Table 3. *Interatomic distances in* Zr_2Al_3

Distances in the Zr co-ordination polyhedron (13 atoms) (Å)

Zr–Al (*a*): 2·83, 2·89, 3·22
Zr–Al (*b*): 2·88, 2·91, 2·93, 2·97, 3·00 (twice)
Zr–Zr: 3·40 (twice), 3·43 (twice)

Distances in the general Al co-ordination polyhedron (10 atoms) (Å)

Al–Al (*a*): 2·67, 2·71
Al–Al (*b*): 2·77 (twice)
Al–Zr: 2·88, 2·91, 2·93, 2·97, 3·00 (twice)

Distances in the special Al co-ordination polyhedron (10 atoms) (Å)

Al–Al (*b*): 2·67 (twice), 2·71 (twice)
Al–Zr: 2·83 (twice), 2·89 (twice), 3·22 (twice)

The co-ordination polyhedra do not have any simple form. Their shapes can be obtained from the bonding shown in Fig. 1, where contacts outside the puckered triangular nets are shown as dotted lines and the bonds within the nets are shown as full lines.

No simple relation has been found between the structure of Zr_2Al_3 and that of $ZrAl_2$ (Wilson, 1959). The basic symmetry operations in the two structures are different, and, although there is a three-fold net in $ZrAl_2$ also, it is made up of Al atoms forming a planar 4-connected net—the net 4*a* of Wells (1956) or the kagomé net of Frank & Kasper (1959)—with Zr atoms symmetrically above and below the hexagonal holes in this plane. These considerations support one's general conception of a metal, that there is no preferred polyhedron around any particular atom, but that any arrangement which satisfies the space group and radius-ratio and gives a reasonably large co-ordination number around each atom is a likely structure.

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The Separation of Short Range Order and Size Effect Diffuse Scattering

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Short range order diffuse scattering in binary substitutional solid solutions is often obscured by modulations associated with the fact that the two kinds of atoms are of different sizes. A method is described for the separation of these two components of the diffuse scattering, and it is illustrated by its application to CuAu. It is suggested that a determination of the size effect coefficients along with the short range order parameters will provide a greater insight into the short range structure of an alloy.

Introduction

If the atoms of a binary substitutional solid solution are arranged on the atomic sites such that there is no long range order, superstructure reflections disappear and are replaced by diffuse scattering. The Fourier transform of this short range order diffuse intensity gives the short range order parameters, or the average relative populations of the two kinds of atoms in the various coordination shells about an atom at the origin. Roberts (1954) discovered that the diffuse scattering for the alloy CuAu was modulated in a way not compatible with the cosine Fourier series representation of short range order, and Warren, Averbach & Roberts (1951) showed that these modulations are associated with small static displacements of the atoms from the sites of the average lattice. Such displacements are due, in most metallic solid

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solutions, to the disorderly arrangement of atoms of two sizes on a set of sites. These size effect modulations have since been observed in a number of other solid solutions, and have caused ambiguities in the determination of short range order parameters.

It is the purpose of this paper to describe a method for the separation of the size effect modulations from the short range order diffuse scattering, and to show how the modulations may be interpreted quantitatively to give, along with the order parameters, a considerably more detailed description of the short range structure of an alloy than has hitherto been attempted.

Description of the method

Consider a close-packed cubic crystal, the sites of which are populated by two kinds of atoms, A and B. The atoms may be arranged with a degree of short range order, but because the order is not perfect, each atom may be statically displaced from its lattice site. Then Warren, Averbach & Roberts (1951) have shown that the diffuse X-ray scattering may be written

$$I/[Nm_Am_B(f_A-f_B)^2] = \sum_{lmn} \alpha_{lmn} \cos 2\pi(h_1l+h_2m+h_3n) - \sum_{lmn} \beta_{lmn} 2\pi(h_1l+h_2m+h_3n) \sin 2\pi(h_1l+h_2m+h_3n)\ . \tag{1}$$

Here, I/N is the diffuse intensity in electron units per atom, m_A is the fraction of the total number of atoms in the crystal which have atomic scattering factor f_A, and m_B and f_B are similar quantities for B atoms. The position of any atom relative to the origin site is given by $l\mathbf{a}_1/2+m\mathbf{a}_2/2+n\mathbf{a}_3/2$, where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are vectors along the cubic unit cell edges. For a close-packed cubic material, the integers lmn must have an even sum. The quantity α_{lmn} is the short range order parameter associated with the lmn coordination shell. $\alpha_{lmn}=1-(p_{lmn}/m_A)$ where p_{lmn} is the probability of finding an A atom in the lmn coordination shell of a B atom. The continuous variables $h_1h_2h_3$ define a particular position in reciprocal space. At the Bragg maxima they take on values equal to half the Miller indices.

The coefficients β_{lmn} are associated with the fact that the equilibrium positions of the atoms do not correspond precisely to lattice sites. If the interatomic distances for AA, AB, and BB pairs are equal and correspond to lattice translations, then all β_{lmn} are zero.

The derivation of equation (1) is dependent on the assumption that the displacement $\boldsymbol{\delta}$ of an atom from its site is sufficiently small that the approximation

$$\exp\,[2\pi i[(\mathbf{s}-\mathbf{s}_0)/\lambda]\,.\,\boldsymbol{\delta}] \cong 1+2\pi i[(\mathbf{s}-\mathbf{s}_0)/\lambda]\,.\,\boldsymbol{\delta} \tag{2}$$

holds. The consequences of this assumption will be discussed in a later section. The unit vectors $\mathbf{s}_0$ and $\mathbf{s}$ define the directions of the incident and scattered beams.

If data are gathered only in the plane $h_3=0$ in reciprocal space, as is often done, then equation (1) may be written

$$I'(h_1h_2) = \sum_{lm} A_{lm} \cos 2\pi(h_1l+h_2m) - \sum_{lm} B_{lm} 2\pi(h_1l+h_2m) \sin 2\pi(h_1l+h_2m)\ , \tag{3}$$

where

$$I'(h_1h_2) = \frac{I(h_1h_20)}{Nm_Am_B(f_A-f_B)^2}\ ,$$

$$A_{lm} = \sum_n \alpha_{lmn},\quad B_{lm} = \sum_n \beta_{lmn}\ .$$

We wish to separate the two series of equation (3) from each other with no assumptions. We form the function $Q(h_1h_2)=I'(h_1h_2)-I'(h_1,\,h_2+1)$. From (3) it is clear that

$$Q(h_1h_2) = \sum_{lm} B_{lm} 2\pi m \sin 2\pi(h_1l+h_2m)\ . \tag{4}$$

From this expression may be obtained

$$P(h_1h_2) = h_2Q(h_1h_2)+h_1Q(h_2h_1) = \sum_{lm} B_{lm} 2\pi(h_1l+h_2m) \sin 2\pi(h_1l+h_2m)\ . \tag{5}$$

From equations (3) and (5) there results

$$I'(h_1h_2)+P(h_1h_2) = \sum_{lm} A_{lm} \cos 2\pi(h_1l+h_2m)\ . \tag{6}$$

The size effect is thus eliminated from the data without the determination of the parameters B_{lm} and without any assumptions concerning their relative magnitudes.

The measurements of Roberts (1954) of the diffuse scattering for the alloy CuAu are excellent data to demonstrate the method. Shown in Fig. 1(a) is the measured intensity for this alloy quenched from 500 °C., corrected for f^2 and polarization dependence, in the h_1h_20 plane. For best short range order parameter determinations, it is desirable to perform the separation as near to the origin as possible. Here the size effect modulations are small, and all effects due to thermal motion are minimized. The area in the h_1h_20 plane given by $\frac{1}{2} \leq h_1 \leq 1$ and $0 \leq h_2 \leq 1$ was used for this case.

Fig. 1(b) shows the function given by equation (6) as determined from the contour map of Fig. 1(a) without the evaluation of the size effect coefficients B_{lm}.

Discussion

Though the above described method may be used to determine directly the parameters A_{lm}, which is the usual object of a diffuse scattering experiment, it should be pointed out that the quantities B_{lm} may also be obtained by Fourier inversion of equation (4). Both sets of coefficients then determine not only the probability of finding AA, BB, and AB pairs of atoms

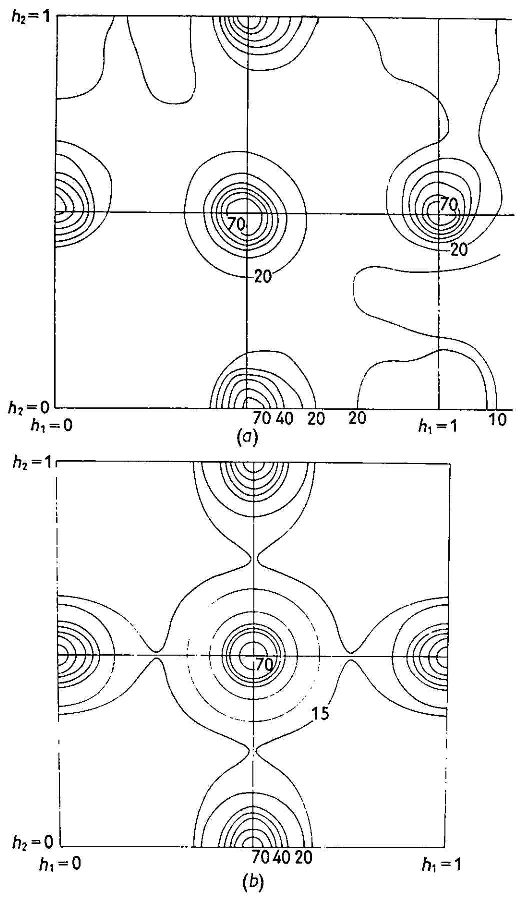

Fig. 1. (*a*) Diffuse intensity distribution in the h_1h_20 plane for CuAu quenched from 500 °C. as measured by Roberts (1954). High intensity contours near the fundamental Bragg maxima have been omitted. (*b*) Diffuse intensity distribution for CuAu after correction for the size effect modulations. Contours near the fundamental Bragg maxima have been omitted.

in any given coordination shell, but as well they provide a measure of how the distance between the three types of pairs deviate from the average distance as given by the lattice constant. Such a treatment of diffuse scattering should provide a new quantitative insight into the short range structure of an alloy. In particular it should be useful for the study of precipitation hardening systems in an early state of ageing.

It is interesting to notice how the size effect modulations distort and obscure the short range order diffuse intensity distribution. Discussing the intensity distribution of Fig. 1(*a*), Roberts (1954) observes that 'in CuAu the diffuse peaks due to short range order are roughly spherical rather than having the pronounced disk shape which Cowley (1950) found for Cu_3Au.' Fig. 1(*b*) shows that after the size effect modulations are removed, the disk-like character of the intensity distribution as found by Cowley is quite apparent.

If one neglects the effect of order on the size effect, the magnitude of the modulations relative to the Laue monotonic scattering (the leading term of the short range order Fourier series) should increase as the concentration of the atoms with larger f increases. The measurements of Cowley for Cu_3Au and those of Batterman (1957) for $CuAu_3$ confirm this expectation. In electron units, the Laue monotonic scattering for these two alloys should be the same. However Batterman's diffuse scattering measurements are so distorted by the size effect that, without correction, a determination of short range order parameters is almost impossible. It is fortunate that early measurements in this system were begun with copper-rich alloys.

The approximation of equation (2) used by Warren, Averbach & Roberts omits an effect considered by Huang (1947) and, in modified form, by Borie (1957, 1959). It may be shown that the quadratic term omitted in (2) gives rise to a decrease in intensity of the Bragg maxima and a diffuse scattering, an effect similar to that due to thermal motion. However, such Huang diffuse scattering is concentrated in the vicinity of the fundamental diffraction maxima, a region obscured by temperature diffuse scattering as well. The above described treatment of the data may usually be carried out omitting this region with no serious loss. For the purposes of this paper, the Warren–Averbach–Roberts theory is more useful than that of Huang, since it invokes no elastic model for the computation of the coefficients β_{lmn}. Such a general representation of the static atomic displacements is applicable to systems in which the displacements may be due to atomic properties other than simple atomic size.

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