space residuals, R_1, R_3 and R_4, leads to values which are in good agreement with each other. The following points seem noteworthy.

1. There is considerable evidence that the Luzzati method leads to overall values of $|\overline{\Delta r}|$ which are consistent with the actual differences in the model coordinates. Some overestimation of $|\overline{\Delta r}|$ may be caused by the application of 'acentric equations' to the overall data. Our results have shown that different reciprocal-space residuals give results consistent with each other. We have therefore confirmed that these methods may be useful in the determination of $|\overline{\Delta r}|$ in those cases where direct comparison of coordinates is impossible (*e.g.* medium-resolution studies).

2. Our results confirm that Wilson's statistics may be applied successfully to both low- and high-angle protein diffraction data. Hence, the results of Parthasarathy & Parthasarathi (1972) may be used to calculate $|\overline{\Delta r}|$.

3. We have found that the methods used gave consistent results for the region $|s| > 0{\cdot}21$ Å^{-1}. R_3 was found to be the least-noisy function in this region.

4. We have confirmed that the low-angle data is significantly affected by solvent scattering, which is also the cause of high background intensity.

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Interference Effects Among Variants*

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Abstract

There have been several recent efforts to account for the broadening of the superstructure Bragg maxima and their displacements in reciprocal space observed for partially transformed b.c.c. solid solutions containing the ω phase. They have been concerned with intensity calculations from models for which the ω regions are defective in a variety of senses. All of the models include only one ω variant, while in fact the system must contain four equally likely variants. A method to correct the calculated intensity for interference effects among the variants, omitted from these models, is described. It is applied to a specimen model. Possible applications of the method are discussed.

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Though the concept is illustrated by its application to the ω phase, it is readily generalized to any multivariant system.

Introduction

A common phenomenon in solid-state transformations is the partial decomposition of a simple structure to one less symmetrical, oriented in a special way to the parent material. An example which has been of recent interest is the transformation upon cooling of b.c.c. solid solutions based on Ti or Zr, containing elements such as V or Nb, to the ω phase. It is understood by considering the primitive rhombohedral cell of the b.c.c structure in terms of a hexagonal basis. Then $c/a = (3/8)^{1/2}$; atomic positions are 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$; and the structure factor vanishes unless $-h + k + l$ is a multiple of three. The c axis of the hexagonal cell is one-half of a body diagonal of the cubic cell. Upon transformation the cell dimensions appear unchanged, but the atomic positions become 0,0,0; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3} + u$; $\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{3} - u$. The parameter u is about $\frac{1}{6}$ or less depending on the composition. The rhombohedral extinction constraint is relaxed and all hkl appear in the diffraction pattern.

However, the new diffraction maxima associated only with the transformed material (here called superstructure maxima) are diffuse and slightly displaced from their expected positions in reciprocal space. Fig. 1, a contour map of diffuse neutron intensity measured by Moss, Keating & Axe (1974) from a Zr–20 wt % Nb alloy, illustrates these effects. A very similar map was observed with X-rays by Lin, Spalt & Batterman (1976).

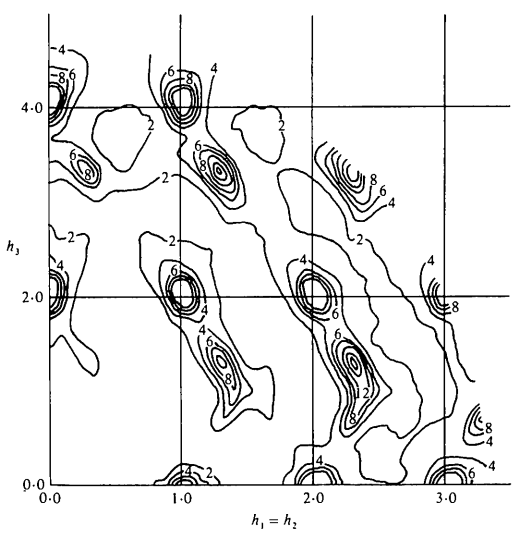

Fig. 1. Contour map of the diffuse neutron intensity distribution at 300 K for Zr–20 wt % Nb quenched from 1273 K. The continuous variables h_1, h_2, and h_3 become the b.c.c. Miller indices at the fundamental Bragg maxima. The map is for the plane $h_1 = h_2$.

Attempts to understand the structural meaning of this intensity distribution have primarily consisted of interference calculations from models of the ω structure into which a variety of defects are introduced. Examples are those of Borie, Sass & Andreassen (1973*a*,*b*; subsequently referred to as BSA*a* and BSA*b*), Kuan & Sass (1976), and Pynn (1978). Horovitz, Murray & Krumhansl (1978) have attempted to describe the defect as a soliton.

An aspect of this transformation is that there are four equally likely orientations for the transformed regions, since there are four body diagonals of the cubic cell which may be parallel to the c axis of the ω structure. These are the four variants of the system. Diffuse intensity from two of these is clearly visible in the map of Fig. 1. Though most of the diffuse intensity in this map is related to the variant whose c axis is parallel to the b.c.c. [111] direction, the tails apparent at approximately $h_3 = 0{\cdot}7$ and $h_1 = h_2 = 1{\cdot}3$ and $2{\cdot}3$ result from the variant whose c axis is associated with the b.c.c. [11$\bar{1}$]. Within any one of them there are three possible choices of the origin atom which remains undisplaced on transformation. Each of these corresponds to a subvariant. The model calculations generate diffuse and shifted ω superstructure maxima by the introduction of defects within an ω region which allow transitions among the subvariants, so they are all equally likely.

Hence from the point of view of accounting for interference effects, the system is rather complicated. There are thirteen orientationally different kinds of regions: there are the essentially isotropic untransformed cubic regions, the four variants, and within each of these three subvariants.

None of the model calculations have dealt with this complication. Diffuseness and shifts of the superstructure maxima result from consideration only of interference effects among the subvariants within a single variant. At most the model atomic array is taken to be a single variant within a matrix of untransformed material.

It is the purpose of this contribution to consider the diffraction consequences of the interference effects of the thirteen orientationally different kinds of regions within partially transformed alloys containing the ω phase. Though the theory will be developed within the context of that system, it should be readily generalized to others.

Theory

We identify the variants with the index p. We let v_{pm} be unity if site $\mathbf{r}_m$ (the atomic position before transformation) is in region p, otherwise zero. Let α_{pm} be unity if the atom at site $\mathbf{r}_m$ is undisplaced on transformation, $\exp[i\mathbf{k}.\boldsymbol{\delta}_p]$ if the site is displaced $+\boldsymbol{\delta}_p$ parallel to the c axis of the pth variant, and $\exp[-i\mathbf{k}.\boldsymbol{\delta}_p]$ if the

displacement is $-\delta_p$ ($\mathbf{k}$ is the diffraction vector). This scheme is illustrated in Fig. 2. With the atomic scattering factor taken to be unity, the scattering amplitude in electron units from the crystal is then

$$A = \sum_m \exp[i\mathbf{k}.\mathbf{r}_m] \left\{1 + \sum_{p=1}^{4} (\alpha_{pm} - 1)\, v_{pm}\right\}. \quad (1)$$

We assume the model, the intensity distribution from which we seek to correct, has treated the crystal as though it were composed of only one variant, say $p = 1$, the rest of the crystal being untransformed. In effect, the transformed regions for $p = 2$, 3, and 4 have been excised and replaced by untransformed b.c.c. material. The fictitious scattering amplitude from the model is then

$$A_1' = \sum_m \exp[i\mathbf{k}.\mathbf{r}_m] \{1 + (\alpha_{1m} - 1)\, v_{1m}\}.$$

To account for all variants it has been common to take the computed intensity to be

$$I' = \sum_{p=1}^{4} A_p' A_p'^* = \sum_{p=1}^{4} \sum_m \sum_n \exp[i\mathbf{k}.(\mathbf{r}_m - \mathbf{r}_n)] \times \{1 + (\alpha_{pm} - 1)\, v_{pm}\} \{1 + (\alpha_{pn}^* - 1)\, v_{pn}\}. \quad (2)$$

We wish to know the residual intensity $\Delta I = I - I'$, I being AA^* computed from (1), and I' as given by (2). We have

$$\Delta I = \sum_m \sum_n \exp[i\mathbf{k}.(\mathbf{r}_m - \mathbf{r}_n)] \left\{\left[1 + \sum_{p=1}^{4} (\alpha_{pm} - 1)\, v_{pm}\right] \times \left[1 + \sum_{q=1}^{4} (\alpha_{qn}^* - 1)\, v_{qn}\right] - \sum_{p=1}^{4} [1 + (\alpha_{pm} - 1)\, v_{pm}]\, [1 + (\alpha_{pn}^* - 1)\, v_{pn}]\right\}$$

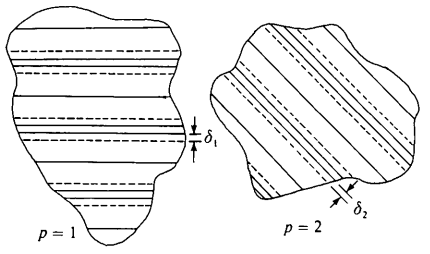

Fig. 2. A schematic illustration of a partially transformed region containing variants $p = 1$ and $p = 2$. Dotted lines indicate atomic plane positions before transformation. Planes in the untransformed b.c.c. matrix have been omitted since they may be drawn parallel to the planes of either regions 1 or 2. In region 1, v_{1m} for all m is unity, otherwise zero.

or

$$\Delta I = \sum_m \sum_n \exp[i\mathbf{k}.(\mathbf{r}_m - \mathbf{r}_n)] \times \sum_{\substack{p=1 \\ (p \neq q)}}^{4} \sum_{q=1}^{4} (\alpha_{pm} - 1)(\alpha_{qn}^* - 1)\, v_{pm}\, v_{qn} - 3I_\beta, \quad (3)$$

where I_β is the kinematic intensity sum before transformation:

$$I_\beta = \sum_m \sum_n \exp[i\mathbf{k}.(\mathbf{r}_m - \mathbf{r}_n)].$$

By the usual means we reduce the double sum over m and n to a single sum. We are able to form many mn pairs in the crystal such that $\mathbf{r}_m - \mathbf{r}_n = \mathbf{r}_j$. Let N_j be the number of such pairs. Let the volume fraction of the crystal associated with one particular variant be x, and let $w_{pq}(\mathbf{r}_j)$ be the probability that after first having found site n in variant q, we translate from it $\mathbf{r}_j$ to site $\mathbf{r}_m$ and find it in variant p. We assume that there is no correlation between subvariants for different variants; that is,

$$\langle(\alpha_{pm} - 1)(\alpha_{qn}^* - 1)\rangle \text{ (constant } \mathbf{r}_j) = \langle\alpha_p - 1\rangle \langle\alpha_q - 1\rangle.$$

The averages on the right of the above expression are over all sites associated with a particular variant, hence the α's carry only a single subscript identifying that variant. Then (3) becomes

$$\Delta I = \sum_j N_j \exp[i\mathbf{k}.\mathbf{r}_j] \times \sum_{\substack{p=1 \\ (p \neq q)}}^{4} \sum_{q=1}^{4} x w_{pq}(\mathbf{r}_j) \langle\alpha_p - 1\rangle \langle\alpha_q^* - 1\rangle - 3I_\beta. \quad (4)$$

We note that $w_{pq}(\mathbf{r}_j)$ must approach x for large $\mathbf{r}_j$. We add and subtract an appropriate quantity to the triple sum of (4) to separate it into sharp and diffuse parts. For the diffuse part we also make the 'infinite crystal' approximation. Then

$$\Delta I = Nx^2 \sum_j \exp[i\mathbf{k}.\mathbf{r}_j] \times \sum_{\substack{p=1 \\ (p \neq q)}}^{4} \sum_{q=1}^{4} \langle\alpha_p - 1\rangle \langle\alpha_q^* - 1\rangle \left\{\frac{w_{pq}(\mathbf{r}_j)}{x} - 1\right\} + I_\beta \left\{x^2 \sum_{\substack{p=1 \\ (p \neq q)}}^{4} \sum_{q=1}^{4} \langle\alpha_p - 1\rangle \langle\alpha_q^* - 1\rangle - 3\right\}. \quad (5)$$

We are primarily interested in the diffuse part of (5), the intervariant interference correction to the diffuse intensity distribution computed from a fictitious single-variant model. We are further interested in expressing it only in terms of parameters that are determined by the model.

Consider $w_{pq}(\mathbf{r}_j)$, the probability (in the real multivariant partially transformed crystal) that after finding a site in variant q, the site $\mathbf{r}_j$ from it is in variant p. In

the single-variant (say variant q) model crystal, let $W(\mathbf{r}_j)$ be the probability that after finding a site in the variant, the site at $\mathbf{r}_j$ from it is in the untransformed region. If we assume that there are no correlations among the variants in the real crystal, the chance that the site at $\mathbf{r}_j$ was really in variant p, but was among those replaced by untransformed material to generate the single-variant model, is simply the total number of sites that are p divided by the total number of sites that are not q: $x/(1-x)$. Hence within that assumption, $w_{pq}(\mathbf{r}_j) = xW(\mathbf{r}_j)/(1-x)$.

We may now write the diffuse part of (5) in terms of model-dependent parameters only:

$$\Delta I_D = Nx^2 \left\{ \sum_{p=1}^{4} \sum_{q=1}^{4} \langle \alpha_p - 1 \rangle \langle \alpha_q - 1 \rangle \right\} \times \left\{ \sum_j \exp\left[i\mathbf{k}.\mathbf{r}_j \right] \left[\frac{W(\mathbf{r}_j)}{1-x} - 1 \right] \right\}. \quad (6)$$

The computation of the trigonometric function corresponding to the double sum over p and q is straightforward. Suppose that the fraction of atoms undisplaced within a variant is S. Note that it need not be one-third; it will depend on the character of the defects which allow transitions from one subvariant to another and their density. The atomic displacements within a defective region also need not be the same as those within perfect ω regions. However, if they are,

$$\begin{aligned} \langle \alpha_p - 1 \rangle &= S + (1-S)\cos(\mathbf{k}.\boldsymbol{\delta}_p) - 1 \\ &= (1-S)\left[\cos(\mathbf{k}.\boldsymbol{\delta}_p) - 1\right] \\ &= -2(1-S)\sin^2(\mathbf{k}.\boldsymbol{\delta}_p/2). \end{aligned}$$

For the variant related to the cell diagonal $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$ (the $\mathbf{a}_n$'s being the b.c.c. basis vectors), $\boldsymbol{\delta}_p = (u/2)(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. If $\mathbf{k} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3)$ (the $\mathbf{b}_n$'s being reciprocal to the $\mathbf{a}_n$'s, and the h_n's continuous variables which become the Miller indices at the b.c.c. reciprocal-lattice nodes), then

$$\langle \alpha_p - 1 \rangle = -2(1-S)\sin^2\left[\frac{\pi u}{2}(h_1 + h_2 + h_3)\right].$$

Analogous expressions for the other three variants are readily found and combined to give the double sum over p and q of (6).

Note that the Fourier series given by the sum over j in (6) is in general negative since $W(0) = 0$. Since $\langle \alpha_p - 1 \rangle \langle \alpha_q - 1 \rangle$ is always positive, ΔI_D will be negative.

Application of the theory

We have devised a single-variant model for a partially transformed crystal containing the ω phase which is an elaboration and extension of those described in BSA*a*,*b*. As in those calculations the crystal is taken to be a three-dimensional mosaic of 'bricks' of different but commensurate dimensions: (1) ω unit cells, containing three atoms and of height c. (2) Structural elements for the untransformed regions, containing one atom and of height $c/3$. (The model described in BSA*a* is a mosaic of only these two kinds of bricks; the intensity distribution associated with it exhibits broadened and shifted superstructure maxima, but in the wrong sense.) (3) Defective elements, containing two atoms and of height $2c/3$. (BSA*b* is a description of the intensity calculation from a mosaic of bricks of types 1 and 3; its superstructure maxima are broadened and shifted in the correct sense. However, note that since these elements may not be derived either from the ω or untransformed structures, the model crystal contains no untransformed material.) Our new model is an extension of the earlier calculations in that the crystal is taken to be a composite of all three kinds of structural elements.

Fig. 3 is a diffuse intensity contour map computed from this model essentially by the methods described in BSA*a*,*b*. It is a multivariant map generated from a single-variant model *via* the tactic of (2). It therefore exhibits no interference effects among the variants of the system. We defer to a subsequent contribution a description of the details of the model and the diffuse intensity calculation. Fig. 4 shows a contour map of ΔI_D, the intervariant interference correction for the map of Fig. 3, found from (6) and the specific parameters of the model.

Discussion

An interesting feature of the map shown in Fig. 3 is that, in addition to the diffuse and shifted superstructure

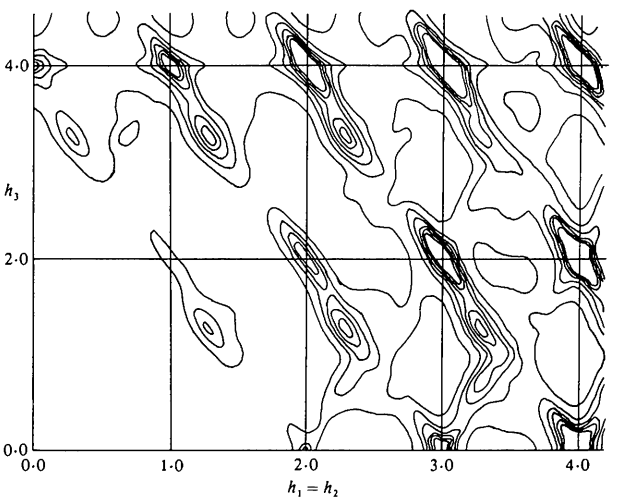

Fig. 3. The relative diffuse intensity distribution in the plane $h_1 = h_2$ for the single-variant model described in the text. Closely spaced contours in the immediate neighborhood of the fundamental maxima have been omitted.

maxima, the model has generated diffuse maxima under the sharp fundamental reflections associated both with the ω phase and its b.c.c. ancestor. Both of the calculations described in BSA*a*,*b* failed to achieve this result. The maxima are apparent in the experimentally determined contour map of Fig. 1. The main difference between the model giving rise to Fig. 3 and the earlier calculations is that it consists of ω regions, rendered defective so that all subvariants are active, imbedded in a matrix of untransformed material. Interference among the subvariants, controlled by the nature of the defects, appears adequate to generate the general features of the diffuse intensity distribution in the neighborhood of the superstructure positions in reciprocal space (BSA*b*). However, the maxima centered on the b.c.c. reciprocal-lattice nodes seem dependent on interference between defective ω regions and the b.c.c matrix. The contribution of Kuan & Sass (1976), in which the problem of computing a diffraction pattern from a model is approached from a very different point of view, is nevertheless concerned with the intensity distribution resulting from defective transformed regions imbedded in b.c.c. material. Like our model, their calculation considers only one variant and in effect generates a multivariant result *via* (2). It is interesting and suggestive that their result also exhibits diffuse maxima at the fundamental reciprocal-lattice nodes. Both their model, however, and that responsible for Fig. 3 fail to reproduce the relative strengths of these maxima shown in Fig. 1. The possibility that this part of the scattering pattern may reveal details concerning the sizes of the defective ω regions and their distribution in the untransformed matrix is very interesting.

The intensity map of Fig. 4 for ΔI_D shows negative diffuse peaks at just the above discussed places in reciprocal space: the fundamental Bragg maxima. That this should be so is not surprising since these are the only regions where all of the variants are simultaneously 'turned on'. Clearly the interference correction here discussed must be accounted for before any attempt quantitatively to interpret such maxima from model calculations is undertaken.

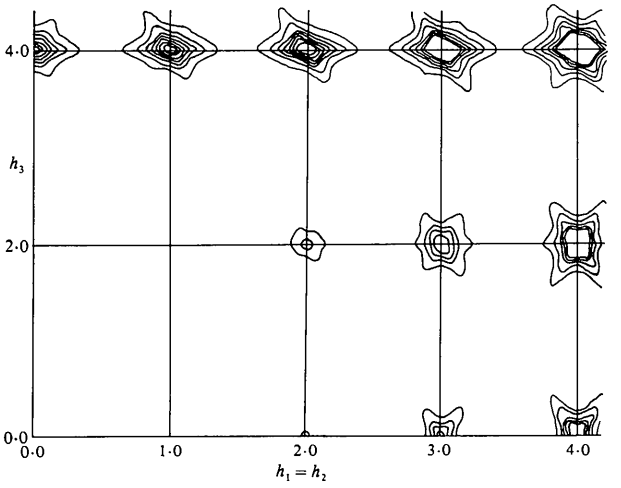

Fig. 4. A contour map of the correction ΔI_D. This intensity distribution must be subtracted from that of Fig. 3 to correct for interference effects among the variants.

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