

A New Type of Disordered Structure of AuCu₃

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X-ray diffuse scattering with an intensity distribution of one-dimensionally elongated shape in reciprocal space is observed for a single crystal of AuCu₃, which is in a transient state around the order-disorder transition point. The analysis is carried out on the basis of Wilson's model for the disordered structure of AuCu₃. The probability that a unit cell at a given position is displaced by half the diagonal of the unit-cell cube is derived as a function of the position of unit cell, and is found to be expressed by an exponential function.

Introduction

It has previously been reported (Doi, Masaki & Kamada, 1969) that an unusual type of X-ray diffuse scattering with a cross-like distribution in reciprocal space was observed for a single crystal of a Au-Cu alloy,

having a composition close to that of AuCu₃. A single crystal of Au₂₇Cu₇₃ [the composition being determined by the lattice parameter $a = 3.757 \pm 0.005$ Å (Pearson, 1958)] was annealed in vacuum maintained at a temperature of about 900°C for 3 days and then cooled down to room temperature in about 20 hours. Passage through the order-disorder transition point (390°C) was made with the cooling rate of 50°C.hr⁻¹; therefore the structure concerned may not necessarily correspond to a structure in thermal equilibrium. Intensity distribution was measured quantitatively and analysed using a technique similar to that developed for the structure analysis of a Guinier-Preston (G.P.) zone in an Al-Cu alloy (Doi, 1960). Cu K α radiation, monochromated by the 101 reflexion of curved quartz, was used. Scattered intensities on a plane perpendicular to the [001] axis and passing through the reciprocal origin were recorded by a NaI(Tl) scintillator with pulse-height discrimination. The results obtained are shown in Fig. 1. Superlattice reflexions described previously (Doi *et al.*, 1969) were too weak to be measured quantitatively and are neglected in the following analysis.

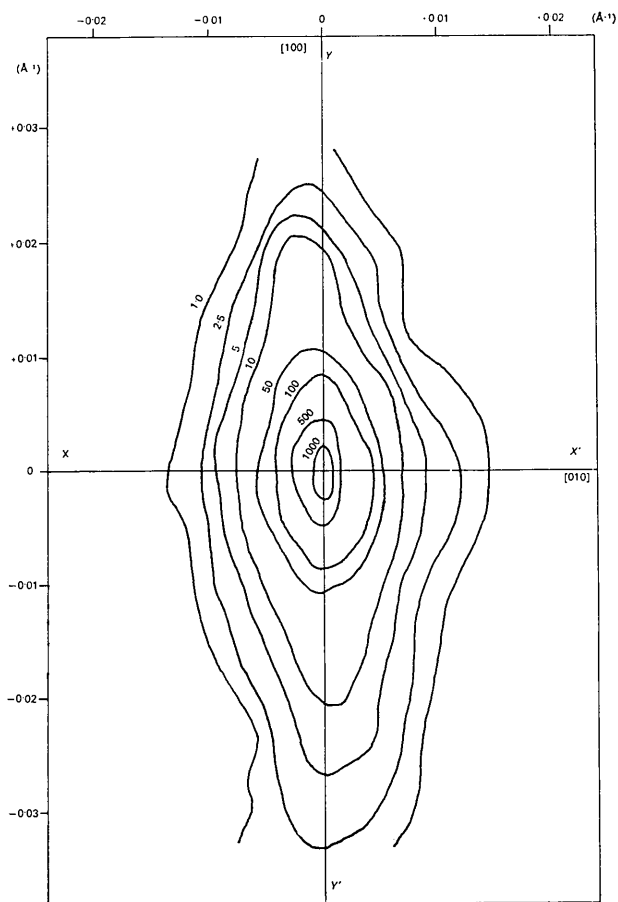


Fig. 1. Intensity distribution around the relpoint 010, on the plane perpendicular to [001]. The heights of contours are expressed in arbitrary units.

Structure analysis

Since the diffuse scattering concerned has a one-dimensional distribution, the corresponding structural disorder should also be of a one-dimensional nature, as first discussed by Wilson (1962) for the disordered structure of AuCu₃.

Into the ordered structure of AuCu₃, in which Au atoms occupy the cube corners and Cu atoms the face centres, a structural disorder is introduced by displacing a unit cell by a vector \mathbf{d} in the (100) plane (see Fig. 2):

$$\mathbf{d} = \frac{1}{2}(\mathbf{a}_2 + \mathbf{a}_3), \quad (1)$$

where \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are the unit translations. The displacements give rise to an elongation of, for example, the 010 relpoint along the [100] direction. Displacements of the same nature may also occur in the (010) and (001) planes, and the diffuse scattering will be of

the shape calculated by Wilson (1947, 1962). He has also remarked that the intensity distribution tends to be cross-like for the points far away from the relpoint 010.

If, as assumed by Wilson (1947, 1962), the displacements take place in a completely random and independent way, the intensity profile along the line YY' passing through the 010 relpoint (Fig. 1) should be of the Lorentzian form. Fitting of the observed profile with Lorentzian curves, however, proved unsuccessful, suggesting the existence of short-range correlations between the displacements. (Fitting with Gaussian curves, proposed by Edmunds & Hinde (1952), was also unsuccessful.)

The intensity $I(\mathbf{s})$ of the scattered X-rays at a point \mathbf{s} on a line YY' (Fig. 2) is expressed as

$$I(\mathbf{s}) = A(\mathbf{s})A^*(\mathbf{s}). \quad (2)$$

If $\omega(\mathbf{s})$ is the phase factor of scattered rays at the position \mathbf{s} in the reciprocal space, the amplitude $A(\mathbf{s})$ is expressed as:

$$\begin{aligned} A(\mathbf{s}) &\equiv A(s_{010}, s_2) \equiv A(s_2) = [I(s_2)]^{1/2} \exp i\omega(s_2) \\ &= \int_{-x_1}^{+x_1} \int_{-x_2}^{+x_2} \varrho(x_1, x_2) \exp 2\pi i(s_{010}x_1 + s_2x_2) dx_1 dx_2 \\ &= \int_{-x_2}^{+x_2} \left[\int_{-x_1}^{+x_1} \varrho(x_1, x_2) \exp 2\pi i s_{010} x_1 dx_1 \right] \\ &\quad \times \exp 2\pi i s_2 x_2 dx_2 \\ &= \int_{-x_2}^{+x_2} F_{010}(x_2) \exp 2\pi i s_2 x_2 dx_2 \end{aligned} \quad (3)$$

where $\mathbf{x} = (x_1, x_2)$ and $\mathbf{s} = (s_1, s_2)$ are position vectors in direct and reciprocal spaces, axes 1 and 2 being taken parallel and perpendicular to the [010] axis, respectively [cf. Fig. 2(a) and (b)]. In the last row of equation (3), $F_{010}(x_2) dx_2$ denotes the 010 structure factor for the electron distribution $\varrho(x_1, x_2)$ contained within $(x_2, x_2 + dx_2)$. It should be noted that, because of the finite resolving power in direct space, the coordinate x_2 has a positional uncertainty Δx_2 . This uncertainty, in the present case is estimated to be about 15 Å from the limit of integration $(-S_2, +S_2)$ in (6), which will be derived from (3) by an inversion. $F_{010}(x_2)$ is therefore regarded as a mean value of the 010 structure factor for the electrons contained between $x_2 - \frac{1}{2}\Delta x_2$ and $x_2 + \frac{1}{2}\Delta x_2$.

Now let $p(x_2)$ be the probability that a unit cell at a position x_2 is displaced by the vector \mathbf{d} of equation (1), then $F_{010}(x_2)$ can be expressed as

$$F_{010}(x_2) = (f_{\text{Au}} - f_{\text{Cu}}) [1 - 2p(x_2)]$$

where the 010 structure factor is $f_{\text{Au}} - f_{\text{Cu}}$ for a non-displaced unit cell, and $-(f_{\text{Au}} - f_{\text{Cu}})$ for a displaced cell (Fig. 2). Here f_{Au} and f_{Cu} denote the atomic form factors of Au and Cu atoms, respectively. With equations (2), (3) and (4), the Fourier transform of the intensity distribution $I(s_2)$ is given as

$$\begin{aligned} I(s_2) &= F_{010}(x_2) * F_{010}(x_2) \\ &= (f_{\text{Au}} - f_{\text{Cu}})^2 [1 - 4 \int p(x_2) dx_2 + 4p(x_2) * p(x_2)] \end{aligned} \quad (5)$$

where the symbol $*$ means a convolution product of functions. Because the disorders involved seem to be correlated in a rather complicated way, as suggested by the failure of the Lorentzian curve fitting, the quantity in the right-hand side of (5) cannot lead to a very clear conclusion regarding the nature of the disorder. On the other hand, if the phase factor $\omega(\mathbf{s})$ can be assigned for diffuse scatterings in some reasonable way, as in the case of the structure analysis of G.P. zones (Doi, 1960; James & Liedl, 1965) and of the analysis of atomic size effects in disordered alloys (Doi, 1964), then from (3), the Fourier transform of amplitude distribution $A(s_2)$ gives

$$p(x_2) = \frac{1}{2} \left[1 - \frac{1}{f_{\text{Au}} - f_{\text{Cu}}} \int_{-S_2}^{+S_2} ds_2 A(s_2) \exp -2\pi i s_2 x_2 \right] \quad (6)$$

It has, in fact, been shown that the phase assignment for the diffuse scatterings is feasible if the statistical

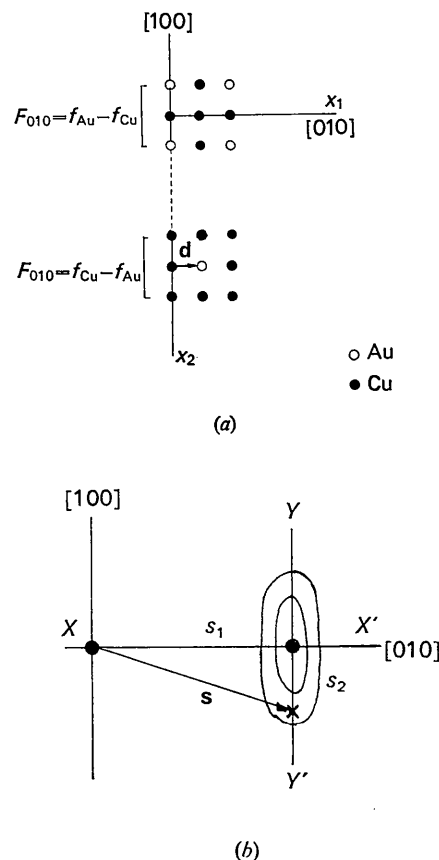


Fig. 2. (a) Model of disordered structure of AuCu₃ projected onto a plane perpendicular to [001]. The upper unit cell represents a non-displaced cell while the lower one is displaced by a vector \mathbf{d} defined by equation (1). (b) The corresponding reciprocal space schematically represented.

centrosymmetry (Doi, 1960), described below, is assumed.

It is noted that in practice the integration in the right-hand side of (6) is replaced by a summation:

$$\overline{p(x_2)}^L = \frac{1}{2} \left[1 - \frac{1}{f_{Au} - f_{Cu}} \sum_{-N}^{+N} A(s_2^{(n)}) \exp -2\pi i s_2^{(n)} x_2 \right] \quad (7)$$

where $s^{(n)}$ is the position of the point (n) sampled discretely in reciprocal space. When these points are sampled at regular separations, $\Delta s_2 = 1/a^*L$ in reciprocal space, where L is to be determined in accordance with the resolving power with which we observe the reciprocal space, then the value of $\overline{p(x_2)}^L$ defined by (7) will represent the function $p(x_2)$ averaged over the points $x_2, x_2 \pm aL, x_2 \pm 2aL, x_2 \pm 3aL, \dots, x_2 \pm maL, \dots$, m be-

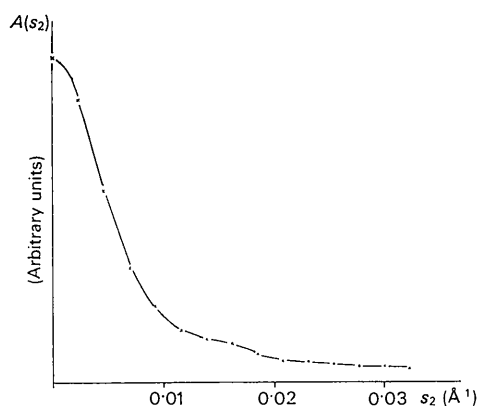


Fig. 3. Amplitude profile $A(s_2)$, derived from the intensity distribution along the line YY' in Fig. 1. The ordinate is in arbitrary units. Crosses show the points sampled, and the continuous curve gives the results of least-square curve-fitting which are used to derive the coefficients $\overline{p(x_2)}^L$ given in Fig. 4.

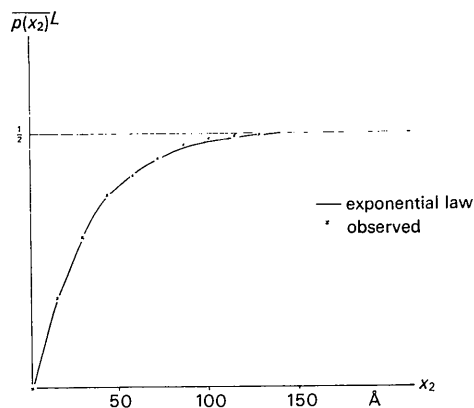


Fig. 4. The parameter $\overline{p(x_2)}^L$ against x_2 . $\overline{p(x_2)}^L$ measures the probability that a unit cell at position x_2 is displaced by a vector \mathbf{d} . Small crosses represent the values derived directly from the observed scatterings, and the continuous curve represents the values calculated from equation (14).

ing an integer (Doi, 1960). Now, by statistical centrosymmetry we understand that

$$\overline{p(x_2)}^L = \overline{p(-x_2)}^L, \quad (8)$$

whereas the centrosymmetry, in its exact meaning, requires the relation

$$p(x_2) = p(-x_2). \quad (9)$$

In the present observation, since the interval Δs_2 is about $(450 \text{ \AA})^{-1}$, L of equation (7) is estimated as $450 \text{ \AA} / 3.76 \text{ \AA} = 120$, so that the average is taken over the range as large as 120 unit cells. Since the size of coherent domains (mosaics) in this crystal, estimated from the width of the fundamental 020 reflexion, is found to be very much larger than the above-estimated value of L , the statistical centrosymmetry (8) may well be expected to hold, although the exact centrosymmetry (9) is by no means valid for disordered structures.

For assumption (8), the phase factor $\exp i\omega(\mathbf{s})$ is restricted to either $+1$ or -1 for $\mathbf{s} = \mathbf{s}^{(n)}$. If we assume for the 010 relpoint that

$$\exp i\omega(\mathbf{s}) = +1, \quad \mathbf{s} = \mathbf{s}_{010} \quad (10)$$

the same phase is to be allotted to every sampling point surrounding the relpoint 010 (Doi, 1960). Condition (10) implies that, in the crystal (or more exactly, in each of coherent domains (mosaics) in the crystal), the total number of non-displaced cells is larger than that of displaced cells. We put the origin of direct space on one of those non-displaced cells, *viz*,

$$p(x_2) = 0, \quad x_2 = 0 \quad (11)$$

where, as remarked above, the expression $x_2 = 0$ is understood to involve an uncertainty Δx_2 . Note that if the numbers of both kinds of cells were exactly equal, the scattered intensity would vanish at the 010 relpoint.

As a result of the averaging operation discussed above in relation to the statistical centrosymmetry (8), the condition (11) should be rewritten as:

$$\overline{p(x_2)}^L = 0, \quad x_2 = 0. \quad (12)$$

Condition (12) means that, in direct space all points at a distance maL from the origin (m being an integer) are occupied by non-displaced unit cells. This will not be the case with disordered structures, and we can assume *a priori* only that

$$\overline{p(x_2)}^L < \frac{1}{2}, \quad x_2 = 0 \quad (12')$$

which simply implies that more non-displaced cells than displaced ones exist in the crystal, and that the origin of the direct space coincides with one of those non-displaced cells. If a displaced unit cell occurs at a distance maL from the origin, in contrast with condition (12), the origin can be moved so that a non-displaced cell again occurs at a distance maL from the origin.

The value of aL concerned (450 \AA) is certainly much longer than the distance within which the presence of non-displaced cell at the origin affects the nature of other cells, but, on the other hand, the distance re-

quired for a non-displaced cell to be present in the vicinity of the maL position is in general within the limit of uncertainties in direct space (Δx_2 being about 15 Å, or 3 to 4 unit translations). We can thus expect the validity of condition (12) to a fair approximation. Indeed, it is seen that, with (12) we can convert the observed amplitude into an electron unit, *viz*,

$$\sum_n A(s_2^{(n)}) = (f_{\text{Au}} - f_{\text{Cu}}). \quad (13)$$

If absolute measurements were made with sufficient precision, we could examine to what extent condition (12) holds. Later, it will be seen that the conclusion of the present analysis is essentially unaffected by the arbitrariness of the scale for observed intensities or amplitudes.

Fig. 3 shows $A(s_2)$ plotted as a function of (s_2) and is derived from the intensity profile $I(s_2)$ using equation (2), condition (10) and the statistical centrosymmetry (8). This function may be substituted into (7) to obtain the probability parameter $\overline{p(x_2)^L}$. In order to avoid termination error in the summation of (7), a least-square fitting was made with a FORTRAN program written for the IBM 7044 computer, and the most probable values of $\overline{p(x_2)^L}$ were derived and are shown in Fig. 4 by small crosses. The value of $\overline{p(x_2)^L}$ for $x_2=0$ is fixed to be zero in accordance with (12), or (13).

Discussion

In Fig. 4, we have a non-displaced cell at the origin $x_2=0$. At points as distant as about 150 Å from the origin, both displaced and non-displaced cells are found with equal probabilities, corresponding to $\overline{p(x_2)^L} = \frac{1}{2}$. In other words, the influence from the non-displaced cell at the origin ceases to be effective at points as distant as 150 Å from the origin. At intermediate distances behaviours of $\overline{p(x_2)^L}$ are found to be characteristic. In Fig. 5 we plot the logarithm of $\frac{1}{2} - \overline{p(x_2)^L}$ against x_2 , the value of $\frac{1}{2}$ being asymptotic value of $\overline{p(x_2)^L}$. The plots, which are well approximated by a straight line as seen in Fig. 5, suggest that $\overline{p(x_2)^L}$ may be expressed as

$$\overline{p(x_2)^L} = \frac{1}{2}(1 - e^{-lx_2}) \quad (14)$$

with $l=(30 \text{ Å})^{-1}$. The continuous curve in Fig. 4, representing equation (14), reproduces the observed values (crosses) fairly well. It was remarked in the previous section that the assumption (12) was equivalent to the normalization of $A(s_2)$ by (13), and both of those were expected to hold only approximately. Here it will be seen readily from (7) that even when the normalization by (13) is not exactly correct, the exponential form of $\overline{p(x_2)^L}$ is still valid, although the coefficients in (14) may vary with the normalization factor to $A(s_2)$. The right-hand side of (13) is multiplied by this factor so that the observed values of $A(s_2)$ are expressed in an electron unit.

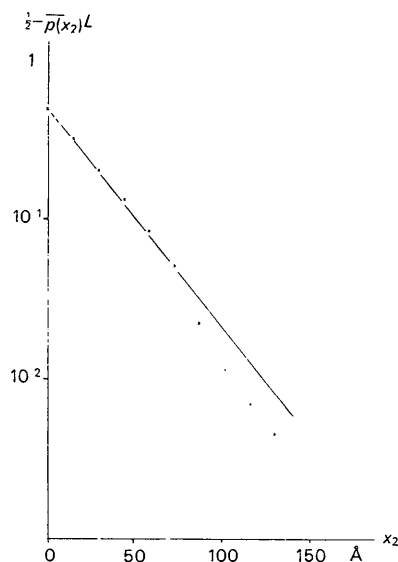


Fig. 5. Logarithmic plot of $\frac{1}{2} - \overline{p(x_2)^L}$ against x_2 , $\frac{1}{2}$ being the asymptotic value of $\overline{p(x_2)^L}$.

The exponential law as expressed by (14) should not be compared with the exponential expression derived by Wilson (1962) for two-body correlation parameters, which is related to the Lorentzian form of the intensity profile, discussed in the previous section. The parameter $\overline{p(x_2)^L}$ discussed here represents N -body correlation, N being as large as L ($=120$ in the present analysis).

The implication of the exponential law (14) is not immediately obvious. It may, however, be inferred that equation (14) reveals a certain aspect of the mechanism in the kinetics of ordering in the alloy when it is cooled through the transition point. As noted above, the structure described does not correspond to a thermal equilibrium but is a result of a passage through the order-disorder transition point on cooling.

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