

Structure factors and the critical voltage effect in ordered BCC (B2) alloys: I. A model for the structure factors and atomic mean-square displacements

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Received 24 November 1982, in final form 10 March 1983

Abstract. The systematic critical voltage phenomena observed in high-voltage electron diffraction provide a sensitive method for determining submicroscopic alloy parameters such as Debye temperatures, the extent of long-range order, and atomic scattering factors. Only a very limited number of critical voltages can be observed in the voltage range usually available, 100–1200 kV, so that quantitative interpretation of the data must be based on a few-parameter model which incorporates all the pertinent factors. A satisfactory model has been developed which can be used to interpret or compute the critical voltage of ordered BCC binary alloys as functions of composition, temperature and long-range order. This model can also be used to analyse the Debye–Waller factors of these alloys measured by x-ray or neutron diffraction techniques, and thus provide supplementary information about the vibrational behaviour of these systems.

1. Introduction

The use of the critical voltage technique to measure structure factors in metals and alloys is well established (see for example Lally *et al* 1972, Hewat and Humphreys 1973, Sinclair *et al* 1975, Shishido and Tanaka 1976, Shirley and Fisher 1979, Sellar *et al* 1980). This method involves the observation of a particular Bragg excited reflection in a given systematic row over a range of accelerating voltages, and the measurement of the voltage at which this reflection is a minimum. Associated with this minimisation are asymmetry changes of Kikuchi lines and rocking curve profiles which can lead to an accurate determination of the critical voltage, V_c .

The value of a critical voltage measured in a systematic row depends on the values of the structure factors at the reciprocal lattice positions corresponding to the set of atomic planes (the systematic reflections). The structure factors for an alloy depend on the following: (i) the values of the atomic scattering factors for the reflection concerned, (ii) composition and long-range order (LRO), and (iii) mean-square static and thermal displacements from average sites, which cause a Debye–Waller type attenuation of the scattering factors. To utilise the critical voltage effect one must employ an appropriate

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model which characterises all or some of the above effects by a few well chosen parameters. Some of these parameters may be fixed beforehand (e.g. composition by chemical analysis, or LRO by heat treatment) and others may be determined. For example, Hewat and Humphreys (1973) and Shishido and Tanaka (1976) used measured values of the Debye-Waller factors for Si and Ge and determined the low-angle atomic scattering factors from V_c measurements, in order to examine the electron charge distribution associated with the covalent bonding in these materials. On the other hand, Shirley and Fisher (1979) determined the low-angle atomic scattering factors in pure metals, and considered these unchanged on alloying in primary solid solutions. They then determined the atomic mean-square displacements (MSD) for solid solution alloys from critical voltage measurements, and used a simple nearest-neighbour (NN) central force model to analyse the results.

The present paper is the first of two on the theory and analysis of structure factors and critical voltage measurements in ordered BCC alloys and outlines a theory based on the ideas of Shirley and Fisher (1979) for the structure factors and atomic MSD in disordered binary alloys. In the second paper (Fox 1983) the theory is used to analyse critical voltage measurements in α FeCo, β' CoAl and β' NiAl. The model can also be used to obtain information from Debye-Waller factors measured by x-ray or neutron diffraction. The preliminary results of this work have been reported by Shirley and Fisher (1980) and Fox (1980).

2. Outline of the model for the structure factors of ordered BCC alloys

In a fully ordered stoichiometric B2 alloy (AB), there are equal numbers of A and B atoms. The A atoms are all on a simple cubic sublattice designated α and the B atoms are all on a sublattice designated β . It will be shown later that if there is no short-range order (SRO), then the atomic MSD will depend only on the sublattice (α or β) and not on the type of atom occupying it. On this basis, the structure factors, F , for an arbitrary B2 alloy with substitutional defects are given by (Warren 1969).

$$F = \begin{cases} \bar{f}(e^{-M_\alpha} + e^{-M_\beta}) + \frac{1}{2}\Delta f S(e^{-M_\alpha} - e^{-M_\beta}) & \text{(fundamental)} \\ \bar{f}(e^{-M_\alpha} - e^{-M_\beta}) + \frac{1}{2}\Delta f S(e^{-M_\alpha} + e^{-M_\beta}) & \text{(superlattice)} \end{cases} \quad (1a) \quad (1b)$$

where $\bar{f} = m_A f_A + m_B f_B$, $\Delta f = f_A - f_B$ and

$$M_\alpha = \frac{8}{3}\pi^2 \langle u_\alpha^2 \rangle s^2 \quad M_\beta = \frac{8}{3}\pi^2 \langle u_\beta^2 \rangle s^2. \quad (1c)$$

In these equations, $s = \sin \theta / \lambda$, where θ is the Bragg angle and λ the electron (or x-ray) wavelength. The atom fraction of A atoms (or B atoms) is m_A (or m_B) and their atomic scattering factors are f_A and f_B . The MSD for α and β sites are $\langle u_\alpha^2 \rangle$ and $\langle u_\beta^2 \rangle$ respectively and S is the LRO parameter. When $S=0$ in equations (1), $F=0$ in equation 1(b) and equation 1(a) reduces to the structure factor for the disordered case.

Expressions for $\langle u_\alpha^2 \rangle$ and $\langle u_\beta^2 \rangle$ will now be developed using the ideas of Shirley and Fisher (1979). Essentially this theory uses the harmonic approximation and assumes that NN central forces predominate. The following definitions for the B2 lattice form the starting point for this derivation.

y_α and y_β are the fractions of α and β sites and therefore

$$y_\alpha = y_\beta = \frac{1}{2}. \quad (2)$$

The fractions of correctly and wrongly occupied α sites are r_α and w_α respectively, and similarly the fractions of correctly and wrongly occupied β sites are r_β and w_β . Therefore

$$r_\alpha + w_\alpha = 1 \quad r_\beta + w_\beta = 1. \quad (3)$$

Using the definition of the LRO parameter, S , due to Warren (1969) and equations (3) gives

$$r_\alpha = m_A + \frac{1}{2}S \quad r_\beta = m_B + \frac{1}{2}S \quad (4a)$$

$$w_\alpha = m_B - \frac{1}{2}S \quad w_\beta = m_A - \frac{1}{2}S. \quad (4b)$$

Correlations of the type σ_i^A and σ_i^B used by Shirley and Fisher (1979) in their derivation for solid solutions can be used in a similar manner for B2 alloys. In this case, account must be taken of the two sublattices α and β , and so

$$\sigma^A(i_\alpha) = \begin{cases} 1 & \text{for an A atom on site } i \text{ in the } \alpha \text{ sublattice} \\ 0 & \text{for a B atom on site } i \text{ in the } \alpha \text{ sublattice} \end{cases}$$

with similar definitions for $\sigma^B(i_\alpha)$, $\sigma^A(i_\beta)$ and $\sigma^B(i_\beta)$. $\sigma^A(i_\alpha)$ and $\sigma^B(i_\alpha)$ can both be expressed in terms of one correlation $\sigma(i_\alpha)$ and also $\sigma^A(i_\beta)$ and $\sigma^B(i_\beta)$ can be expressed in terms of $\sigma(i_\beta)$ where

$$\sigma(i_\alpha) = \begin{cases} 2w_\alpha & \text{for an A atom on } (i_\alpha) \\ -2r_\alpha & \text{for a B atom on } (i_\alpha) \end{cases} \quad (5a)$$

$$\sigma(i_\beta) = \begin{cases} -2w_\beta & \text{for a B atom on } (i_\beta) \\ 2r_\beta & \text{for an A atom on } (i_\beta) \end{cases} \quad (5b)$$

and so from equations (4)

$$\sigma(i_\alpha) = \begin{cases} 2m_B - S & \text{A on } (i_\alpha) \\ -2m_A - S & \text{B on } (i_\alpha) \end{cases} \quad (6a)$$

$$\sigma(i_\beta) = \begin{cases} 2m_B + S & \text{A on } (i_\beta) \\ -2m_A + S & \text{B on } (i_\beta). \end{cases} \quad (6b)$$

It should be noticed that these reduce to the disordered definition, $\sigma_i = (2m_B, -2m_A)$ when $S=0$, the definition used by Shirley and Fisher (1979) for primary solid solutions. From these definitions it follows that

$$\sigma^A(i_\alpha) = r_\alpha + \frac{1}{2}\sigma(i_\alpha) \quad \sigma^B(i_\alpha) = w_\alpha - \frac{1}{2}\sigma(i_\alpha) \quad (7a)$$

$$\sigma^A(i_\beta) = w_\beta + \frac{1}{2}\sigma(i_\beta) \quad \sigma^B(i_\beta) = r_\beta - \frac{1}{2}\sigma(i_\beta). \quad (7b)$$

The mean field theory of Clapp and Moss (1966) can now be used for each sublattice to find $\langle u^2(i_\alpha) \rangle_A$, the MSD of A atoms on α sites; and similarly for $\langle u^2(i_\alpha) \rangle_B$, $\langle u^2(i_\beta) \rangle_A$ and $\langle u^2(i_\beta) \rangle_B$. The MSD of A atoms on α sites is found by summing the displacements for all configurations where A atoms are on α sites; thus

$$\langle u^2(i_\alpha) \rangle_A = \sum_i \sigma^A(i_\alpha) u^2(i_\alpha) \left(\sum_i \sigma^A(i_\alpha) \right)^{-1} \quad (8)$$

and using the first part of equation 7(a)

$$\langle u^2(i_\alpha) \rangle_A = \langle u^2(i_\alpha) \rangle + (2r_\alpha)^{-1} \langle \sigma(i_\alpha) u^2(i_\alpha) \rangle. \quad (9a)$$

Similarly,

$$\langle u^2(\alpha) \rangle_B = \langle u^2(\alpha) \rangle - (2w_\alpha)^{-1} \langle \sigma(\alpha) u^2(\alpha) \rangle \quad (9b)$$

$$\langle u^2(\beta) \rangle_A = \langle u^2(\beta) \rangle + (2w_\beta)^{-1} \langle \sigma(\beta) u^2(\beta) \rangle \quad (9c)$$

$$\langle u^2(\beta) \rangle_B = \langle u^2(\beta) \rangle - (2r_\beta)^{-1} \langle \sigma(\beta) u^2(\beta) \rangle. \quad (9d)$$

Shirley (1974) showed how the MSD in solid solutions could be split into thermal and static parts; this procedure can be applied equally to ordered BCC alloys, and so

$$\langle u^2(\alpha) \rangle = \langle u^2(\alpha) \rangle_t + \langle u^2(\alpha) \rangle_s \quad (10a)$$

$$\langle \sigma(\alpha) u^2(\alpha) \rangle = \langle \sigma(\alpha) u^2(\alpha) \rangle_t + \langle \sigma(\alpha) u^2(\alpha) \rangle_s \quad (10b)$$

and similarly for $\langle u^2(\beta) \rangle$ and $\langle \sigma(\beta) u^2(\beta) \rangle$.

The $\langle \sigma(\alpha) u^2(\alpha) \rangle_t$ which arise as a result of the defects are an order of atomic radius mismatch smaller than $\langle u^2(\alpha) \rangle_t$ and $\langle u^2(\beta) \rangle_t$ (as discussed by Shirley and Fisher (1979) for solid solutions). Because of this, and because $\langle \sigma(\alpha) u^2(\alpha) \rangle_t$ and $\langle \sigma(\beta) u^2(\beta) \rangle_t$ will be experimentally inseparable from $\langle u^2(\alpha) \rangle_t$ and $\langle u^2(\beta) \rangle_t$, the following definitions will be made:

$$\langle u_\alpha^2 \rangle_t = \langle u^2(\alpha) \rangle_t \quad (\text{for both A and B atoms}) \quad (11a)$$

$$\langle u_\beta^2 \rangle_t = \langle u^2(\beta) \rangle_t \quad (\text{for both A and B atoms}). \quad (11b)$$

Expressions for $\langle u_\alpha^2 \rangle_t$ and $\langle u_\beta^2 \rangle_t$ can be obtained by considering the nature of the average NN force constant for the α and β sublattices, and for simplicity the effects of SRO will be ignored. An examination of the force constants of BCC alkali metals (Flocken and Hardy 1969) and for the B2 alloy β' NiAl (Georgopoulos and Cohen 1981) shows that NN central forces make by far the largest contribution to the MSD in these systems, and second NN central force constants make the next largest contribution. Angular and higher order force constants account for only a small part of the MSD. As central forces arise predominantly from core electrons they are unlikely to be affected by alloy composition as discussed by Shirley (1975). The force constants between A–A, B–B and A–B atom pairs are therefore assumed to be independent of composition in their contribution to the MSD.

This procedure implies the use of the harmonic approximation, and it should be born in mind that there will be anharmonic contributions to the MSD which can be important at higher temperatures. A quasi-harmonic approximation which takes account of thermal expansion will be outlined later, but such a correction requires knowledge of the volume expansion coefficient and the Gruneisen parameter, which may not be available. The average NN force constant for an α site can be written as

$$k_\alpha = k_{AA} r_\alpha w_\beta + k_{AB} r_\alpha r_\beta + k_{BB} w_\alpha r_\beta + k_{AB} w_\alpha w_\beta \quad (12)$$

where k_{AA} is the force constant between NN A atoms, k_{BB} is the force constant between NN B atoms, and k_{AB} is the NN force constant between an A–B atom pair. If $\mathcal{S} = S/2$, then substituting equations (4) gives

$$k_\alpha = k_{AA} (m_A^2 - \mathcal{S}^2) + k_{BB} (m_B^2 - \mathcal{S}^2) + 2k_{AB} (m_A m_B + \mathcal{S}^2). \quad (13)$$

For k_β , the average NN force constant for β sites, the equivalent expression is

$$k_\beta = k_{AA} w_\beta r_\alpha + k_{BB} r_\beta w_\alpha + k_{AB} r_\alpha r_\beta + k_{AB} w_\beta w_\alpha. \quad (14)$$

It can be seen from equations (14) and (12) that $k_\alpha = k_\beta = k$, i.e. the average interatomic force constant is the same for both sublattices.

For BCC alloys with 'normal' phonon dispersion characteristics where anomalous behaviour such as the ω -phase transformation is absent, in the classical regime, the thermal MSD are proportional to the temperature and inversely proportional to the average interatomic force constant:

$$\langle u_{\alpha}^2 \rangle_t = \langle u_{\beta}^2 \rangle_t = \langle u^2 \rangle_t = CKT/k \quad (15)$$

where C is a constant, K is the Boltzmann constant and T is the absolute temperature. When $S=0$ in equation (13), $\langle u^2 \rangle_t$ can be described by the Debye formula as pointed out by Krivoglaz (1969) and Shirley and Fisher (1979). This is

$$\langle u^2 \rangle_t = \frac{9\hbar^2}{KA} \left(\frac{T\varphi(\theta/T)}{\mu\theta^2} + \frac{1}{4\mu\theta} \right) \quad (16)$$

where $\varphi(\theta/T)$ is the Debye function, θ is the Debye temperature, $\mu = m_A\mu_A + m_B\mu_B$ where $\mu_{A(B)}$ is the atomic weight of an A (B) atom and \hbar , K and A have their usual meanings. As the classical and quantum results must agree for $T = \infty$ then $k \propto \mu\theta^2$ in equation (15). When a BCC system is ordered it is well known that the Debye formula is not a good representation of $\langle u_{\alpha}^2 \rangle_t$ and $\langle u_{\beta}^2 \rangle_t$ at low temperatures, unless the atoms A and B have similar masses. However, a comparison of the classical and quantum theories (equations (15) and (16)) shows that if $T \geq 0.6\theta$ when $\theta \geq 300$ K (which is true for a majority of metals and alloys) then the difference in $\langle u^2 \rangle_t$ predicted by these two equations is at most 2%. Hence, above $T = 0.6\theta$ the quantum effects on $\langle u_{\alpha}^2 \rangle_t$ and $\langle u_{\beta}^2 \rangle_t$ are small and $\langle u_{\alpha}^2 \rangle_t = \langle u_{\beta}^2 \rangle_t = \langle u^2 \rangle_t$ given by equation (16) is a good approximation. Unfortunately, there are very few accurate measurements of Debye-Waller factors in alloys at any temperature to check this assertion. However, a review of the x-ray measurements of the Debye-Waller factors in B2 alkali halides given by Agrawal *et al* (1975) shows that $\langle u_{\alpha}^2 \rangle_t$ and $\langle u_{\beta}^2 \rangle_t$ for these systems have similar but not exactly equal values for $T \geq 0.6\theta$, even when θ is less than 300 K; this also indicates that equation (16) is a good approximation for this temperature range. The reason for the two sublattices not having exactly equal thermal MSD in B2 alkali halides at higher temperatures, near θ , is because of the contributions of second and possibly higher nearest neighbours, since the second NN distance in BCC lattices is only 1.195 times greater than the first NN distance.

At lower temperatures the effect of the different masses of atoms A and B becomes important, and there are no simple quantum expressions such as equation (16) to describe the behaviour of $\langle u_{\alpha}^2 \rangle_t$ and $\langle u_{\beta}^2 \rangle_t$. Govindarajan (1973) and Agrawal *et al* (1975) have used model potentials which fitted measured phonon dispersion curves to calculate the low-temperature Debye-Waller factors in B2 alkali halides, and they obtained good agreement with experiment. From this work it can be seen that, at low temperatures, the sublattice which contains the atoms of the higher mass has a lower value of the thermal MSD than the other sublattice, and this statement will apply equally to any binary B2 system with atoms of different mass. Because no simple model expressions can be derived for $\langle u_{\alpha}^2 \rangle_t$ and $\langle u_{\beta}^2 \rangle_t$ in B2 alloys at low temperatures, it is better to make measurements of these temperatures above 0.6θ so that equation (16) can be used with reasonable accuracy.

To calculate the static displacements for the α and β sublattices in BCC ordered systems the method of Shirley and Fisher (1979) will be used. Their equation (12) shows that the static displacement of an atom at site j due to atoms at sites k can be written as

$$u_j = -\sum_k \xi_{jk} \cdot \sigma_k \quad (17)$$

This equation can be modified to incorporate the existence of two sublattices, thus

$$\mathbf{u}(\gamma^j) = -\sum_k \xi(\gamma^j \delta^k) \sigma(\delta^k). \quad (18)$$

Here γ or δ specifies the sublattice (α or β) while j and k are indices summing over a simple cubic lattice. In the derivation leading to expressions for the static MSD for solid solutions, it was found by Shirley and Fisher (1979) that the displacement due to one substitutional defect for an atom at the origin, ξ_{0i} , was proportional to the ratio of the NN force on the defect, $F(1)$, to the NN force constant, α_1 . ξ_{0i} was then expressed as a function of concentration and SRO only, by assuming that NN central forces predominated. Shirley and Fisher (1979) expressed ξ_{0i} as

$$\xi_{0i} = \frac{1}{4} \gamma a \eta T_{0i} \quad (19)$$

where a is the lattice parameter, $\eta = d \ln a / d m_A$, γ is the static amplitude displacement factor which is derived to be equal to 1.0, and T_{0i} is an element of a dimensionless displacement field tabulated in the $\langle 100 \rangle$ directions for a BCC lattice in table 1. Now since $\sigma(\alpha^j)$ and $\sigma(\beta^j)$ reduce to the disordered definition $\sigma_i = (2m_B, -2m_A)$ for $S=0$ (full disorder), the displacements for the ordered case can be written down directly by comparison with equation (19); thus,

$$\xi(\alpha^j \alpha^k) = \frac{1}{4} \gamma a \eta T(\alpha^j \alpha^k). \quad (20)$$

The problem now is the evaluation of $\langle u^2(\alpha^j) \rangle_s$, $\langle u^2(\beta^j) \rangle_s$, $\langle \sigma(\alpha^j) u^2(\alpha^j) \rangle_s$ and $\langle \sigma(\beta^j) u^2(\beta^j) \rangle_s$. Now,

$$\langle u^2(\alpha^j) \rangle_s = \sum_{\substack{\delta^k \\ (\beta^k)}} \xi(\alpha^j \delta^k) \cdot \xi(\delta^k \alpha^j) \langle \sigma(\delta^k) \sigma(\alpha^j) \rangle_s. \quad (21)$$

Table 1. Dimensionless displacement field T_{0i} for a BCC lattice.

lmn	$T_x(lmn)$	$T_y(lmn)$	$T_z(lmn)$
111	0.2470	0.2470	0.2470
200	-0.2597	0	0
220	0.0717	0.0717	0
222	0.1341	0.1341	0.1341
311	-0.0326	-0.0147	-0.0147
331	0.0403	0.0403	0.0022
333	0.0775	0.0775	0.0775
400	-0.0341	0	0
420	-0.0027	-0.0010	0
422	-0.0089	0.0034	0.0034
440	0.0276	0.0276	0
442	0.0257	0.0257	0.0032
444	0.0460	0.0460	0.0460
511	-0.0125	-0.0015	-0.0015
531	0.0010	0.0016	0.0013
533	0.0017	0.0085	0.0085
551	0.0188	0.0188	0.0014
555	0.0284	0.0284	0.0284
600	-0.0105	0	0
620	-0.0052	-0.0018	0
622	-0.0063	0.0008	0.0008
640	0.0025	0.0026	0

Therefore

$$\langle u^2(\alpha^i) \rangle_s = \sum_{kl} \xi(\alpha\alpha^{ik}) \cdot \xi(\alpha\alpha^{il}) \langle \sigma(\alpha^k) \sigma(\alpha^l) \rangle + 2 \sum_{kl} \xi(\alpha\alpha^{ik}) \cdot \xi(\alpha\beta^{il}) \langle \sigma(\alpha^k) \sigma(\beta^l) \rangle + \sum_{kl} \xi(\alpha\beta^{ik}) \cdot \xi(\alpha\beta^{il}) \langle \sigma(\beta^k) \sigma(\beta^l) \rangle. \quad (22)$$

For simplicity, the effects of SRO will now be ignored. This will be done for two reasons: (i) by suitable heat treatment it is often possible to produce an alloy with zero SRO when LRO is present; (ii) if an alloy shows LRO the effects of accompanying SRO will be less than in a disordered alloy, and in a B2 system where LRO is a maximum only second NN SRO can exist which, as shown by Shirley and Fisher (1979), makes only a small contribution to the MSD.

If there is no short-range correlation between an atom on (δ^k) and an atom on (γ^l) , $\langle \sigma(\delta^k) \sigma(\gamma^l) \rangle$ will vanish except with $(\delta^k) = (\gamma^l)$ for which $\xi(\delta^k) = \xi(\gamma^l) = \xi(0) = 0$ and therefore $\langle \sigma(\alpha^k) \sigma(\beta^l) \rangle = 0$. A similar argument applies to an atom on (α^i) and an atom on (α^k) , but this time (α^i) can be equal to (α^k) and in this case, from equations (5) and (6),

$$\begin{aligned} \langle \sigma^2(\alpha^k) \rangle &= r_\alpha 4w_\alpha^2 + w_\alpha 4r_\alpha^2 = 4r_\alpha w_\alpha \\ &= 4m_A m_B + 2(m_B - m_A)S - S^2 = A. \end{aligned} \quad (23a)$$

Also, following a similar argument,

$$\begin{aligned} \langle \sigma^2(\beta^k) \rangle &= r_\beta 4w_\beta^2 + w_\beta 4r_\beta^2 = 4r_\beta w_\beta \\ &= 4m_A m_B - 2(m_B - m_A)S - S^2 = B \end{aligned} \quad (23b)$$

and so from equations (20), (22) and (23)

$$\langle u^2(\alpha^i) \rangle_s = \frac{1}{16} \gamma^2 a^2 \eta^2 \left(A \sum_k T(\alpha\alpha^{ik}) T(\alpha\alpha^{ik}) + B \sum_k T(\alpha\beta^{ik}) \cdot T(\alpha\beta^{ik}) \right). \quad (24)$$

The sums $\sum_k T(\alpha\alpha^{ik}) T(\alpha\alpha^{ik})$ and $\sum_k T(\alpha\beta^{ik}) \cdot T(\alpha\beta^{ik})$ can be evaluated from table 1. The value of the first sum is 1.071 and that of the second sum 1.766, so that

$$\langle u^2(\alpha^i) \rangle_s = \frac{1}{16} \gamma^2 a^2 \eta^2 (1.071A + 1.766B). \quad (25a)$$

A similar procedure gives

$$\langle u^2(\beta^i) \rangle_s = \frac{1}{16} \gamma^2 a^2 \eta^2 (1.766A + 1.071B). \quad (25b)$$

If there is no SRO then both $\langle \sigma(\alpha^i) u^2(\alpha^i) \rangle_s$ and $\langle \sigma(\beta^i) u^2(\beta^i) \rangle$ vanish, since

$$\langle \sigma(\alpha^i) u^2(\alpha^i) \rangle = \sum_{\substack{(\delta^k) \\ (\gamma^l)}} \xi(\alpha\delta^{ik}) \langle \sigma(\alpha^i) \sigma(\delta^k) \sigma(\gamma^l) \rangle \quad (26)$$

and for zero SRO the only non-zero triplet requires that $(\alpha^i) = (\delta^k)$ and $(\alpha^i) = (\gamma^l)$ for which $\xi(\alpha\delta^{ik}) = \xi(0)$ and $\xi(\alpha\gamma^{il}) = \xi(0)$ which are both zero. This is also true for $\langle \sigma(\beta^i) u^2(\beta^i) \rangle_s$.

From this, and equations (9) and (15), it is easy to see that the static MSD depend only on the site (α or β), and *not* on the type of atom occupying it. This result was also found by Shirley and Fisher (1979) for disordered alloys with zero SRO. Therefore

$$\langle u^2(\alpha^i) \rangle_A = \langle u^2(\alpha^i) \rangle_B = \langle u_\alpha^2 \rangle \quad (27a)$$

$$\langle u^2(\beta^i) \rangle_A = \langle u^2(\beta^i) \rangle_B = \langle u_\beta^2 \rangle. \quad (27b)$$

It should be pointed out that equations (25) reduce to the zero SRO disordered case when $S=0$ (equation (22) of Shirley and Fisher (1979) with all $C_n = 0$).

2.1. Effects of maximum LRO

2.1.1. *Stoichiometry.* For a fully ordered stoichiometric B2 alloy $S=1$ and $m_A = m_B = \frac{1}{2}$ so that equations (1) for the structure factor become

$$F = \begin{cases} (f_A + f_B)e^{-M} & \text{(fundamental)} \\ (f_A - f_B)e^{-M} & \text{(superlattice).} \end{cases} \quad (28a) \quad (28b)$$

Equation (13) for the average interatomic force constant is now given by $k = k_{AB}$ and equation (15) for the thermal MSD becomes

$$\langle u^2 \rangle_t = CKT/k_{AB}. \quad (29)$$

Since the quantum expression (16) and the classical formula (29) must agree as $T \rightarrow \infty$ then $k_{AB} \propto \mu_s \theta_s^2$ where θ_s and μ_s are the Debye temperature and atomic weight of the stoichiometric alloy. In equations (25) $A=B=0$ and so $\langle u_\alpha^2 \rangle_s = \langle u_\beta^2 \rangle_s = 0$, i.e. there are no static contributions to the MSD at stoichiometry, and all the strain due to atomic radius mismatch has been relieved.

2.1.2. *A rich substitutional alloys.* A B rich substitutional alloy will have equations identical to those of the A rich alloy except that all the subscripts referring to A atoms will become those for B atoms. For an A rich alloy with maximum LRO $S=2m_B$ and from equations (1) the structure factors are

$$F = f_A e^{-M\alpha} \pm [(m_A - m_B)f_A + 2m_B f_B] e^{-M\beta} \quad (30)$$

where the plus sign refers to a fundamental reflection and the minus sign to a superlattice reflection. From equation (13) the average interatomic force constant is

$$k = (m_A - m_B)k_{AA} + 2m_B k_{AB} \quad (31)$$

and $\langle u^2 \rangle_t$ is given by equation (16). Since $k \propto \mu\theta^2$ and $k_{AB} \propto \mu_s \theta_s^2$ equation (31) can be written in terms of the Debye temperatures; thus

$$\mu\theta^2 = \{[(m_A - m_B)/\tau'] + 2m_B\} \mu_s \theta_s^2 \quad (32)$$

where $\tau' = k_{AB}/k_{AA}$.

The static displacements are (from equations (25))

$$\langle u_\alpha^2 \rangle_s = 0.883\gamma^2 a^2 \eta^2 m_B (m_A - m_B) \quad \langle u_\beta^2 \rangle_s = 0.5355\gamma^2 a^2 \eta^2 m_B (m_A - m_B). \quad (33)$$

In many instances the static displacements are small and the averaging approximation

$$\langle u^2 \rangle_s = \langle u_\alpha^2 \rangle_s = \langle u_\beta^2 \rangle_s = 0.7093\gamma^2 a^2 \eta^2 m_B (m_A - m_B) \quad (34)$$

can be used, so that $M_\alpha = M_\beta = M$.

3. Potential application of the model to structure factor measurements

The analysis of structure factors in any binary alloy system requires values of the atomic scattering factors, f_A and f_B , and a mathematical relationship between the NN atomic

force constants k_{AA} , k_{AB} and k_{BB} expressed in terms of one unknown, which is then determined along with the static-amplitude displacement factor γ . During any such analysis, the effects of anharmonicity or the existence of any anomalous vibrational behaviour should be considered.

3.1. The atomic scattering factors f_A and f_B

Measurements of Debye–Waller factors by x-ray diffraction are usually made from the integrated intensities from high-angle reflections, which means that tabulated values of the atomic scattering factors, f_A and f_B , can be used with reasonable accuracy. Debye–Waller factor measurements by neutron diffraction do not require a knowledge of scattering factors.

In the case of the systematic critical voltage effect, f_A and f_B for the first-order and sometimes the second-order reflections are not necessarily accurately given by tables and so these must be determined in some way. Shirley and Fisher (1979) pointed out that the electronic contributions to the stability of primary solid solutions are minimal, so that the low-angle scattering factors in the pure elements could be considered to be unchanged on alloying. For an ordered BCC alloy which arises from a disordered primary solid solution, there may be some electronic contributions to the ordering process, which could alter the values of the low-angle atomic scattering factors.

Most B2 alloys, however, do not arise as a result of the ordering of primary solid solutions, but are of the β type. These are intermediate phases which have strong electronic contributions to their stability and rely on the electron-to-cell ratio being a constant value of three. The elements which comprise these alloys often have different structures to the β phase, as well as having a different electron charge distribution, which means that the first-order and sometimes the second-order low-angle atomic scattering factors of a systematic row in these alloys must be considered to be unknown during a critical voltage analysis.

3.2. The interatomic force constants k_{AA} , k_{BB} and k_{AB}

For a primary solid solution Shirley and Fisher (1979) used the parameter $\tau = 2k_{AB}/(k_{AA} + k_{BB})$ in conjunction with the Debye temperatures of the pure elements to produce a mathematical expression for the Debye temperature of the alloy. This assumes that the system is an isostructural, continuous solid solution, and so a B2 alloy which arises as a result of the ordering of such a solid solution will probably have interatomic force constants with values similar to those in the solid solution. The reason for this is that k_{AA} , k_{AB} , k_{BB} and therefore τ depend predominantly on NN central forces (core–core interactions), which are unlikely to be changed significantly by the long-range ordering process, as such changes will depend on the outer electrons which are responsible for cohesion, although there may be some force constant changes associated with the strain relief of ordering.

In β -phase alloys no pure element information can be used to estimate k_{AA} or k_{BB} and all three types of interatomic force constant must be considered to be unknown when analysing MSD measurements made on these systems; this is not a difficulty as equations (28) and (31) show that, at most, only two of these are unknown in a fully ordered alloy.

3.3. γ -static amplitude displacement factor

As discussed by Shirley and Fisher (1979), this parameter is of the order of unity and

should be relatively independent of composition. To measure this parameter it is necessary to prepare an alloy with minimal SRO and a maximum number of substitutional defects, and to measure the structure factors at various temperatures.

3.4. The effects of anharmonicity

With increasing temperature, the interatomic force constants weaken and this means that the thermal MSD increase more rapidly with increasing temperature than they would in the absence of anharmonic effects. A detailed review of the effects of anharmonicity on the thermal MSD has been given by Krivoglaz (1969) and by Willis and Pryor (1975). They point out that the effects of anharmonicity can be accounted for over a large range of temperatures purely by considering thermal expansion. The quasi-harmonic correction derived by Willis and Pryor (1975) for the thermal MSD is

$$\langle u^2 \rangle_t = \langle u^2 \rangle_{tm} / (1 + 2\beta\gamma_1 T) \quad (35)$$

where $\langle u^2 \rangle_{tm}$ is the measured value of the thermal MSD, $\langle u^2 \rangle_t$ is the corrected value, β is the volume expansion coefficient, γ_1 is the Gruneisen parameter and T is the absolute temperature. Unfortunately, for many alloy systems there are no values of γ_1 and β available, so that it is preferable to make measurements at lower temperatures where anharmonic effects are small.

The effects of anharmonicity due to thermal expansion on the static MSD as embraced by the quasi-harmonic approximation are less, since these depend on the ratio of the NN force on the defect to the NN force constant, α_1 , where these two will both decrease proportionately with increasing temperature.

3.5. BCC systems and the ω -phase transformation

Contributions to the MSD in some quenched BCC solid solutions based on Zr, Ti and Hf can also come from the ω phase (see for example Kuan and Sass 1976, De Fontaine *et al* 1971). Associated with this contribution to the MSD are diffuse intensity streaks close to the traces of the $\{111\}$ planes in reciprocal space, and the maxima of this diffuse intensity occur at the $\frac{1}{3}(112)$ reciprocal lattice positions. Below a certain temperature, T_ω , these diffuse intensity regions sharpen into reflections characteristic of the ω phase (Sass 1972, Dawson and Sass 1970). There have been several theories proposed to explain the ω phase (see for example Borie *et al* 1973, Pynn 1978, Horovito *et al* 1978, Cook 1975). Of these only Cook (1975) made quantitative predictions. He proposed that ω was homogeneously nucleated by the collapse of $\{111\}$ planes arising from large-amplitude displacement waves (phonons) propagating in $\langle 111 \rangle$ directions; these were considered to arise from strong anharmonic terms in the expression for the free energy of the system which contained the ω phase. Kuan and Sass (1976) found that such a model did not adequately fit the observed diffuse intensity effects and proposed that ω is heterogeneously nucleated by thermal vacancy point defects. In this case $\{111\}$ planar collapse is limited to the region of the point defects, i.e. a low-frequency phonon or phonon group is trapped by the defect.

Recently Prasetyo *et al* (1976), Ortiz and Epperson (1979), Kirchgaper and Gerold (1978) and Georgopoulos and Cohen (1977, 1981) have detected ω -like transformations in the B2 alloys β' CuZn, β' CoGa and β' NiAl, and this work has shown that substitutional defects as well as vacancy defects can nucleate ω in these systems.

Above T_ω the phonon trapping process increases the static displacements and reduces the thermal displacements so that the latter cannot be described by equations (16) and

modifications to the model for the MSD must be considered in these cases. Below T_{ω} , an ω -containing alloy is two-phase so that the structure factors cannot be described by equations (1), and no simple theory is applicable.

4. Summary and conclusions

A simple model has been developed for analysing structure factor measurements in ordered BCC (B2) alloy systems. This model is based on the ideas of Shirley and Fisher (1979) who developed expressions for the MSD of solid solutions to analyse critical voltage measurements in these.

The potential application of this model to Debye–Waller factor measurements made by x-ray or neutron diffraction and structure factor determinations made by the critical voltage method have been discussed, and in addition to the usual effects of static displacements due to atomic radius mismatch, LRO and anharmonicity, the possible effects of the ω phase have been examined.

In the following paper (Fox 1983) this model will be used to analyse critical voltage measurements in three ordered BCC (B2) alloys: these arise from the ordering of a primary BCC solid solution, a β' phase and a β'' phase which contains diffuse ω .

Acknowledgments

The authors would like to thank the following organisations for the provision of time, resources and financial support: The United States Steel Corporation and Motorola Inc. in the USA, and Foseco International Ltd, The University of Birmingham and The Science Research Council in the UK.

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