(2) The crystals form as needles parallel to the *c* axis, which is the direction of the Pb–N spirals.

(3) The needles form as thin plates perpendicular to the *b* axis, consistent with the weak bonding between the sheets of spirals.

(4) The needles are easily deformed and show plastic behaviour. This arises from flexibility of the spirals and many crystals were observed in which the direction of the *c* axis was not constant. In one case a Weissenberg photograph for oscillation about the *a* axis showed that the *c* axis direction varied continuously over a range of about 10° within the length of the crystal (about 200 μ).

(5) Optical absorption is greatest for the direction of the *a* axis which is the direction towards which all the N–C–N groups are aligned.

(6) Thermal decomposition results in the evolution of cyanogen, but the powder pattern of the material is not appreciably altered. This corresponds to bond fission between the Pb and N(2) atoms and between the N(1) and C atoms so that C–N(2) units from adjacent groups form cyanogen and the –Pb–N– spirals remain unchanged. The Pb–N(2) and the N(1)–C bonds are the weakest in the structure.

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A Direct Analysis of Atomic Displacement in Disordered Alloys from X-ray Diffuse Scattering

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The displacements of lattice points around a Cu atom in perfectly disordered $AuCu_3$ are derived by means of a Fourier transformation of diffuse scattering *amplitude*, without making any assumptions as to the nature of the distortion field.

The results show that the displacement $\boldsymbol{\delta}_{mn}$ of lattice point n at the position $\mathbf{r}_{mn}$ with respect to the distortion centre m is expressed by

$$\boldsymbol{\delta}_{mn} = c_A(\mathbf{r}_{mn}/|\mathbf{r}_{mn}|^3) - \mathbf{K}$$

where c_A is a constant and $\mathbf{K}$ is an additive term which may be identified with the image term as discussed by Eshelby (*J. Appl. Phys.* (1954) **25**, 255).

The possibility of deriving the Zernike parameter of the order–disorder phenomena, when they are accompanied by size effect lattice distortions, is suggested.

The present author has suggested (Doi, 1960*b*, 1961) that with a Fourier transformation of diffuse scattering *amplitude* distribution the order–disorder phenomena of binary alloys can be discussed from a new point of view, *i.e.* that of the propagation of order (Zernike, 1940), which may open a way accessible to the 'exact solution' in the sense of Onsager (1944) as pointed out by Ashkin & Lamb (1943).

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In order to attain this object, however, the so-called size effect modulation must be estimated and, if possible, eliminated so that the diffuse scattering subject to the Fourier treatment be regarded as purely due to the substitutional disorders. In this paper a possible approach to this problem will be described.

Moreover information on the lattice deformation around a point imperfection in an f.c.c. alloy crystal will be obtained in a less arbitrary way than that previously adopted.

Theory

Borie has given an expression of the diffuse scattering for perfectly disordered f.c.c. alloys assuming that the size effect displacements are small quantities (equation (7) of Borie, 1959):

$$\frac{I_D}{m_A m_B N} = \left\{(f_A-f_B)+\frac{m_A f_A+m_B f_B}{m_B}\,.\,i\sum_{n\neq m}\mathbf{s}\,.\,\boldsymbol{\delta}_{mn}\exp\,(i\mathbf{s}\mathbf{r}_{mn})\right\}^2 \quad (1)$$

with

$$\boldsymbol{\delta}_{mn}=c_A(\mathbf{r}_{mn}/|\mathbf{r}_{mn}|^3),\quad c_A m_A=-c_B m_B\,. \quad (1a)$$

Here the position of the lattice point n is given by a vector $\mathbf{r}_{mn}+\boldsymbol{\delta}_{mn}$ starting from the origin m, $\boldsymbol{\delta}_{mn}$ being the displacement of the lattice point n caused by the presence of a particular kind of atom, say A, at the origin m. f_A, f_B and m_A, m_B mean the form factors and concentrations of A and B atoms, and c_A, c_B measure the strength of the distortion center m when it is occupied by an atom A or B respectively. $\mathbf{s}$ is a reciprocal space vector and N stands for the total number of atoms.

It is recognized that the quantity in the bracket of (1) is real if

$$\boldsymbol{\delta}_{mn}=-\boldsymbol{\delta}_{m,-n} \quad (1b)$$

and we can define the *amplitude of diffuse scattering* such that

$$A(\mathbf{s}) = \left|(f_A-f_B)+\frac{m_A f_A+m_B f_B}{m_B}\,i\sum_{n\neq m}\mathbf{s}\,.\,\boldsymbol{\delta}_{mn}\exp\,(i\mathbf{s}\,.\,\mathbf{r}_{mn})\right| \times\exp\,\{i\omega(\mathbf{s})\} \quad (2)$$

where $\omega(\mathbf{s})$ means the phase angle at the position $\mathbf{s}$. When we take the origin of the direct space at the distortion centre m, then

$$\exp\,\{i\omega(\mathbf{s})\}=\pm 1$$

and the right-hand side of (2) can be rewritten, assuming $\boldsymbol{\delta}_{mn}$'s as small quantities,

$$A(\mathbf{s}) = \pm\left|\frac{f_A-\bar{f}}{m_B}+\frac{\bar{f}}{m_B}\left[\sum_{n\neq m}\exp\,\{i\mathbf{s}\,.\,(\mathbf{r}_{mn}+\boldsymbol{\delta}_{mn})\}-\sum_{n\neq m}\exp\,\{i\mathbf{s}\,.\,\mathbf{r}_{mn}\}\right]\right| \quad (2a)$$

with

$$\bar{f}=m_A f_A+m_B f_B\,. \quad (2b)$$

Equation (2a) means that $m_B A(\mathbf{s})$ is the diffuse scattering amplitude produced by atoms of form factor $\bar{f}$ placed at $\mathbf{r}_{mn}+\boldsymbol{\delta}_{mn}$ $(m\neq n)$, and an atom A at the origin m. Taking the Fourier transform of $m_B[\mp A(\mathbf{s})-(f_A-f_B)]/\bar{f}$ we have:

$$\int\frac{m_B[\mp A(\mathbf{s})-(f_A-f_B)]}{\bar{f}}\exp\,\{i\mathbf{s}\,.\,\mathbf{r}\}dv_{\mathbf{s}} = \sum_{n\neq m}[\delta(\boldsymbol{\delta}_{mn}+\mathbf{r}_{mn}-\mathbf{r})-\delta(\mathbf{r}_{mn}-\mathbf{r})] \quad (3)$$

where $\delta(\mathbf{r})$ means the delta function in direct space. It is seen from (3) that if we can have the values of $A(\mathbf{s})$ with their signs in the whole of the reciprocal space, we can derive the values of $\boldsymbol{\delta}_{mn}$ for every n without any assumptions like (1a), which is, however, not feasible in practice.

In this respect the author has developed (Doi, 1957, 1960a) a method which consists of a Fourier transformation of amplitude distribution in a limited region of a reciprocal space, in particular, in the neighbourhood of a relpoint where phase angles are easily assigned (Doi, 1957) assuming the *statistical centrosymmetry*:

$$\overline{\varrho(\mathbf{r})}^{L_1L_2L_3} = \overline{\varrho(-\mathbf{r})}^{L_1L_2L_3}\,. \quad (4)$$

In equation (4), $\overline{\varrho(\mathbf{r})}^{L_1L_2L_3}$ means the electron density averaged over the points

$$(r_1+n_1L_1a_0,\ r_2+n_2L_2a_0,\ r_3+n_3L_3a_0;\quad n_1, n_2, n_3=0,\ \pm1,\ \pm2,\ \pm3,\ etc.\ \ldots),$$

where a_0 means the period of the f.c.c. lattice. In the present case the statistical centrosymmetry is implied by the condition (1b) and the phases are limited either +1 or −1. Let

$$K(\mathbf{s})=K(s_1, s_2, s_3) = \frac{\sin\frac{1}{2}(a_0/2)s_1}{s_1/2}\,\frac{\sin\frac{1}{2}(a_0/2)s_2}{s_2/2}\,\frac{\sin\frac{1}{2}(a_0/2)s_3}{s_3/2} \quad (5)$$

and define a function:

$$\varphi_{(200)}(\mathbf{r}) = \int\frac{m_B[\mp A(\mathbf{s})-(f_A-f_B)]}{\bar{f}} \times K(\mathbf{s}-\mathbf{s}_{(200)})\exp\,\{i\mathbf{r}\,.\,(\mathbf{s}-\mathbf{s}_{(200)})\}dv_{\mathbf{s}} \quad (6)$$

where $\mathbf{s}_{(200)}$ means the relpoint (200). It is shown using the convolution theorem (Doi, 1957, 1960a, b) that

$$\varphi_{(200)}(\mathbf{r}) = \int\sum_{n\neq m}\delta(\mathbf{r}_{mn}+\boldsymbol{\delta}_{mn}-\mathbf{r})-\delta(\mathbf{r}_{mn}-\mathbf{r}) \times\Delta(\mathbf{r}'-\mathbf{r})\exp\,[-i\mathbf{s}_{(200)}\,.\,\mathbf{r}']dv_{\mathbf{r}'} \quad (7)$$

with

$$\Delta(\mathbf{r}) = \int K(\mathbf{s})\exp\,[i\mathbf{s}\,.\,\mathbf{r}]dv_{\mathbf{s}} = \begin{cases}1. & \text{for } |r_1|<\frac{1}{4}a_0,\ |r_2|<\frac{1}{4}a_0,\ |r_3|<\frac{1}{4}a_0\,,\\ 0 & \text{otherwise.}\end{cases} \quad (8)$$

From (7) and (8) we have:

$$\begin{aligned}\varphi_{(200)}(\mathbf{r}_{ijk}) &= \exp\{i[\mathbf{s}_{(200)}\,.\,\delta_{ijk}]\}-1\\ &\simeq -i\sin[\mathbf{s}_{(200)}\,.\,\delta_{ijk}]\end{aligned} \tag{9}$$

where δ_{ijk} is the displacement of the face centered lattice point: $\mathbf{r}_{ijk}(ia_0/2, ja_0/2, ka_0/2)$. As the left-hand side of (9) can be determined from the experimental data only in the neighbourhood of (200) (Doi, 1957), we can derive the component of δ_{ijk} in the direction of $\mathbf{s}_{(200)}$ without any recourse to a hypothesis such as (1*a*). The only assumption to be made, in addition to the smallness of δ_{ijk}'s, is the condition (1*b*) or the statistical centrosymmetry (4).

Example

For the sake of simplicity let us consider a zero-level section of reciprocal space perpendicular to [001]:

$$A(\mathbf{s}_{\shortparallel}) = \pm\left|\frac{f_A-\bar{f}}{m_B}+\frac{\bar{f}}{m_B}\times\left\{\sum_{i,j}\exp\left(i[\mathbf{s}_{\shortparallel}\,.\,(\mathbf{r}_{ij}+\delta_{ij})]\right)-\sum_{i,j}\exp\left(i\mathbf{s}_{\shortparallel}\,.\,\mathbf{r}_{ij}\right)\right\}\right|, \tag{10}$$

where two-dimensional vectors $\mathbf{s}_{\shortparallel}$ and $\mathbf{r}_{ij}$ represent the projections of $\mathbf{s}$ and $\mathbf{r}_{ijk}$ onto the (001) plane respectively, and

$$\delta_{ij} = \sum_k[\delta_{ijk}]_{\shortparallel} \tag{11}$$

with $[\delta_{ijk}]_{\shortparallel}$ as the projection of δ_{ijk} onto the (001) plane. Here also we assume that δ_{ijk}'s are small quantities. We define a two-dimensional analogue of $\varphi_{(200)}(\mathbf{r})$ (equation (6)) constructed from $A(\mathbf{s}_{\shortparallel})$ of (10):

$$\varphi_{(200)}(\mathbf{r}_{\shortparallel}) = \int\frac{m_B[\mp A(\mathbf{s}_{\shortparallel})-(f_A-f_B)]}{\bar{f}}K(\mathbf{s}_{\shortparallel}-\mathbf{s}_{(200)})\times\exp\{i[\mathbf{r}_{\shortparallel}\,.\,(\mathbf{s}_{\shortparallel}-\mathbf{s}_{(200)})]\}dv_{\mathbf{s}\shortparallel}, \tag{12}$$

which proves to be

$$\simeq -i\sin[|\mathbf{s}_{(200)}|\,.\,|\delta_{ij}|\cos\alpha_{ij}] \tag{12a}$$

where $\mathbf{r}_{\shortparallel}$ means the component of $\mathbf{r}$ parallel to the (001) plane, and α_{ij} is the angle between $\mathbf{s}_{(200)}$ and δ_{ij}. Throughout the following calculation f_A, f_B and $\bar{f}$ are supposed to have the same dependencies upon $\mathbf{s}$.

The observed values of $I_D(\mathbf{s}_{\shortparallel})/Nf_A^2$ for disordered $AuCu_3$ in the neighbourhood of (200) were given by Borie (1957). The sampling of these values were made with a mesh of $1/28a_0\times1/28a_0$.

The phase angles at the sampling points, being limited either to 0 or π according to the condition (1*b*) (Doi, 1957), were assigned in accordance with Borie's calculation (1959), *i.e.* the value π was given for the low-angle side of (200) and 0 for the high-angle side, there being a nodal line crossing [100] at the (200) relpoint. This implies that the atom A at the origin is a Cu atom.

A constant corresponding to $(f_A-f_B)/\bar{f}$ in (12) was added to $\sqrt{(I_D/Nf_A^2)}$ so that the function subject to the Fourier transformation become antisymmetric with respect to the (200) relpoint (equation (2)). Though we have no reliable values of I_D in the close neighbourhood of the relpoint (200), because of the confusion with the normal Bragg reflexion, the interpolation was made rather easily in view of the antisymmetry of the integrand of (12) with respect to the relpoint (200). The diffuse scatterings in the neighbourhoods of the other relpoints (000), (400), (220), ... *etc.* ... could be neglected because the kernel $K(\mathbf{s}_{\shortparallel}-\mathbf{s}_{(200)})$ in (12) has no appreciable values in the neighbourhoods of those relpoints.

The function $\varphi_{(200)}(\mathbf{r}_{\shortparallel})$ was thus calculated which proved imaginary in accordance with (12*a*). The scalar product $|\mathbf{s}_{(200)}|\,.\,|\delta_{ij}|\cos\alpha_{ij}$, being derived therefrom for each lattice point (ij), will give the displacement vector δ_{ij} *when the vector is supposed collinear with the distortion centre* (00). The results are shown in Fig. 1. Values of $|\delta_{ij}|$'s on the [010] axis could not be determined, as the scalar products are identically zero ($\alpha_{0j}\equiv\frac{1}{2}\pi$).

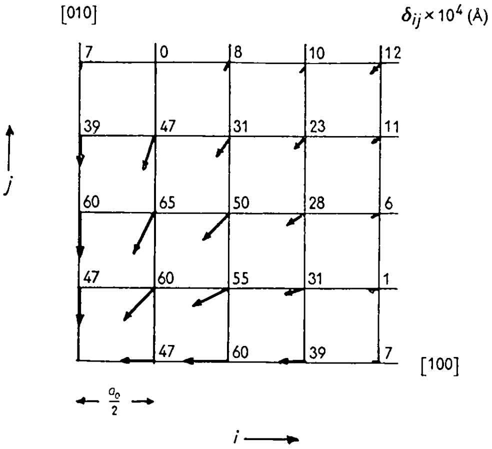

Fig. 1. The displacement of the lattice site $(ia_0/2, ja_0/2)$ of disordered $AuCu_3$ projected onto the (001) plane:

$$\delta_{ij} = \sum_k[\delta_{ijk}]_{\shortparallel}$$

expressed in the unit of 10^{-4} Å. The origin (0, 0) is occupied by a Cu atom. The arrows indicate the directions and magnitudes of δ_{ij}'s (the latter being exaggerated).

Other pairs of $|\delta_{ij}|$'s and $|\delta_{ji}|$'s, which must be equal in accordance with the f.c.c. lattice symmetry, were determined independently. The discrepancies between them may thus measure the errors in $|\delta_{ij}|$'s other than those due to the series-termination effects. All δ_{ij}'s are found directed *toward* the distortion centre giving rise to a lattice contraction around the atom A (=Cu).

Discussion

It is seen that the results represented in Fig. 1 are obtained without any assumptions as to the nature of the distortion field. What we have assumed is that δ_{ij}'s are small, collinear with the distortion centre (00) and symmetric with respect to the centre (00) (equation (1*b*)). It may thus be interesting to compare the values of Fig. 1 with those expected after the inverse-square law (1*a*), in order to see to what extent the elastic continuum model can explain the real distortion field.

Substituting (1*a*) into (11), we have

$$|\delta_{ij}| = \frac{4c_A}{a_0^2}\sum_n \frac{r}{(r^2+4n^2)^{3/2}}, \quad r=\sqrt{(i^2+j^2)}, \qquad (13)$$

which is approximated, when r is large, as

$$\simeq \frac{4c_A}{a_0^2}\int_{-\infty}^{\infty}\frac{r}{(r^2+4n^2)^{3/2}}\,dn = \frac{4c_A}{a_0^2}\cdot\frac{1}{r}. \qquad (13a)$$

In Fig. 2 $|\delta_{ij}|$'s are plotted as a function of $2/a_0r$, for [110], [100] and [210] directions. We see that the values of δ_{ij}'s for larger values of r are found on the straight lines, as expected after equation (13*a*), while those for smaller values of r deviate therefrom very appreciably. We cannot conclude, however, whether these deviations are real ones or simply due to the series-termination errors and/or the approximations adopted in effecting the summation of (13). It is worth noting that the constant c_A determined from the slopes of the straight lines in Fig. 2 is $c_A = -0{\cdot}07 \pm 0{\cdot}005$ Å^3 for the three independent crystallographic directions, while the value determined by Borie (1957) was $c_A = -0{\cdot}072$ Å^3.

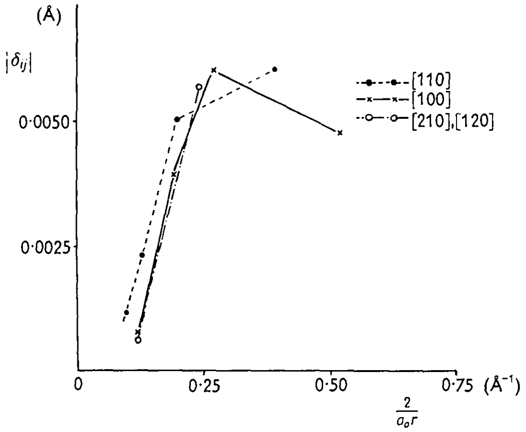

Fig. 2. The values of $|\delta_{ij}|$'s plotted against $2/a_0\sqrt{(i^2+j^2)}$, the reciprocal of the distance from the distortion centre, along the various directions.

The fact that contradicts the assumption (1*a*) is that the straight lines do not pass through the origin of Fig. 2. We can take account of these facts by making a slight modification in (1*a*), so that

$$\delta_{mn} = c_A(\mathbf{r}_{mn}/|\mathbf{r}_{mn}|^3) - \mathbf{K}. \qquad (14)$$

One cannot know with the present results whether the modulus of additive term **K** is a constant or it depends on the orientation [*hkl*]. It is expected that the term may possibly be identified with the image term as discussed by Eshelby (1954).

Concluding remarks

It is to be noted that the method of analysis here developed is not necessarily restricted to the perfectly disordered structure but applies to the partially ordered states as well, where we have diffuse scatterings in the neighbourhoods of the superlattice points, and the function $\varphi_{(200)}(\mathbf{r})$ becomes in general complex.

We need then only to replace (7) by

$$\varphi_{(200)}(\mathbf{r}) = \int \sum_{n\neq m} [(f_n/\bar{f})\,.\,\delta(\mathbf{r}_{mn}+\delta_{mn}-\mathbf{r}) - \delta(\mathbf{r}_{mn}-\mathbf{r})] \times \Delta(\mathbf{r}'-\mathbf{r}) \exp\{i-[\mathbf{s}_{(200)}\,.\,\mathbf{r}']\}dv_{r'}, \qquad (15)$$

and the real and imaginary parts of $\varphi_{(200)}(\mathbf{r})$ will enable us to determine independently both f_n and δ_{mn}, where f_n means the form factor of the atom occupying the lattice site $\mathbf{r}_{mn}$. It is seen that f_n's are related to the Zernike parameters specifying the state of order in the structure (Doi, 1961). This means that the substitutional disorder can be discussed in quite an independent way from the lattice distortions which accompany it inevitably. It also means that an approach to the 'exact solution' of the problem, *i.e.* to derive the partition function from the diffraction data by the intermediate of the Zernike parameter (Ashkin & Lamb, 1943) may be possible even if the appreciable size effects are present in the diffraction data.

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