}_{lmn}F \\ &\times \sin 2\pi(h_1l+h_2m+h_3n) \end{aligned} \tag{18}$$

where

$$\begin{aligned} F = [(f'_{A1}-f'_{A2})\{f_{A0}+f'_{A1}-f_B\}\{f_{A0}+f'_{A2}-f_B\} \\ +\{f_{A0}+f'_{A2}-f_B\}(f''_{A1})^2-\{f_{A0}+f'_{A1}-f_B\} \\ \times(f''_{A2})^2]\,. \end{aligned}$$

As a special case, when λ_2 is far away from the resonance region, $f''_{A2}\simeq 0$ and f'_{A2} is very very small. Then the expression for F gets considerably simplified.

$$F\simeq(f_{A0}-f_B)\{f'_{A1}(f_{A0}+f'_{A1}-f_B)+(f''_{A1})^2\}\,.$$

It is clear from (18) that a Fourier transformation of $\Psi_2(h_1,h_2,h_3)$ yields M^{AA}_{lmn} directly. A similar procedure can be followed to extract L^{AA}_{lmn} and N^{AA}_{lmn} by constructing suitable functions Ψ_1 and Ψ_3 respectively. A Fourier inversion of either $\{Q_2(h_1,h_2,h_3)\}_{\lambda_1}$ or $\{Q_2(h_1,h_2,h_3)\}_{\lambda_2}$ gives the combination of M^{AA}_{lmn} and M^{BB}_{lmn} so that M^{BB}_{lmn} can be separated by combining the data from (18). Thus all the six components of the static displacement of AA and BB pairs of atoms can be separated by combining the intensity data at two wavelengths.

Conclusion

It has been shown that using anomalous scattering of either X-rays or neutrons, one can separate the individual contributions of the AA and BB pair of atoms towards the static displacement diffuse scattering. The use of resonant elastic scattering of thermal neutrons has the added advantage in the enchancement of the diffuse intensity at the expense of Bragg reflexions. Since the diffuse intensity associated with short-range order and static displacement of atoms depends on the difference in the scattering lengths between the two types of atoms, it is clear from equations (7) and (12) that by making $(f_{A0}+f'_A)$ negative (in the region lying in the long wavelength side of the resonant peak) one can considerably increase the diffuse intensity.

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