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The Structure Analysis of a Guinier–Preston Zone by Means of a Fourier Method

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The structure of a G.–P. zone in Al–Cu alloy was analysed using a Fourier transformation of the *amplitude* distribution near the reciprocal lattice point (200). For each atomic plane composing the zone, the content of Cu atoms and the displacement from the net plane of the matrix crystal have been determined. The Cu content was found to vanish after the second plane from the origin, giving the zone a quasi-two-dimensional structure. A displacement of about 0·15 Å toward the zone origin takes place for the first plane, and displacements for the other planes are found to be negligible. The results are compared with those previously obtained by Toman and by Gerold.

Introduction

The analysis of scattering patterns produced by imperfections in crystals has been carried out usually either by (i) the comparison of observed intensities with those calculated on more or less arbitrary structure models by trial and errors, or by (ii) Fourier transformation of the observed *intensity* distribution (see, for example, Guinier, 1956). The second method can be carried out with less detailed assumptions than the first, though the information it furnishes is related only to the atom pairs present in the crystal and not directly to the atomic arrangement.

The present author (Doi, 1957) proposed previously a method of analysing the disordered structures by Fourier transformation of the *amplitudes* of scattered X-rays in a limited region of reciprocal space, e.g. the region surrounding a relpoint, and showed that the information concerning the atomic arrangement in the disordered crystal may be obtained to some extent directly from the intensity distribution of the scattered X-rays, as the phase angles of the amplitudes in the region concerned may be determined by a similar method to that applied by Li & Smoluchowski (1954) for the analysis of small-angle scattering. In the present paper the theory is applied to the structure analysis of the Guinier–Preston zone (which is quoted hereafter as G.–P. zone).

2. Principle of analysis

Let us consider the following function related to a one-dimensional structure of unit translation a,

$$\varphi_H(x) = \int_{-\infty}^{+\infty} A(s)K(s-s_H)\exp 2\pi i x(s-s_H)ds\ , \quad (1)$$

where

$$K(s) = \frac{\sin \pi a s}{\pi s} \quad (2)$$

in place of the usual expression for electron densities

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$$\varrho(x) = \int_{-\infty}^{+\infty} A(s) \exp 2\pi i x s ds , \quad (3)$$

where $A(s)$ is the structure amplitude at the position s in reciprocal space, and

$$s_H = \frac{1}{a} \times H \quad (H=0, \pm 1, \pm 2, \ldots, \text{etc.}). \quad (4)$$

Using the convolution theorem (see, for example, James, 1954), we have

$$\varphi_H(x) = \int_{-\infty}^{+\infty} \varrho(x')\Delta(x-x') \exp(-2\pi i x' s_H) dx', \quad (5)$$

where

$$\Delta(x) = \int_{-\infty}^{+\infty} K(s) \exp 2\pi i x s ds$$
$$= \int_{-\infty}^{+\infty} \frac{\sin \pi a s}{\pi s} \exp 2\pi i x s ds . \quad (6)$$

Since $\Delta(x)=1$ for $|x| < \frac{1}{2}a$, and $\Delta(x)=0$ for $|x| > \frac{1}{2}a$, it is seen that $\varphi_H(x)$ is interpreted as *the structure factor of index* (H) *for the electron density contained in the region between* $x+\frac{1}{2}a$ *and* $x-\frac{1}{2}a$. The integration of (1) requires only the knowledge of $A(s)$ in the neighbourhood of s_H because the kernel $K(s-s_H)$ decreases rapidly with the deviation of s from s_H and, in particular, it vanishes exactly at relpoints other than the Hth where $s=s_H$.

The integration in (1) is practically replaced by summations due to the finite resolution of intensity measurement (Doi, 1957), thus we obtain

$$\Phi_H(x) = \sum_n A(s_n)K(s_n-s_H) \exp 2\pi i x(s_n-s_H) , \quad (7)$$

where s_n's mean the descrete values of s. The effects of the replacement are estimated as follows (Doi, 1957; Ino, 1957). Let the sampling of s_n be made at regular intervals,

$$s_n - s_H = n/aL , \quad (n=0, \pm 1, \pm 2, \ldots, \pm M) , \quad (8)$$

where L is a positive integer greater than 1.

$\Phi_H(x)$ is then written as

$$\Phi_H(x) = \int_{-\infty}^{+\infty} \varphi_H(x')R(x-x')dx', \quad (9)$$

where

$$R(x) = \frac{\sin [2\pi(M+\frac{1}{2}) . x/aL]}{\sin [\pi . x/aL]} . \quad (10)$$

The function $R(x)$ is a peak function having the maxima at

$$x = aL \times n \quad (n=0, \pm 1, \pm 2, \ldots, \text{etc.}) , \quad (11)$$

provided that M is sufficiently large. Whence it is shown

$$\Phi_H(x) \propto \overline{\varphi_H(x)}^L, \quad (12)$$

where $\overline{\varphi_H(x)}^L$ is the average value of $\varphi_H(x)$'s at $x, x \pm aL, x \pm 2aL, \ldots$, etc. Let $\overline{\varrho(x)}^L$ represent the electron density averaged over the points at $x, x \pm aL, x \pm 2aL, \ldots$, etc., then it follows from (5) that

$$\overline{\varphi_H(x)}^L = \int_{-\infty}^{+\infty} \overline{\varrho(x')}^L \Delta(x-x') \exp(-2\pi i x' s_H) dx' . \quad (13)$$

Since $A(s_n)$'s for regularly sampled s_n's (see equation (8)) are the Fourier transforms of $\overline{\varrho(x)}^L$, they are real if

$$\overline{\varrho(x)}^L = \overline{\varrho(-x)}^L. \quad (14)$$

The structure satisfying this condition shall be called *statistically centrosymmetric*.

As $A(s)$ is a continuous function of s (Li & Smoluchowski, 1954), the real function $A(s)$ should pass a zero point $|A(s)|=0$ when $A(s)$ changes its sign. Under the condition of statistical centrosymmetry (14), we can then assign the same sign to all points in a range containing no zero point of $|A(s)|$ (Doi, 1957).

3. The transformation of observed amplitude distribution and the interpretations in terms of structure model

G.–P. zones in Al–Cu alloys are composed of the Cu atoms precipitated from the solid solution and forming an assembly of Cu-rich atomic planes parallel to the (100) plane of the matrix crystal of aluminium.

To start the structure analysis, we assume that the rth plane in the zone be fully described by a set of two parameters; m_r, the Cu-content in the rth plane, and ε_r, the displacement of that plane from the position of the corresponding matrix net plane. Thus we have $2N$ parameters altogether to be determined for the G.–P. zone composed of N planes. The structure amplitude on the relrod [100], divided by the atomic form factor of aluminium f_{Al}, is expressed by

$$\hat{A}(s) = \frac{A(s)}{f_{\text{Al}}} = \sum_r \frac{f_{\text{Cu}} m_r + f_{\text{Al}}(1-m_r)}{f_{\text{Al}}} \times \exp\left[-2\pi i \left(\frac{r a_0}{2} + \varepsilon_r\right) s\right]$$
$$= \sum_r \beta_r \exp\left[-2\pi i \left(\frac{r a_0}{2} + \varepsilon_r\right) s\right] \quad (15)$$

with

$$\beta_r = -m_r + \varkappa m_r + 1 , \quad (16)$$

$$\varkappa = f_{\text{Cu}}/f_{\text{Al}} , \quad (17)$$

where f_{Cu} is the atomic form factor of the Cu atom, $\varkappa$ a constant assumed to be independent of s, and a_0 the cell edge of the matrix crystal.

Put

$$f_r = \beta_r \exp[-2\pi i s \varepsilon_r] , \quad (18)$$

then $\hat{A}(s)$ of (15) is written

$$\hat{A}(s) = \sum_r f_r \exp\left[-2\pi i \frac{r a_0}{2} s\right] . \quad (19)$$

It is seen from (19) that the structure amplitude $\hat{A}(s)$ is equivalent to that for the structure represented in Fig. 1(*a*), where each atomic plane of infinitesimal thickness is situated exactly at the position of each matrix net plane but with the complex structure amplitude f_r as given by (18).

When the statistical centrosymmetry (14) is assumed, the square root of the observed intensity, which is necessarily real, may be proportional to $A(s)$ in (15). There are, however, two kinds of symmetric G.-P. zones as pointed out by Toman (1955): one is the *odd zone* having the centre of symmetry *on* one of the atomic planes, and the other the *even zone* having the centre of symmetry *at the midpoint* between two neighbouring planes. Toman, however, concluded from the intensity distribution in the neighbourhood of the relpoint (110) that the presence of an even zone is less probable. In the following analysis, therefore, the contribution of the even zones to the intensity distributions are neglected. It then follows that the signs of $A(s_n)$ are positive at the relpoints (200) and (400) when the origin of direct space is taken at the statistical centre of symmetry, and further, the signs of $A(s_n)$ may be taken as positive at every point surrounding the relpoints (200) and (400) so long as there is found no zero point of $|A(s_n)|$.

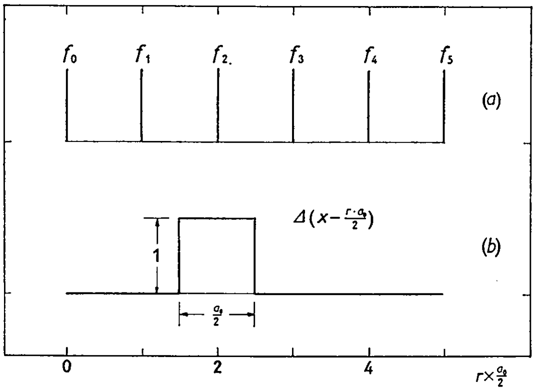

Fig. 1. (*a*) Representation of the G.-P. zone in terms of f_r, the complex structure factor of the *r*th atomic plane (equation 18). (*b*) The function $\Delta(x-ra_0/2)$ for $r=2$.

When we put $a=\frac{1}{2}a_0$, $s_H=s_{(200)}$ in (1) and (2), then the breadth of $\Delta(x)$ of (6) is equal to $\frac{1}{2}a_0$ (Fig. 1(*b*)), and the function $\varphi_{(200)}(x)$ is interpreted as the structure factor of index (200) for the electronic distribution contained between $x+\frac{1}{4}a_0$ and $x-\frac{1}{4}a_0$. Thus we have the relation (Figs. 1(*a*), (*b*)).

$$\varphi_{(200)}\left(\frac{ra_0}{2}\right)=f_r\,,\quad (r=0,\ \pm1,\ \pm2,\ \ldots,\ \text{etc.})\,. \tag{20}$$

The parameters m_r's and ε_r's are readily derived from $\varphi_{(200)}(x)$ using the relations (20), (18) and (16). In order to have the unique solutions for ε_r's, however, we must assume

$$|\varepsilon_r|<\frac{a_0}{4}\,, \tag{21}$$

because the solution of equation (18) for ε_r is many-valued.

The experiments give the function $\Phi_{(200)}(x)$ (equation (7)) in place of $\varphi_{(200)}(x)$, and it is seen from (12), (13) and (20) that

$$\Phi_{(200)}\left(\frac{ra_0}{2}\right)\propto \bar{f}_r^L\,,\quad (r=0,\ \pm1,\ \pm2,\ \ldots,\ \pm L)\,, \tag{22}$$

where $\bar{f}_r^L$ is the complex structure factor of the *r*th atomic plane in the averaged structure $\overline{\varrho(x)}^L$. From

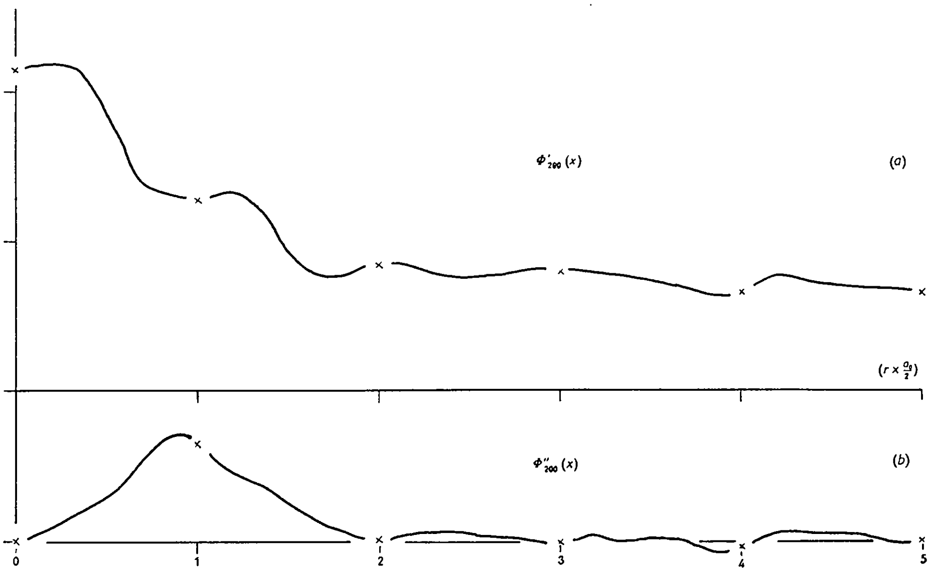

Fig. 2. The function $\Phi_{(200)}(x)$, its real (*a*) and imaginary (*b*) parts. Crosses represent the points sampled. The abscissa is expressed in units of $\frac{1}{2}a_0$.

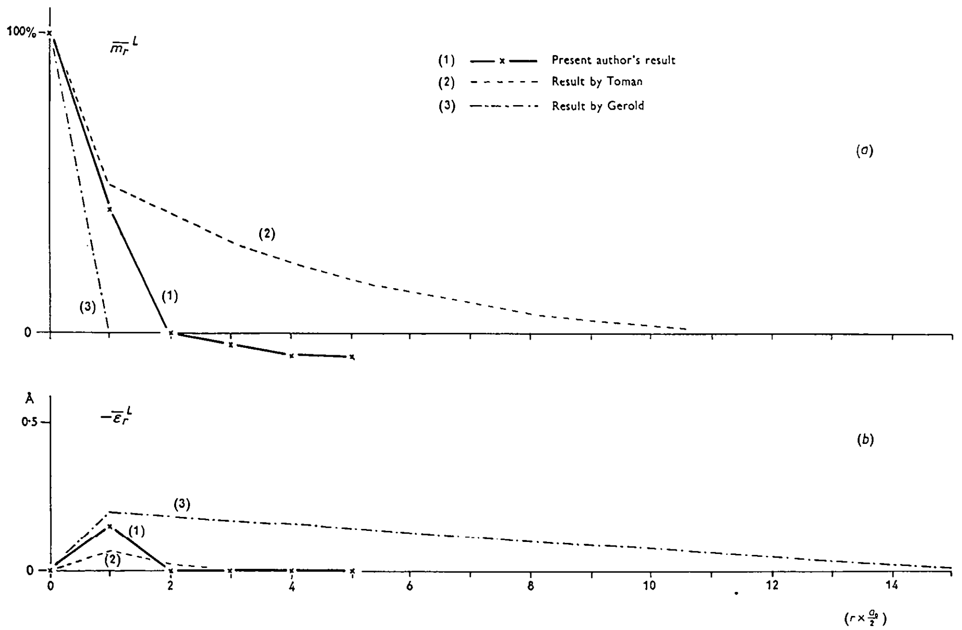

Fig. 3. The results of structure analyses by the present author (Curves 1), by Toman (Curves 2) and by Gerold (Curves 3). (*a*) The parameter $\overline{m}_r^L$, the atomic composition of Cu in the *r*th plane in the zone. (*b*) The parameter $-\overline{\varepsilon}_r^L$, the displacement of the *r*th plane toward the zone origin.

the relation (22) the parameters for the averaged structure $\overline{m}_r^L$ and $\overline{\varepsilon}_r^L$ are derived in the same way as m_r and ε_r are derived from f_r.

The intensity distribution along the relrod [100] of the aged Al–Cu crystal was measured by Toman (1957). By using his intensity data for the range from $s_{(\bar{1}00)}$ to $s_{(500)}$, and with the condition $L=5$ in (8),* $\Phi_{(200)}(x)$ was calculated assuming that the positive square roots of the observed intensities give $A(s_n)$ in (7). The real part $\Phi'_{(200)}(x)$ and the imaginary one $\Phi''_{(200)}(x)$ are represented in Figs. 2(*a*) and (*b*) respectively. It is to be noted that $\Phi_{(200)}(x)$ contains information on atomic planes up to the fifth from the origin, the intervals of peaks in $R(x)$ (equation (11)) being equal to $L.a_0=5.a_0$ in this case.

The parameters $\overline{m}_r^L$ and $\overline{\varepsilon}_r^L$ ($L=5$) were determined using the relation (22). The results are represented by the curves (1) in Figs. 3(*a*) and (*b*). The values of $\overline{m}_r^L$'s were normalized so that $\overline{m}_0^L=100\%$.

Some of the values of $\overline{m}_r^L$'s are found to be negative, which contradicts the definition of $\overline{m}_r^L$. This may be attributed to experimental errors in the intensity measurements, especially those for $s=s_{(200)}$ where the intensity was estimated by extrapolation (Toman, 1957); such errors will affect appreciably the values of $\overline{m}_r^L$ for large *r*. The negative values of $\overline{\varepsilon}_r^L$ mean that the planes are displaced *toward* the zone origin, resulting in a lattice contraction.

4. Discussion

The results obtained by Toman (1955, 1957) and by Gerold (1954, 1958) are shown in Fig. 3 by curves (2) and (3) respectively. In our result (curve (1), Fig. 3(*a*)), the concentration of Cu atoms is 100% at $r=0$ and almost vanishes for $r \geq 2$, a fact which distinguishes the present result from that of Toman (curve (2), Fig. 3(*a*)). The displacement of atomic planes takes its maximum value of about 0·15 Å at $r=1$ and almost vanishes for $r \geq 2$ in our result (curve (1), Fig. 3(*b*)), which is in a tolerable agreement with Toman's result (curve (2), Fig. 3(*b*)). On the contrary, the result by Gerold (curves (3), Figs. 3(*a*), (*b*)) proves to be similar to ours with respect to the Cu concentration, but different from ours with respect to the displacement.

As pointed out by Gerold (1958), Toman's treatment may be subject to errors due to the intensity distribution in the near neighbourhood of the origin. It is to be noted here that in our calculation the contribution from the small-angle scattering turns out to be of little importance, because the kernel $K(s-s_{(200)})$ has no appreciable values near $s=0$. Moreover, Toman has made use of an approximation neglecting the third and the higher powers of ε_r's, which is much more severe than the approximation due to the condition (21) adopted in our calculation. We can then understand why in Toman's result the Cu concentration is greater, and the displacement of atomic planes is in general smaller than both Gerold's and our values. On the other hand, Gerold's result gives the greatest

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* The detailed discussion for the modes of samplings in reciprocal space is found in the previous paper by the author (Doi, 1957).

values of plane displacement, and zero value of Cu concentration except for $r=0$. These results are, however, regarded as being due to his trial and error method assuming $m_0=100\%$, $m_r=0$ $(r \geq 1)$ and $\varepsilon_1=0{\cdot}20$ Å.

In Toman's result the intensity distribution, including that in the small-angle region, is explained by the arrangement of the Cu atoms rather than by the lattice deformations, ε_r's being assumed as small quantities; on the other hand, in Gerold's treatment the explanation of the intensity distribution is given in terms of the lattice deformation, the distribution of Cu atoms in the zone being highly simplified in his initial assumptions.

As the model here obtained with the aid of the intensity distribution modulated by the function $\{K(s-s_{(200)})\}^2$, is based on less restrictive assumptions than those of the previous treatments, it is seen that the intensity distribution, so far as the neighbourhood of (200) is concerned, is most reasonably explained in terms of our structure model.

The same procedure may be applied to the intensity distribution near the relpoints (400), (600), ..., etc., when the observation is extended sufficiently, and it should give the same result as the present one, so long as m_r and ε_r suffice to describe the rth atomic plane in the zone. If this is not the case, the structure model of the G.–P. zone should be further refined by introducing some new parameters so that a consistent model may be obtained for different regions of reciprocal space.

It is worth noting that our results as represented by curves (1) in Figs. 3(*a*) and (*b*) are both found to be the intermediate of Toman's and Gerold's results. The zone structure as represented in our results is much more two-dimensional than expected from Toman's results, while Gerold's one corresponds to a purely two-dimensional structure.

The author is grateful to Dr R. Sadanaga for his valuable discussions.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

International Tables for X-ray Crystallography. Errata

Volume II. *Errata*

p. 46 Last sentence: for *the last two cases* read *cases* (*c*) *and* (*d*)
p. 186 The diagram is inverted: correction needed in the legend: for *bottom* read *top*
|| *pp. 418–429* *Table 8.5 D.* For *Change sign* (heading on right side of each page) read *Change sign for* $h=4n+2$; *sign as given for* $h=4n$

Volume I. *Additional Errata*

p. 20 4th line from bottom: R_{obs} should be R_{obv}
p. 52 8th line from bottom: *Zeit. f. Kryst.* should be *Z. Kristallogr.* (elsewhere *Zeit. f. Krist.* and *Zeits. Krist.* would be better written as *Z. Kristallogr.*)
p. 275 Symmetry diagram. Add 2 sets of horizontal screw axes at $z=\frac{1}{12}, \frac{5}{12}$ respectively, passing respectively through

$(\frac{1}{6}, \frac{1}{3}, \frac{1}{12};\ \frac{1}{6}, \frac{5}{6}, \frac{1}{12})$ $(\frac{1}{6}, \frac{1}{3}, \frac{1}{12};\ \frac{2}{3}, \frac{5}{6}, \frac{1}{12})$ $(\frac{1}{6}, \frac{5}{6}, \frac{1}{12};\ \frac{2}{3}, \frac{5}{6}, \frac{1}{12})$

and

$(\frac{1}{3}, \frac{1}{6}, \frac{5}{12};\ \frac{5}{6}, \frac{2}{3}, \frac{5}{12})$ $(\frac{1}{3}, \frac{1}{6}, \frac{5}{12};\ \frac{5}{6}, \frac{1}{6}, \frac{5}{12})$ $(\frac{5}{6}, \frac{1}{6}, \frac{5}{12};\ \frac{5}{6}, \frac{2}{3}, \frac{5}{12})$

p. 346 3rd line from bottom: 4.4.2 should be 4.4.3
p. 423 In space group $I4_1/a$, the second set of structure factor formulae should refer to $h+k+l=2n$ and not, as given, to $h+k+l=n$
p. 428 In space group no. 94, $|(Fhkl)|$ should be $|F(hkl)|$
p. 542 4th reference: *Ibid.* should read *Z. Kristallogr.*

All these corrections are relatively minor except the one affecting the twelve pages 418–429 of Volume II. This correction should be inserted at once on each page. The Kynoch Press is printing gummed labels for this purpose, which will be sent to all purchasers as soon as possible.

K. Lonsdale
General Editor