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Diffraction by Crystals with Planar Faults. II. Magnesium Fluorogermanate

BY J. M. COWLEY

Department of Physics, Arizona State University, Tempe, Arizona 85281, *U.S.A.*

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Continuous streaks and the displacement of diffraction maxima from the perfect-crystal positions, observed in electron diffraction patterns of magnesium fluorogermanate suggest the existence of planar faults at which the *c*-axis dimension of the unit cell is contracted by 25%. High-resolution electron microscope images of thin crystals confirm this deduction. It is shown that even in the presence of strong dynamical-diffraction effects, electron diffraction patterns from thin crystals can be interpreted, within well defined limitations, by use of a kinematical theory such as is given in part I [Cowley (1976). *Acta Cryst.* A32, 83–87]. Using this kinematical theory calculations of diffraction intensity are made for reasonable assumptions of the form of the faults. The effect of the modification of the structure at the fault planes on the peak intensities is shown to be small so that structure analyses based on peak intensities only should give the structure of the unfaulted crystal.

1. Introduction

Clear evidence of planar faulting appeared in electron diffraction patterns of magnesium fluorogermanate supplied to the author by Dr Peter Kunzmann and subsequently in similar patterns and electron microscope images obtained by Sumio Iijima. Continuous streaks appeared parallel to the *c* axis and there were systematic displacements of broadened intensity peaks away from the positions of the diffraction peaks for unfaulted crystals. These observations seemed to provide clear examples of the type of effects reported for many cases of diffraction from extended defects in crystals. An analysis of the patterns was therefore undertaken by use of a formulation of the diffraction problem in terms of a generalized Patterson function. A generalization of this formulation is reported in part I of this series (Cowley, 1976).

The structure analysis carried out by Bless, Von Dreele, Kostiner & Hughes (1972) shows that, on one plane of atoms, perpendicular to the *c* axis, the germanium-atom positions have an occupancy factor of only 0·35, associated with the replacement of neighboring oxygen atoms by fluorine. It appeared probable that the planar faults observed to occur perpendicular to the *c* axis could involve the omission of the plane containing these partially occupied germanium positions. The question therefore arose as to whether the existence of such faults could influence the results of a structure analysis carried out with the usual assumption of a perfect, unfaulted lattice. It seemed intuitively obvious that if, in a fraction α of the unit cells, a fault occurred such that the germanium atoms were missing, the structure analysis should show an occupancy $1-\alpha$ for the corresponding sites. Calculations of intensity were required to test this conclusion.

2. Experimental observations

The electron diffraction pattern provided by Peter Kunzmann is reproduced as Fig. 1. This shows the $0kl$ reciprocal-lattice plane of the orthorhombic unit cell; $a=14{\cdot}343$ (1), $b=10{\cdot}196$ (1), $c=5{\cdot}9075$ (4) Å (Bless *et al.*, 1972). Sharp streaks appear parallel to the c^* axis. The diffraction spots are sharp for the reflections corresponding to the periodicities of the close-packed oxygen (and fluorine) sublattice. Along the c^* axis, the $0,0,4n$ spots are sharp. The $0,0,4n\pm1$ reflections are broadened and displaced away from the $0,0,4n$ reflections. The $0,0,4n\pm2$ reflections are more broadened but undisplaced. From this one may conclude that the close-packed stacking of the oxygen (and fluorine) atoms is unaffected by faulting. The structure defined by the cation positions has planar faults perpendicular to the c^* axis. The nature of the faults is such that the average cell dimension is reduced, giving an outward displacement of the 001 and equivalent reflections, *i.e.*, when the fault planes occur some fraction of the unit cell content is subtracted. Since the $0,0,4n$ reflections are sharp, this fraction must be one quarter.

The content of the magnesium fluorogermanate unit cell (Bless *et al.*, 1972), as viewed down the *a* axis, is suggested in Fig. 2. The cations are distributed on four planes, labelled A,B,C,D with z values 0, 0·25, 0·50 and 0·75. Plane A contains 6 Ge and 4 Mg; planes B and D contain 8 Mg. In plane C the Ge positions have fractional occupancy, r, so that the content is $4r$ Ge and 8 Mg.

If at the faults one of these planes of atoms is omitted, the unit-cell *c* dimension will be reduced by one quarter. As illustrated in Fig. 2, the unit-cell origin will be shifted by the shift vector **S**, which is the translation vector for the close-packed oxygen sublattice. This type of fault is then completely consistent with the form of the diffraction pattern, Fig. 1.

Omission of either the A or the C layer of cations from the unit cell (but not the B or D layer) would allow a reasonable juxaposition of its neighbor layers without any rearrangements of atoms. Omission of the C layer seems more likely than the omission of the A layer because the C layer could well be made unstable by fluctuations of the Ge occupancy.

Fig. 1. Electron diffraction pattern from a thin crystal of magnesium fluorogermanate, taken with the beam parallel to the *a* axis, showing the streaks parallel to the c^* axis. (Courtesy of Dr Peter Kunzmann.)

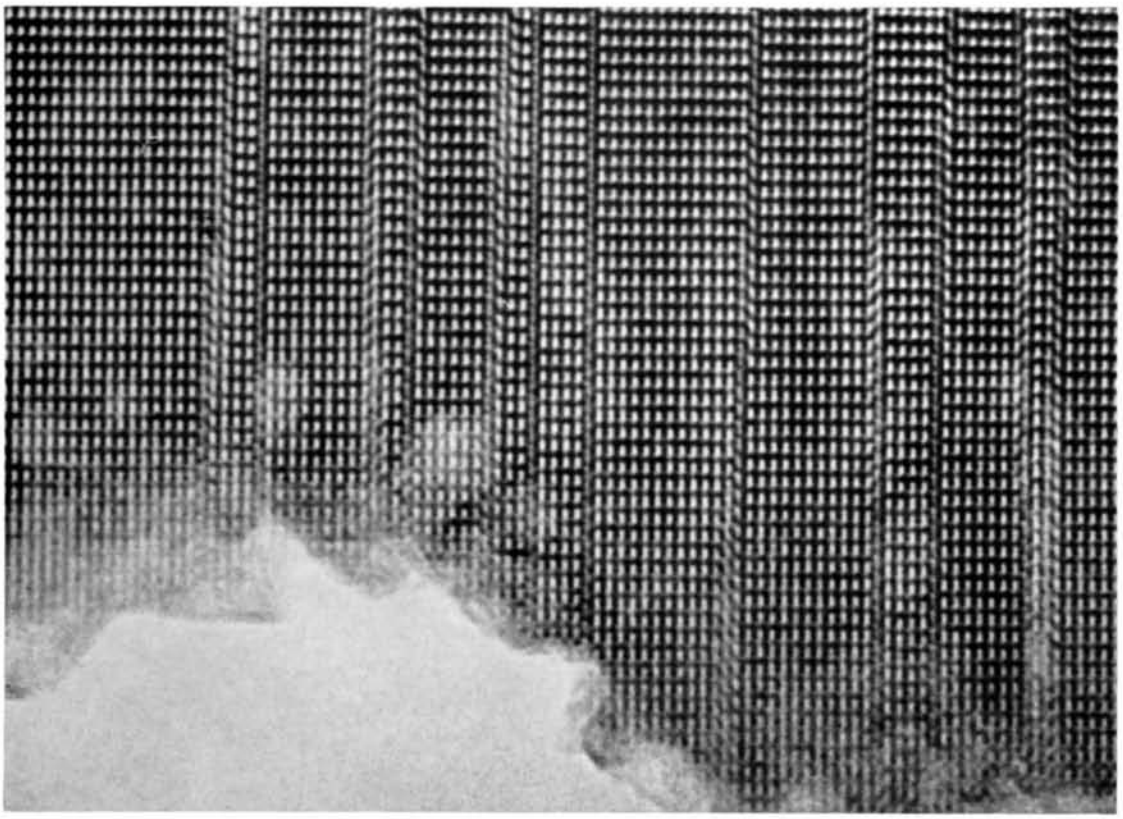

Fig. 3. Electron micrograph of a thin crystal of magnesium fluorogermanate obtained with the beam parallel to the [110] direction, showing the planar faults perpendicular to the *c* axis. The magnification can be deduced from the periodicity $c = 5{\cdot}91$ Å, clearly seen between the faults.

[*To face p.* 88

The proposed form for the planar faults was subsequently confirmed by the high-resolution electron micrographs of thin crystals obtained by Sumio Iijima using the modified JEM-100B electron microscope (Iijima, 1971; Cowley & Iijima, 1975). Fig. 3, for example, shows clearly the contraction of the unit cells at the fault planes and the translation of the lattice across the faults. Electron micrographs of crystals in this and other orientations showed a variety of faults, out-of-phase domain configurations and so on, which will be the subject of a future publication.

3. Dynamical diffraction effects

It is well known that the intensities of electron diffraction patterns are strongly affected by *n*-beam dynamical diffraction. Intensities of reflections vary rapidly and, seemingly, erratically with crystal thickness and orientation and can be calculated and interpreted only under special conditions for which values of these variables are well defined (Cowley, 1969). The assumption that intensity variations in electron diffraction patterns can be interpreted in terms of fault configurations as if the diffraction process were kinematical therefore needs to be justified. In the present case a justification can be given within definable limitations.

When sharp streaks due to planar faults appear in electron diffraction patterns from thin crystals, the incident electron beam is very nearly parallel to the fault planes, as suggested in Fig. 4. The wave function at the exit face of the crystal is given with good accuracy, by applying the 'column approximation'. For 100 keV electrons and crystals a few hundred Å thick, the wave function at any point of the exit surface is determined by the content of the column of crystal above it and the diameter of this column is 5 to 10 Å. For regions between faults, the exit wave function will have the periodicity and symmetry of the projection of the crystal lattice and will give contributions to the diffraction amplitudes described by the structure amplitudes $F(\mathbf{u})$, given by Fourier transform of the wave function within one periodicity and so a continuous function of the reciprocal-space vector **u**. For very weak scattering these will be the kinematical structure amplitudes $F_k(\mathbf{u})$. For stronger scattering these will be dynamical scattering amplitudes, $F_d(\mathbf{u})$. At the positions of the faults, the perturbation of the periodicity will extend over a region of width 5 to 10 Å at most. The perturbed regions will contribute kinematical or dynamical contributions, $G_k(\mathbf{u})$ or $G_d(\mathbf{u})$, to the diffraction amplitudes.

If the average separation of faults is much greater than 10 Å, the contributions from the fault regions can be neglected, particularly in the light of the results obtained below. The main features of the diffraction pattern will be determined by the distribution of faults and the nature of the discontinuities of the lattice at the faults and may be described by a distribution function $D(\mathbf{r})$ or its Fourier transform $D(\mathbf{u})$. Then it can be shown readily that the intensity in the diffraction pattern may be written

$$I(\mathbf{u}) = |F(\mathbf{u})|^2 \,.\, \mathbf{D}(\mathbf{u}) \,. \qquad (1)$$

The function $D(\mathbf{u})$ derives from the deviations from periodicity of the array of unit cells, *i.e.*, it depends on the relationships of vectors which are of greater magnitude than the unit-cell dimensions, and therefore $D(\mathbf{u})$ will determine the fine-scale intensity distribution about the reciprocal-lattice points.

The function $|F(\mathbf{u})|^2$, will vary slowly compared with the reciprocal-lattice dimensions since it is given by Fourier transform of the wave-function fluctuations within a unit cell. The differences between $F_k(\mathbf{u})$ and $F_d(\mathbf{u})$ will therefore affect the relative intensities of the various diffraction maxima but not the shapes or displacements of the maxima or the form of the streaking.

It may be concluded that, for cases such as this, the presence of dynamical diffraction effects will not falsify deductions made using kinematical theory to interpret the form of the streaking and the broadening and displacement of the peaks. It will complicate deductions regarding the arrangement of atoms in the unfaulted or faulted regions.

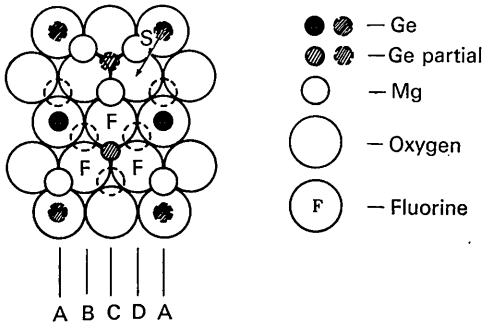

Fig. 2. Diagram of the structure of magnesium fluorogermanate (Bless *et al.*, 1972) indicating the four planes of cations, labelled *A*, *B*, *C*, *D*.

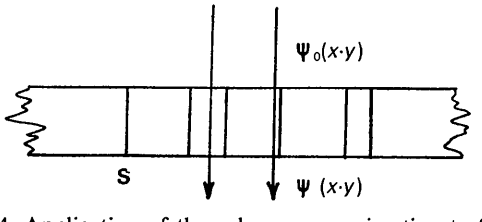

Fig. 4. Application of the column approximation to formulation of the scattering equation for a thin crystal having faults parallel to the beam direction.

4. Kinematical intensity expressions

It was shown in part I that the intensity of diffraction as a function of the reciprocal-space vector **u**, is given for this type of faulting situation as

$$I(\mathbf{u})/N=\alpha(1-\alpha)\,[|F|^2(1-\cos 2\pi\mathbf{u}\,.\,\mathbf{S})$$
$$+(\mathrm{Re}\,F^*G)\,\{1+\cos 2\pi\mathbf{u}\,.\,(\mathbf{R}+\mathbf{S})$$
$$-\cos 2\pi\mathbf{u}\,.\,\mathbf{R}-\cos 2\pi\mathbf{u}\,.\,\mathbf{S}\}$$
$$-(\mathrm{Im}\,F^*G)\,\{\sin 2\pi\mathbf{u}\,.\,\mathbf{R}$$
$$+(1-2\alpha)\sin 2\pi\mathbf{u}\,.\,\mathbf{S}-\sin 2\pi\mathbf{u}\,.\,(\mathbf{R}+\mathbf{S})\}$$
$$+|G|^2(1-\cos 2\pi\mathbf{u}\,.\,\mathbf{R})]$$
$$\times[1-\alpha+\alpha^2-(1-\alpha)\cos 2\pi\mathbf{u}\,.\,\mathbf{R}$$
$$-\alpha\cos 2\pi\mathbf{u}\,.\,(\mathbf{R}+\mathbf{S})+\alpha(1-\alpha)\cos 2\pi\mathbf{u}\,.\,\mathbf{S}]^{-1}, \quad (2)$$

where $F(\mathbf{u})$ is the structure amplitude for the normal layer which has translation vector $\mathbf{R}$ and $G(\mathbf{u})$ is the Fourier transform of the addition to the scattering function at the fault. The faults occur with a probability α and involve a shift in the unit-cell origin by a vector $\mathbf{S}$.

For the case of magnesium fluorogermanate, we may ignore the oxygen–fluorine contributions entirely, take the origin of the unit cell at some convenient point in the C layer and write

$$F(\mathbf{u})=F_C+2F_B\cos 2\pi\mathbf{u}\,.\,(\mathbf{R}/4)+F_A\cos 2\pi\mathbf{u}\,.\,(\mathbf{R}/2),$$
$$G(\mathbf{u})=F_A[\exp\{2\pi i\mathbf{u}\,.\,(\mathbf{R}/4)\}-\exp\{2\pi i\mathbf{u}\,.\,(\mathbf{R}/2)\}]$$
$$+F_B[1-\exp\{2\pi i\mathbf{u}\,.\,(\mathbf{R}/4)\}]-F_C\,, \quad (3)$$

where F_A, $F_B(=F_D)$ and F_C are the structure amplitudes for the A,B,C layers indicated in Fig. 2.

For convenience we deal only with the $00l$ line in reciprocal space and calculate intensities as a function of the continuous variable l. Then $\mathbf{u}\,.\,\mathbf{R}=l$ and $\mathbf{S}=-\mathbf{R}/4$. Since we will not be concerned with accurate intensity values but only the form of the intensity distribution, we make the approximation $f_{\mathrm{Ge}}=2f_{\mathrm{Mg}}\equiv 2f_{\mathrm{M}}$. Then

$$F(l)=8f_{\mathrm{M}}[1+r+2\cos\pi(l/2)+2\cos\pi l],$$
$$G(l)=-8f_{\mathrm{M}}[r+\cos\pi l-i\sin\pi l], \quad (4)$$

where r is the occupancy factor for the germanium sites in the C layer.

With this simplified model, the curves of Fig. 5 were calculated. Fig. 5(*a*) shows the form of the $D(\mathbf{u})$ function of (1), calculated for $G=0$ and $\alpha=0{\cdot}2$. This is seen to represent the general form of the scattering well, with the 001 reflection broadened and displaced outwards, and the 002 reflection broadened twice as much but not displaced. Figs. 5(*b*) and 5(*c*) were calculated for the more extreme case of $\alpha=0{\cdot}3$, with $r=0{\cdot}5$ and 0·35 respectively. In each case the intensity calculated from the full expression (2) is compared with that calculated for $G=0$. The overall decrease of intensities with l due to the form of f_{M} has not been included.

5. Conclusions

Comparison of the calculated curves, Fig. 5, shows agreement with the observations such as Fig. 1. For the particular pattern, Fig. 1, the displacements and widths of the peaks suggest a value $\alpha\simeq 0{\cdot}2$. However, other patterns from material of the same nominal composition showed a wide range of apparent α values, usually smaller than this. The X-ray diffraction patterns used by Bless *et al.* (1972) for their structure analysis showed no signs of streaks or peak displacements (E. Kostiner, private communication). These authors did report the existence of the very weak k-odd reflections, visible in Fig. 1, which suggest a violation of the glide-plane symmetry, presumably associated with the partial occupancy of the Ge positions.

From Fig. 5(*b*) and (*c*) it is seen that the relative intensities of the 001 and 002 reflections depend strongly on the occupancy factor r. Although the intensities of Fig. 1 are strongly affected by dynamical diffraction, the fact that the 002 is consistently equal to or less than the 001 and 003 reflections in intensity favors an r value of 0·35 or less.

The comparison of curves calculated with and without the G contributions suggests that even for the very high value of $\alpha=0{\cdot}3$, the contribution of the modification of structure at the fault to the peak intensities is very small, although away from the peaks the relative

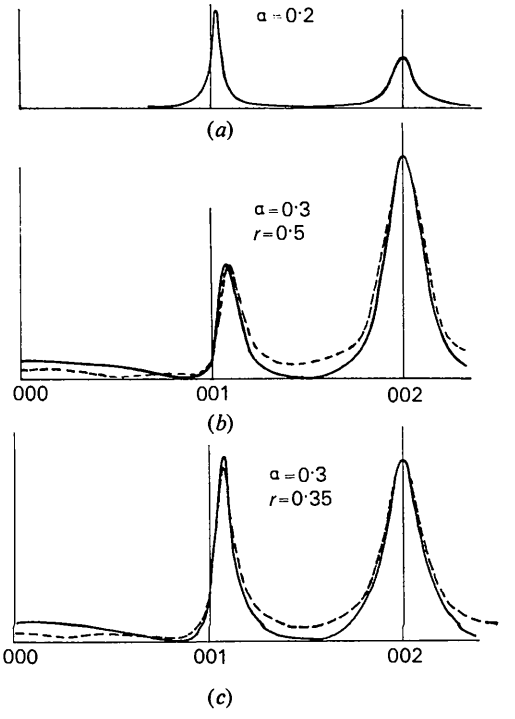

Fig. 5. Calculated variation of intensity along the $00l$ line for magnesium fluorogermanate, ignoring the f^2 decrease in intensity with scattering angle. (*a*) The function $D(\mathbf{u})$ of equation (1) with $\alpha=0{\cdot}2$. (*b*) Calculated intensities for $\alpha=0{\cdot}3$ and occupancy factor $r=0{\cdot}50$ for the germanium sites in the C layer. (*c*) Calculate intensities for $\alpha=0{\cdot}3$, $r=0{\cdot}35$. In (*b*) and (*c*) the full curves are drawn on the assumption that there is no modification of the structure at the faults, *i.e.* $G=0$. The dotted curves are drawn assuming the form of $G(l)$ given in equation (4).

contribution of G to the intensities may be very large. This follows because in the expression (2), the factors which multiply $|G|^2$, (Re $F * G$) and (Im $F * G$) all vanish for $\mathbf{u} \cdot \mathbf{R}$ integral, *i.e.* at the reciprocal-lattice points for the unfaulted structure. The peak intensities can be modified by the factors dependent on G only to the extent that the peaks are displaced or extended away from the reciprocal-lattice points into the region for which these multipliers are non-zero. Since both the peak widths and their displacements are roughly proportional to α it is seen that the contribution of G to the peak intensities may also be roughly proportional to α but will be negligibly small except for very large α values.

Hence the 'intuitively obvious' conclusion that the structure amplitudes for the unit cell will be modified from F to $F+\alpha G$ is shown to be false. In the particular case of magnesium fluorogermanate, the existence of faults of the type discussed should not make any appreciable difference to the value of the occupancy factor r for the Ge sites deduced from the structure analysis.

It is seen from equation (2) and Fig. 5 that information regarding the nature of the modification of the structure at the fault planes can, in principle, be obtained from the diffraction pattern but this would involve the careful measurement and interpretation of the intensities of the weak streaks between the main intensity maxima.

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A Probabilistic Theory of the Cosine Invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$

BY C. GIACOVAZZO

Istituto di Mineralogia e Petrografia, Università di Bari, Italy

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A conditional joint probability distribution is derived in order to estimate the values of the cosine invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ in terms of the magnitudes of $E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{h}+\mathbf{l}}, E_{\mathbf{k}+\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$. The theory leads to values for the cosines which lie anywhere between -1 and $+1$. Some applications of the quartets in procedures for crystal structure determination are described.

I. Derivation of the theory

I.1 *Introduction*

The significance in direct methods of phase determination of the cosine invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ has been stressed in several recent papers.

Starting from semi-empirical observations of Schenk (1973*a*), Hauptman (1974*a*) has developed in $P1$ a probabilistic theory of this cosine invariant which is valid under the assumption that $|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$ are sufficiently small. In particular he derived the negative cosine invariant expression

$$\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}) \simeq -\frac{I_1(B)}{I_0(B)},$$

where $B=2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|/N$. For large values of B this formula gives, in contrast to the estimate for $\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}-\varphi_{\mathbf{h}_1+\mathbf{h}_2})$,

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}} \simeq \pi .$$

A more general probabilistic theory of the invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$, subject to no restrictive conditions, has been given by Hauptman (1974*b*). The theory leads to estimates for the value of the cosine which may lie anywhere between -1 and $+1$. In that paper the joint conditional probability distribution of the pair $\varphi_{\mathbf{k}}, \varphi_{\mathbf{h}_1+\mathbf{k}}$ given $|E_{-\mathbf{h}_3+\mathbf{k}}|, |E_{\mathbf{k}}|, |E_{\mathbf{h}_1+\mathbf{k}}|$ and for fixed $\mathbf{h}_1$ and $\mathbf{h}_3$ was inspected. The vector $\mathbf{k}$ is the sole random variable, which is supposed uniformly distributed over reciprocal space. Hauptman's results seem satisfactory, but the final formulae are rather difficult to deal with.

Independently, Giacovazzo (1975*a*) derived in $P\bar{1}$ probabilistic formulae for $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$.