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A possible approach to the problem of the propagation of order by means of the Fourier transformation of X-ray diffuse scattering.

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The parameters describing the disordered state of solid solutions are, generally speaking, in correspondence to their counterparts in X-ray diffraction phenomena; namely the long-range order parameters are related to the integrated intensities of superlattice reflections, and the *intensity* distributions of X-ray diffuse scattering are interpreted in terms of the short-range order parameters (Cowley, 1950). There are other parameters, however, which specify the state of order more in detail; e.g. we can cite the probability p_i, of finding a particular kind of constituent atom, say, A, at a given site i, which Zernike (1940) made use of in discussing the problem of the propagation of order throughout the lattice (Muto & Takagi, 1955).

On the other hand, there is a method of analyzing the disordered structures by means of the Fourier transformation of the *amplitude* distribution of diffuse scattering (Doi, 1957, 1960*a*). The phase assignment required for deriving the amplitudes is made on the assumption of the *statistical centrosymmetry* for the structure $\varrho(\mathbf{x})$ under examination; i.e.

$$\overline{\varrho(\mathbf{x})}^{\mathbf{L}} = \overline{\varrho(-\mathbf{x})}^{\mathbf{L}}, \tag{1}$$

where $\mathbf{L}$ stands for a triplet of integers (L_1, L_2, L_3) determined in accordance with the resolving power with which we observe the diffuse scattering (Doi, 1957), and $\overline{\varrho(\mathbf{x})}^{\mathbf{L}}$ means the value of the electron density averaged over the points

$$\mathbf{x} + m_1L_1\mathbf{a}_1 + m_2L_2\mathbf{a}_2 + m_3L_3\mathbf{a}_3$$
$$(m_1, m_2, m_3 = \pm 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \ldots,\ \text{etc.})\,,$$

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ being the lattice translations. The results of the analysis can afford more detailed information than that furnished by the intensity distribution and represented by the order parameters mentioned above.

The method was applied (Doi, 1960*b*) to the two-dimensional section of the diffuse scattering observed for $\mathrm{AuCu_3}$ above the critical point (Cowley, 1950), giving as results the fraction of Au atoms at each lattice site forming a two-dimensional lattice which is the (001) projection of f.c.c. structure.

It is readily seen here that when the three-dimensional analysis is made in a similar way, namely using the function $\varphi_H(\mathbf{x})$ as defined:

$$\left.\begin{aligned} \varphi_H(\mathbf{x}) &= \int A(\mathbf{s})K(\mathbf{s}-\mathbf{s}_H)\exp 2\pi i(\mathbf{s}-\mathbf{s}_H.\mathbf{x})dv_s \\ K(\mathbf{s}) &= \frac{\sin \pi a_1 s_1}{\pi s_1}\,\frac{\sin \pi a_2 s_2}{\pi s_2}\,\frac{\sin \pi a_3 s_3}{\pi s_3}\,, \end{aligned}\right\} \tag{2}$$

with proper choices of relpoints H, and a phase assignment for $A(\mathbf{s})$ assuming the statistical centrosymmetry (1), the Au-fraction of each lattice site will be derived with procedures analogous to those used for the two-dimensional analysis (Doi, 1960*b*). In fact $\varphi_H(\mathbf{x})$ can be rewritten:

$$\varphi_H(\mathbf{x}) = \int \varrho(\mathbf{x}')\Delta(\mathbf{x}'-\mathbf{x})\exp -2\pi i(\mathbf{s}_H.\mathbf{x}')dv_{x'} \tag{3}$$

with

$$\Delta(\mathbf{x}) = \begin{cases} 1 & \text{for } |x_1| < \tfrac{1}{2}a_1,\ |x_2| < \tfrac{1}{2}a_2,\ |x_3| < \tfrac{1}{2}a_3 \\ 0 & \text{otherwise,} \end{cases} \tag{4}$$

and the value of $\varphi_H(\mathbf{x}_n)$ for

$$\mathbf{x}_n = \tfrac{1}{2}(2n_1+1)\mathbf{a}_1 + \tfrac{1}{2}(2n_2+1)\mathbf{a}_2 + \tfrac{1}{2}(2n_3+1)\mathbf{a}_3$$
$$(n_1, n_2, n_3 = 0,\ \pm 1,\ \pm 2,\ \ldots,\ \text{etc.}) \tag{5}$$

can be expressed as a linear combination of electronic contents at the 4 neighbouring lattice sites surrounding the point (5) and forming a cube with edges $\tfrac{1}{2}\mathbf{a}_1, \tfrac{1}{2}\mathbf{a}_2, \tfrac{1}{2}\mathbf{a}_3$, which are therefore to be determined from the values of $\varphi_H(\mathbf{x}_n)$'s for 4 independent H's.

The electronic content of each site thus derived is directly related to the Au-fraction at each site, which is to be identified with the probability parameter p_i as defined by Zernike, as it is referred to the averaged structure $\overline{\varrho(\mathbf{x})}^{\mathbf{L}}$ with L_1, L_2, L_3 much smaller in general than the dimensions of coherent domains constituting the crystal under examination.

The feasibility of deriving p_i's from diffraction data depends on the possibility of phase assignment of $A(\mathbf{s})$ in three-dimensional reciprocal space, i.e. the validity of the condition (1). The condition claims that, though the structure $\varrho(\mathbf{x})$ itself is not centrosymmetric, we can put a three-dimensional lattice

$$m_1L_1\mathbf{a}_1 + m_2L_2\mathbf{a}_2 + m_3L_3\mathbf{a}_3$$
$$(m_1, m_2, m_3 = 0,\ \pm 1,\ \pm 2,\ \ldots,\ \text{etc.}) \tag{6}$$

within it so that the structure $\overline{\varrho(\mathbf{x})}^{\mathbf{L}}$ averaged over all the cells of (6) having edges $L_1\mathbf{a}_1, L_2\mathbf{a}_2, L_3\mathbf{a}_3$ proves centrosymmetric. The lattice points of (6) correspond to the origin of $\overline{\varrho(\mathbf{x})}^{\mathbf{L}}$, i.e. the lattice site (000) for which the value of $p(000)$ should be 1·00 after Zernike's definition.

It is not expected, however, that all the lattice points of (6) coincide with atomic sites where Au atoms are always found, unless $\mathbf{L}$ become comparable to the dimensions of coherent domains of which the crystal is constituted. The value of $p(000)$ derived from diffraction data may thus be in general inferior to 1·00. For the greater values of $\mathbf{L}$, $p(000)$ derived would tend to 1·00, but the validity of the condition (1) is not expected to be intact for the greater values of $\mathbf{L}$ comparable to the dimensions of the coherent domains. The deviation of $p(000)$ from the expected value of 1·00 will thus measure the amount of resolution with which we observe the state of order in the structure.

We can therefore conclude that if we can fix the value of $\mathbf{L}$ such that the condition (1) holds and the value of $p(000)$ is not appreciably deviated from 1·00, the probability parameter p_i's as defined by Zernike can be determined, and the problem of the order propagation in solid solutions may be discussed on the basis of the structure analysis made by means of the Fourier transformation of amplitude distribution using the φ-functions given by (2).

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Thermal expansion of sodium fluoride and sodium bromide.

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Published reports on the thermal expansion of sodium fluoride and sodium bromide are few and restricted in scope. (See Krishnan, 1958). On NaF the only results available are those of Henglein (1925) for low temperatures and the room-temperature values quoted by Megaw (1939) and Wooster (1949). For NaBr, besides Henglein's (1925) work there are reports from Baxter & Wallace (1916) and Straumanis, Jevins & Karlsons (1938). The former give average values of cubical expansion for the ranges of temperature 0–25 °C. and 25–50 °C., and the latter give the coefficient of expansion between 15 and 60 °C. as obtained by X-ray method. Recently the author (Deshpande, 1955) has studied both these halides at elevated temperatures by the X-ray method, and the results are reported below.

The experimental set-up and the computational procedure have been described elsewhere (Deshpande & Mudholker, 1960; Deshpande & Sirdeshmukh, 1961). The only special feature of the present work is the hygroscopic nature of NaBr. With careful drying over P_2O_5 in a vacuum dessicator and the use of an air-tight cellophane cover on the specimen, it was possible to obtain quite satisfactory results.

Table 1. *Lattice constants of* NaF *and* NaBr *at different temperatures*

Temperature	Lattice constant of NaF	Temperature	Lattice constant of NaBr
29·6 °C.	4·6340 Å	31·5 °C.	5·9738 Å
68·1	4·6400	82·7	5·9879
108·0	4·6466	119·4	5·9985
148·0	4·6537	160·0	6·0110
176·0	4·6585	252·0	6·0389
208·0	4·6648	—	—
254·0	4·6726	—	—

Lattice constants of the two salts at various temperatures are given in Table 1. The estimated accuracy of the values is ±0·0001 Å. Table 2 gives the coefficients of thermal expansion as defined by $\alpha = 1/a_{20}(\Delta a/\Delta t)$. Least-squares treatment of the $\alpha - t$ data gives the following equations for the temperature dependence of the coefficients of thermal expansion.

Table 2. *Coefficients of thermal expansion of* NaF *and* NaBr

	NaF			NaBr		
Temperature	α (exp.)	α (calc.)	$\Delta\alpha$	α (exp.)	α (calc.)	$\Delta\alpha$
30 °C.	34·00	34·00	0·0	44·84	44·84	0·0
70	34·75	35·17	+0·42	46·89	46·41	−0·48
110	36·60	36·34	−0·26	47·90	47·93	+0·03
150	37·78	37·51	−0·27	49·24	49·70	+0·46
190	38·86	38·68	−0·19	51·83	51·42	−0·41
230	39·94	39·85	−0·09	53·18	53·09	−0·09
250	40·04	40·43	+0·39	—	—	—

NaF:

$$\alpha = 33{\cdot}13 \times 10^{-6} + 29{\cdot}20 \times 10^{-9} . t .$$

NaBr:

$$\alpha = 43{\cdot}69 \times 10^{-6} + 37{\cdot}77 \times 10^{-9} . t + 15{\cdot}21 \times 10^{-12} . t^2 .$$

Values calculated from these equations are also given in Table 2 along with the differences between the experimental and calculated values. The differences are all about 1%.

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