Crystallographic Phase Determination from Dark-Field Electron-Microscope Moiré Patterns

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A proposal is made for a direct experimental method to determine the phases of crystallographic structure factors. The method is based on the observation of electron-microscope dark-field moiré patterns. The kinematical theory of electron diffraction is used in the presentation of the method. Compensation of dynamical effects and instrumental aberrations is briefly discussed.

Introduction

The outstanding problem in crystallography is still that of determining the phases of the diffracted beams in a diffraction experiment. Only the amplitudes of such beams can normally be recorded, and thus only the amplitudes of the Fourier coefficients of the scattering potential can be determined. It is therefore not possible to reconstruct, in a direct way, the spatial distribution of the scattering potential in the crystal, which would be equivalent to determining the structure un-ambiguously. A very large number of structures have, of course, been solved, with a number of different methods for phase assignment. These include the direct methods derived from mathematical properties of Fourier series, Patterson-function methods, iso-morphous replacement, anomalous dispersion, and simple trial and error [see, for example, Lipson & Cochran (1966) and the references cited therein]. In addition, Hoppe (1969*a*,*b*) and Hoppe & Strube (1969), have described a method by which phases could be determined if the primary beam in an electron diffraction experiment has an inhomogeneous intensity distri-bution. This could be obtained, for instance, by using suitable apertures in the illuminating system. A similar idea is the basis for Cotterill, Gerward & Lindegaard-Andersen's (1978) proposal for phase determination with a modified X-ray interferometer technique.

Another approach to direct experimental phase determination is to exploit interference effects. Par-ticularly promising is the very direct approach of multiple-beam lattice imaging with electron microscopy [see, for example, Allpress & Sanders (1973) and the references cited therein]. It should be emphasized, how-ever, that with present-day electron-microscope resolution (approximately 1 Å) fine detail cannot be obtained. In fact, the most fruitful work in this field has been performed on crystals with rather large unit cells, where the observed details have been groups of a few atoms within the unit cell. Improvements in resolution,

on the other hand, could ultimately lead to direct observation of the positions of single atoms within the unit cell by this technique.

Another interference effect which is commonly observed in electron microscopy and which could be used for phase determination is the moiré effect. These patterns were obtained several years before lattice images were observed, and they have been used to a certain extent in the study of crystal defects (Bassett, Menter & Pashley, 1958). The possibility of extracting phase information from moiré patterns does not seem to have attracted much attention. Almost twenty years ago Cowley & Moodie (1959) pointed out the possibility of obtaining the Patterson function of the potential distribution from moiré patterns, but of course this does not give direct phase information. They pointed out that a moiré pattern produced by over-lapping thin crystals yields information on the convolu-tion of the projections of the potential distributions of the two crystals. But this still leaves the unknown potential distribution to be calculated and the structure to be solved.

In this communication a direct experimental method is presented for obtaining the phases of diffracted electron beams. It is based on the observation of dark-field moiré patterns, and it deals with the diffracted beams of different order separately in the recording process. The method is described in terms of the kine-matical theory of diffraction in thin crystals. Dynamical effects are briefly discussed together with other detri-mental effects.

1. Kinematical theory of moiré patterns

1.1 *Phase relations for collinear vectors*

The kinematical theory of electron diffraction pre-dicts the amplitudes and phases of diffracted beams from a crystal illuminated by an incoming beam. A

simple derivation has been presented by Howie (1971). Let the wave function of the incoming beam be

$$\psi_0 = \psi_0 \exp(i\mathbf{k}_0 . \mathbf{r}) \tag{1}$$

and let the crystal have thickness t and the electrostatic potential

$$V(\mathbf{r}) = \sum_g V_g \exp(i g \cdot \mathbf{r}) \tag{2}$$

where the sum is extended to all reciprocal-lattice vectors g. The Fourier coefficients V_g are complex numbers so that

$$V_g = |V_g| \exp(i\alpha_g) \tag{3}$$

where α_g are the desired phases.

The diffracted beams emerging from the crystal are described by the wave functions

$$\psi_g = \psi_0 \frac{i\pi}{\xi_g} \frac{\sin(\frac{1}{2}ts_g)}{\frac{1}{2}s_g} \exp(-\frac{1}{2}its_g)$$

$$\times \exp[i(\mathbf{k}_0 + g + s_g) . \mathbf{r}] \tag{4}$$

where

$$\xi_g = \frac{2\pi h^2 k_0}{2meV_g} \tag{5}$$

$$k_0 = |\mathbf{k}_0|, s_g = |\mathbf{s}_g|. \tag{6}$$

The deviation vectors $\mathbf{s}_g$ are parallel to $\mathbf{k}_0$, and they are subject to the condition

$$|\mathbf{k}_0 + g + \mathbf{s}_g| = k_0. \tag{7}$$

The correction of the effect of the excitation errors s_g is discussed later. For the time being it will be assumed that the s_g for the different diffracted beams are either zero or infinite. We then have to deal only with the diffraction vectors g for which s_g is zero, and the corresponding excited beams. For these, (4) and (5) lead to

$$\psi_g = i\psi_0 CV_g \exp[i(\mathbf{k}_0 + g).\mathbf{r}] \tag{8}$$

where C is a real constant.

Now let two crystals, designated (I) and (II), overlap and suppose that the beam passes first through (I) and then through (II), the latter being a crystal of known structure. In crystal (I) beams with diffraction vector g_I and all integer multiples of g_I are excited. In crystal (II) the same applies for a diffraction vector g_{II}. g_I and g_{II} must be almost identical, that is

$$0 < |g_I - g_{II}| \ll |g_I|. \tag{9}$$

For (9) to be fulfilled g_I and g_{II} must be almost equal. The double layer gives rise to beams diffracted once and twice; these are conveniently described with a double-index notation n_1, n_2 so that ψ_{n_1,n_2} is the beam diffracted by $n_1 g_I$ and thereafter by $n_2 g_{II}$. If either n_1 or n_2 equals zero, no diffraction of the beam occurs in the corresponding crystal. It is assumed that neither the

singly diffracted beams nor the doubly diffracted beams suffer any excitation errors. Then by (8), and taking the constant C to be identical for the two crystals, one obtains

$$\psi_{n_1,0} = \psi_0 i C V_{n_1 g_I} \exp[i(\mathbf{k}_0 + n_1 g_I).\mathbf{r}] \tag{10}$$

$$\psi_{0,n_2} = \psi_0 i C V_{n_2 g_{II}} \exp[i(\mathbf{k}_0 + n_2 g_{II}).\mathbf{r}] \tag{11}$$

$$\psi_{n_1,n_2} = -\psi_0 C^2 V_{n_1 g_I} V_{n_2 g_{II}}$$

$$\times \exp[i(\mathbf{k}_0 + n_1 g_I + n_2 g_{II}).\mathbf{r}]. \tag{12}$$

For the intensity in a dark-field moiré pattern formed with contributions from only $\psi_{n,0}$ and $\psi_{n-1,1}$ one obtains

$$I(\mathbf{r}) = |\psi_{n,0} + \psi_{n-1,1}|^2$$

$$= |\psi_{n,0}|^2 + |\psi_{n-1,1}|^2 + 2 \operatorname{Re}(\psi_{n,0}^* \psi_{n-1,1}), \tag{13}$$

Re designating 'real part of', as usual. Only the last term in this expression is of interest here, the other two terms being constant.

For $n > 1$ one obtains

$$2\operatorname{Re}(\psi_{n,0}^* \psi_{n-1,1}) = 2\operatorname{Re}\left(\psi_0^2 C^3 |V_{ng_I}| |V_{(n-1)g_I}| |V_{g_{II}}|\right.$$

$$\times \exp\left\{-i(\mathbf{k}_0 + ng_I).\mathbf{r} - i\left(\frac{\pi}{2} + \alpha_{ng_I}\right)\right.$$

$$+ i[\mathbf{k}_0 + (n-1)g_I + g_{II}].\mathbf{r}$$

$$\left.\left.+ i[\pi + \alpha_{(n-1)g_I} + \alpha_{g_{II}}]\right\}\right) \tag{14}$$

$$= K \cos\left[(g_{II} - g_I).\mathbf{r} + \frac{\pi}{2}\right.$$

$$\left.+ \alpha_{g_{II}} + \alpha_{(n-1)g_I} - \alpha_{ng_I}\right].$$

The positions $\mathbf{r}_n$ of the maxima in (14) are determined by

$$(g_{II} - g_I).\mathbf{r}_n + \frac{\pi}{2} + \alpha_{g_{II}} + \alpha_{(n-1)g_I} - \alpha_{ng_I} = 2p\pi. \tag{15}$$

For $n = 1$ the moiré pattern is created by interference of singly diffracted beams and (15) is modified to

$$(g_{II} - g_I).\mathbf{r}_1 + \alpha_{g_{II}} - \alpha_{g_I} = 2p\pi. \tag{16}$$

Introducing $\Delta g = g_{II} - g_I$ and subtracting (16) from (15) one obtains

$$\alpha_{ng_I} = \Delta g . (\mathbf{r}_n - \mathbf{r}_1) + \frac{\pi}{2} + \alpha_{(n-1)g_I} + \alpha_{g_I}(+2p\pi). \tag{17}$$

From (17) it is apparent that by measuring the displacements $(\mathbf{r}_n - \mathbf{r}_1)$ of the points of maximum intensity of different orders of dark-field moiré patterns one can obtain the phases α_{ng_I} if α_{g_I} is known. The

displacements can be measured by referring the individual moiré patterns to some fixed points; for instance, some inclusion or hole. It should be borne in mind that Δg might correspond to fringe spacings larger than say 100 Å.

In principle, therefore, all the phases $\alpha_{n g_L}$ can be determined if α_{g_I} is known. In the Appendix it is shown that three α_g corresponding to non-parallel reciprocal vectors can be arbitrarily set to zero and that thereafter all the phases are fixed. One has a method, therefore, of establishing phase relations between Fourier coefficients corresponding to collinear reciprocal vectors.

1.2. *Phase relations for coplanar vectors*

Let g_I, g'_I, and g''_I be three coplanar reciprocal vectors in the unknown crystal (I), and let g_{II}, g'_{II}, and g''_{II} be three coplanar reciprocal vectors in the known crystal (II) each fulfilling conditions like (9) with one of the reciprocal vectors in crystal (I). When moiré patterns are obtained from diffraction in g_I and g_{II}, from g'_I and g'_{II} and from g''_I and g''_{II}, the positions of maximum intensity are r_1, r'_1, and r''_1, respectively, and these fulfil (16).

As the structure of crystal (II) is known, sets of values of the phases $\alpha_{g_{II}}$, $\alpha_{g'_{II}}$, and $\alpha_{g''_{II}}$ are available. The origin of the coordinate system is now chosen to lie close to some fixed point so that the above-mentioned phases have values corresponding to some convenient consistent set of phases for structure (II); see the Appendix. The distance from the fixed point to the origin of the coordinate system need not be larger than the maximum dimension of the unit cell in crystal (II), and it is thus negligible compared with the fringe spacing in the moiré patterns. Therefore, members of a consistent set of phases $\alpha_{g_I}, \alpha_{g'_I}$ and $\alpha_{g''_I}$ can be obtained without appreciable error from the three equations of type (16), with r_1, r'_1, and r''_1 as vectors not from the origin of the coordinate system but from the fixed point. If α_{g_I} and $\alpha_{g''_I}$, say, are known in advance, either because they have been set at zero as members of the set of three phases that can be arbitrarily assigned, or from a similar calculation, the translation vector Δr in ($A3$) of the Appendix can be calculated, and a new consistent value of α_{g_I} emerges. With a known structure used as reference, therefore, a consistent set of phases of the Fourier coefficients corresponding to fundamental reciprocal vectors can be obtained. The word 'fundamental' is used here in the sense of 'shortest in a collinear set'.

1.3. *Phase relations for arbitrary vectors*

An arbitrary diffraction vector can be considered coplanar with a diffraction vector, the phase of which has been arbitrarily assigned, and another diffraction vector in the plane extended by the two remaining diffraction vectors, the phases of which were arbitrarily assigned. Thus, the phases of vectors with arbitrary orientation with respect to the three vectors, the phases of which were arbitrarily assigned, can be determined.

2. Validity of approximations

In the preceding sections a number of approximations have been involved, explicitly or implicitly. The nature of the approximations can conveniently be classified according to whether they concern the diffraction process or the imaging in the instrument.

2.1. *Approximations regarding the diffraction process*

The kinematical theory is in itself an approximate theory but an extra approximation has been involved, namely that of no excitation errors. As seen in (4), excitation errors in the kinematical theory give rise to additional phase shifts, but they can be compensated for by calculation. However, a more systematic approach to the approximations involved in the diffraction process would be to look upon the method described in the previous paragraphs as a means of measuring the actual phases of the diffracted beams at the exit surface of the second crystal. The crystallographic phases would then have to be calculated with dynamical theory. No attempt to solve that formidable problem will be attempted here, but some comments on possible routes to a solution will be given. The converse problem, to calculate the amplitudes and phases of the diffracted beams, has been solved analytically, but not in a closed form, by Cowley & Moodie (1957). An efficient iterative approach, suitable for numerical calculations, has been presented by Goodman & Moodie (1974), and a possible way to obtain the desired crystallographic phases would be to let these be parameters to be optimized in a fit of numerically calculated diffracted beam phases to the measured values. This hardly seems an efficient scheme, and a more attractive method would be to use crystals thin enough for the kinematical theory to be valid. This might require crystals less than say 100 Å thick which are very difficult to manipulate. It might be possible instead to look at differences between the phases of the diffracted beams from crystals with a difference of thickness in that order of magnitude. It should finally be noted that an indication of the significance of dynamical effects in the multi-beam case may be obtained from the dynamical theory of moiré patterns in the two-beam case presented by Hashimoto, Mannami & Naiki (1960) and by Gevers (1962).

2.2. *Approximations regarding the imaging process*

Electron microscopes are not perfect imaging systems; various aberrations set limits to the resolution which can be obtained. Discussions of the resolution limit for electron microscopes are presented by Hirsch, Howie, Nicholson, Pashley & Whelan (1965) and more recently by Hanszen (1971), who uses the theory of transfer functions. The moiré fringe patterns to be observed for determining crystallographic phases can have spacings of several hundred ångstroms, so the method does not depend on very high resolution. However, the same factors that limit resolution and defects of focus introduce phase shifts for the diffracted beams. The phase shifts are known functions of the angle between the optical axis and the diffracted beam.

These angles are in general not the same for the two diffracted beams contributing to a moiré pattern, and therefore errors are introduced if corrections are not performed. As the corrections can easily be calculated, they do not give rise to any problems from the theoretical point of view.

Another approximation about the instrument is that the incoming beam has been considered a plane wave. In fact, the illumination has a finite coherence length (see, for example, Heidenreich, 1964), which must be larger than the fringe spacing for the fringes to be observed. This condition, however, is satisfied if the diffraction spots are distinct. If it is not satisfied, defocusing the illumination or using a smaller condenser aperture is required; unfortunately, both of these measures reduce the intensity.

3. Experimental investigation

In order to test the proposed theory, an investigation of dark-field moiré patterns in talc $[Mg_3Si_4O_{10}(OH)_2]$ was undertaken. This crystal belongs to the monoclinic system and has the space group $C2/c$ (Wyckoff, 1968); the structure thus has a centre of symmetry. Thin flakes of talc were prepared by treating a suspension of talc in alcohol ultrasonically in a commercial cleansing device, and the flakes were then caught on 400-mesh grids. The specimens were examined with a JEM-200 A electron microscope operated at 200 kV.

Rotation dark-field moiré patterns of different orders were obtained with $\mathbf{g}_I = (133)$ and $\mathbf{g}_{II} = (133)$ in two overlapping crystals. The absence of Kikuchi lines in the diffraction pattern (Fig. 1) indicates that the crystals were thin. The dark-field moiré patterns (Figs. 2 and 3) were both obtained with the illumination tilted to bring the contributing diffracted beam to the optical axis of the microscope. The diffraction pattern corresponds to the diffraction condition for the lowest-order moiré pattern. The rotation was very slight and it was impossible to distinguish the splitting of the spots in the diffraction pattern in Fig. 1. As a consequence of this the moiré patterns in Figs. 2 and 3 are the result of interference of $\mathbf{g}_I$ and $\mathbf{g}_{II}$ beams and $2\mathbf{g}_I$ and $2\mathbf{g}_{II}$ beams respectively. The $\mathbf{g}_I + \mathbf{g}_{II}$ beam is of course included in the moiré pattern in Fig. 3, but it is much weaker than either of the $2\mathbf{g}_I$ and $2\mathbf{g}_{II}$ beams. Taking one of the crystals, say the one designated (I), as the known crystal (*i.e.* exploiting the knowledge of the centre of
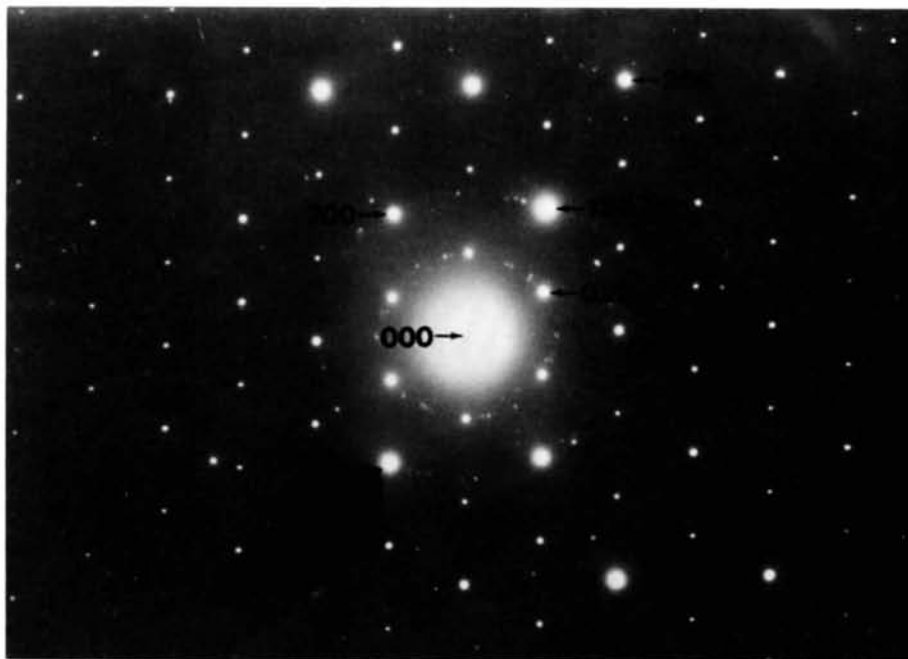

Fig. 1. Indexed diffraction pattern from overlapping talc crystals. The relative rotation of the two crystals can be calculated from the spacing of the moiré pattern in Fig. 2 to be $2 \cdot 3 \times 10^{-3}$ rad ($\sim 7 \cdot 8$ minutes or arc). The splitting of the diffraction spots due to this rotation is imperceptible.

symmetry in this crystal), the phases $\alpha_{\mathbf{g}_j}$ and $\alpha_{2\mathbf{g}_j}$ can be set to zero and zero or π respectively. Then by measuring the displacements of the moiré patterns from Fig. 2 to Fig. 3 the phase $\alpha_{2\mathbf{g}_{11}}$ can be determined when $\alpha_{\mathbf{g}_{11}}$ is set to zero. Fig. 4 clearly demonstrates that the displacements correspond to a phase difference $\alpha_{2\mathbf{g}_1} - \alpha_{2\mathbf{g}_{11}}$ equal to either zero or π because every second moiré fringe in Fig. 3 is coincident with a moiré fringe from Fig. 2. Fig. 4 was obtained by cutting a section from Fig. 3 to obtain edges at a suitable moiré pattern
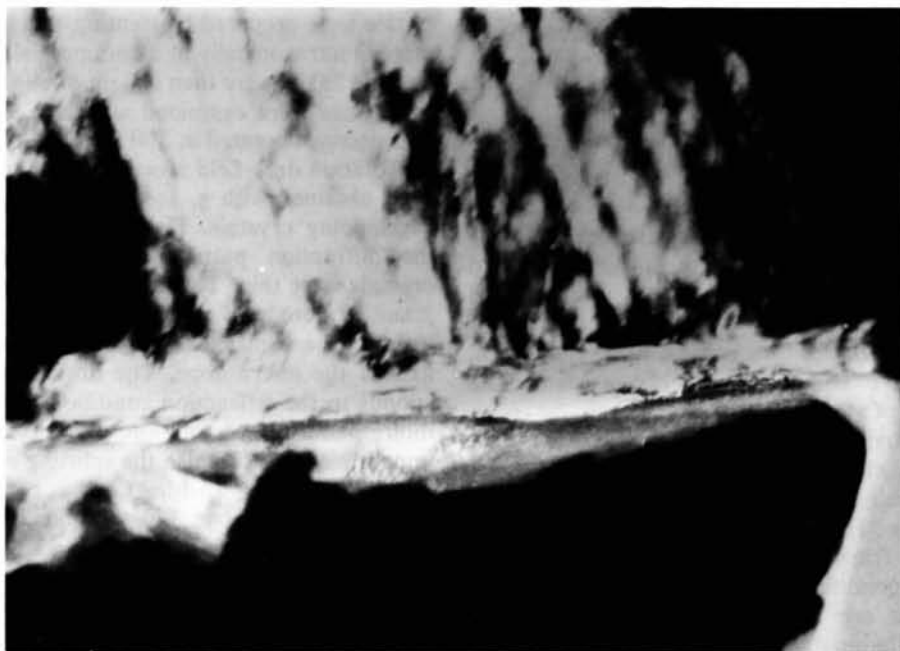

Fig. 2. Dark-field image, corresponding to the 133 reflections, of the area contributing to the diffraction pattern (Fig. 1). Note the widely spaced moiré pattern (spacing ≃ 104 nm).
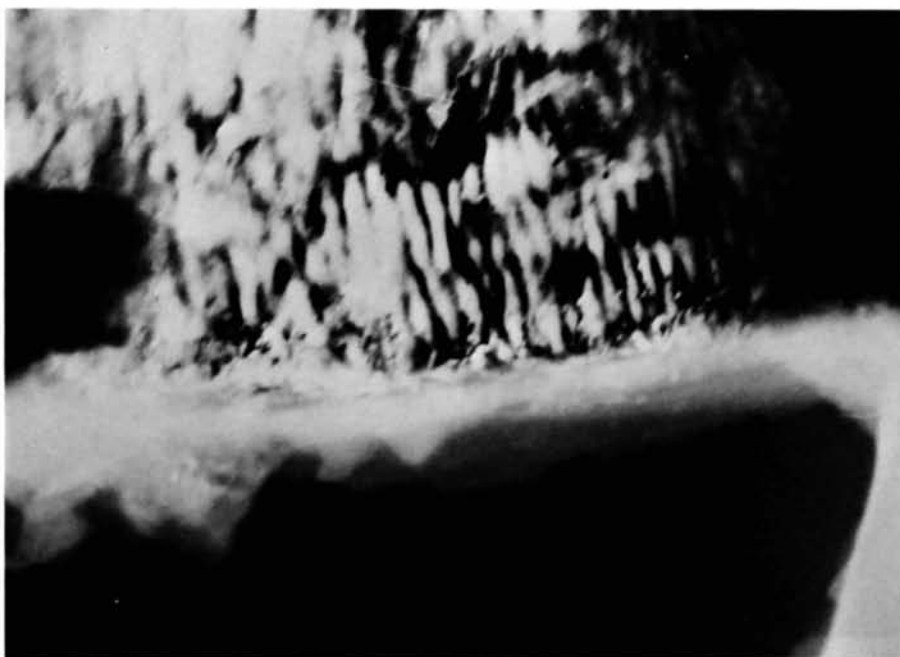

Fig. 3. Dark-field image, corresponding to the 266 reflections, of the same area as seen in Fig. 2 showing moiré pattern with half the spacing seen in Fig. 2 (spacing ∼52 nm).

(arrows marked *M*) and at certain fix points (arrows marked *F*) to assist in the alignment. This section of Fig. 3 was then positioned on Fig. 2, and the composite picture photographed.

What has been done is in effect to measure the phase $\alpha_{2g_{II}}$, which was of course known to be equal to α_{2g_I}, with the choice of α_{g_I} and $\alpha_{g_{II}}$. In the case presented, the result of the measurement is $\alpha_{2g_{II}} = \alpha_{2g_I} + \pi/2 \pm \pi/2$, because of ambiguity of the phase difference being either zero or π. If the moiré pattern resulting from interference between the $2g_I$ and $g_I + g_{II}$ beams had been obtained, this last ambiguity could have been resolved.

Conclusion

A direct experimental method for obtaining the phase of diffracted beams in a diffraction experiment has been presented and an experimental test demonstrating the determination of a known phase has been performed. The method is based on the observation of different orders of dark-field moiré patterns from crystal bilayers consisting of one crystal with known structure and a second crystal the structure of which is to be determined. From a theoretical point of view the phase problem can be considered solvable by this method, although the application of the principle may be quite laborious in the case of structures with large unit cells.

APPENDIX

The lattice potential $V(\mathbf{r})$ has the Fourier expansion

$$V(\mathbf{r}) = \sum_g V_g \exp(i\mathbf{g}\cdot\mathbf{r}) = \sum_g |V_g| \exp[i(\mathbf{g}\cdot\mathbf{r} + \alpha_g)]. \quad (A1)$$

This Fourier series and indeed the function $V(\mathbf{r})$ refer to some choice of origin of the coordinate system and some fixed position of the crystal relative to the origin (positions connected by the space-group symmetry operations are considered to be identical).

If the origin is translated by $\Delta\mathbf{r}$, the potential is described by a new function $V'(\mathbf{r}')$ which is

$$V'(\mathbf{r}') = V(\mathbf{r}' + \Delta\mathbf{r})$$
$$= \sum_g V_g \exp\{i[(\mathbf{r}'+ \Delta\mathbf{r})\cdot\mathbf{g} + \alpha_g]\}. \quad (A2)$$

It is easily seen that the phases are changed to

$$\alpha'_g = \alpha_g + \Delta\mathbf{r}\cdot\mathbf{g}. \quad (A3)$$

Therefore, knowledge of the phase of one Fourier coefficient V_g implies that the origin (or the origin translated by a lattice vector) must lie in a plane normal to $\mathbf{g}$, knowledge of the phases of two coefficients V_{g_1}
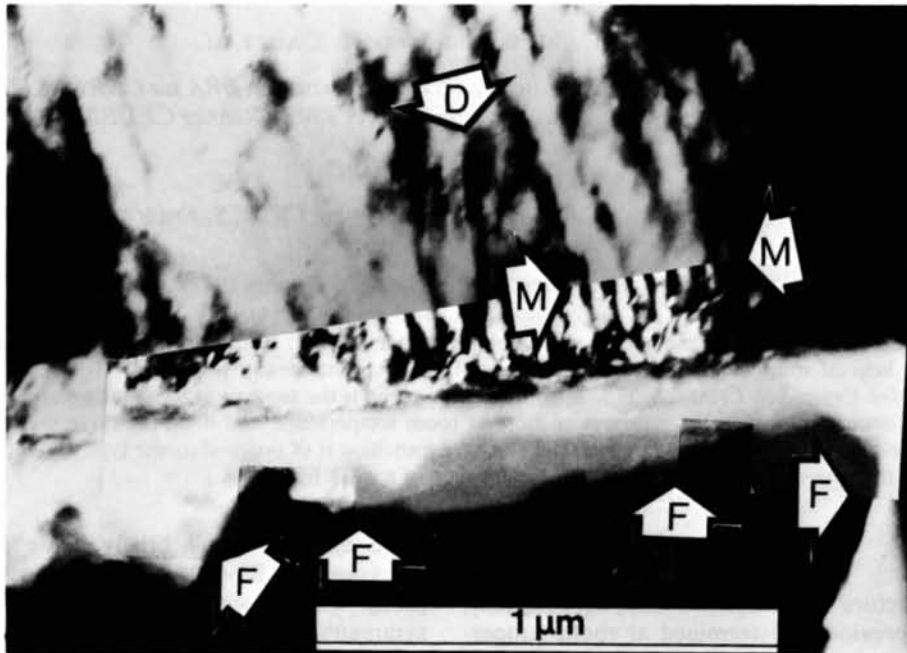

Fig. 4. Part of Fig. 3 superimposed on Fig. 2 with the aid of fiduciary points indicated by arrows marked *F*. Between the arrows marked *M* one sees that every second moiré fringe from Fig. 3 is coincident with a moiré fringe from Fig. 2. The same applies on the other side of the dislocation situated at the arrow marked *D*.

and V_{g_2}, where g_1 and g_2 are non-parallel, implies that the origin (or the origin translated by a lattice vector) is restricted to lie in a line normal to the set of planes defined by g_1 and g_2, and knowledge of the phases of three Fourier coefficients corresponding to non-parallel vectors completely determines the position of the origin (or the origin translated by a lattice vector).

Analogous arguments apply in the case where the lattice is translated by some vector Δr. It can therefore be concluded that when phases are assigned to describe a structure, three of them corresponding to non-parallel vectors can be chosen arbitrarily reflecting the freedom in choice of origin. When this has been done, all the other phases are uniquely determined to be members of a, by definition, consistent set of phases for the structure.

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Order–Disorder Phase Transition in Dichlorodurene

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The structure of dichlorodurene in the ordered phase was determined from neutron diffraction data at 70 K with the help of intra- and intermolecular potential calculations already published [Messager & Sanquer (1974). *Mol. Cryst. Liq. Cryst.* **26**, 373–380]. The space group is the same as at room temperature, $P2_1/a$, but the cell parameters are integer multiples of those at room temperature, and there are three molecules in the asymmetric unit, instead of half a molecule. The phase transition is of order–disorder type and the first-order nature of this transition is established by the observation of a weak hysteresis.

Introduction

The crystal structure of dichlorodurene, $[C_6(CH_3)_4Cl_2]$ or DCD, was previously determined at room temper-

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ature and we recall briefly some important results (Messager & Blot, 1971): DCD crystallizes in space group $P2_1/a$ with two molecules on centres of symmetry in the unit cell of parameters $a = 17.05$ (5), $b = 3.96$ (2), $c = 8.26$ (3) Å, $\beta = 117.5$ (1)°.

Very large thermal-motion parameters and X-ray diffraction observations on equivalent substituents of