

Crystal Structure Analysis from Fine Structure in Electron Diffraction Patterns

BY J. M. COWLEY, P. GOODMAN AND A. L. G. REES

Chemical Physics Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

(Received 6 June 1956)

The fine structure of the electron diffraction spots given by the small cubic crystals of MgO smoke has been studied in detail. The hyperbolic form of the effective 'shape transform' of the dynamic theory has been verified. It is confirmed that the dynamic theory of the fine structure of diffraction spots forms a valid basis for the derivation of structure amplitudes for purposes of structure analysis.

The structure amplitudes, V_{hkl} , for MgO have been derived from the experimental observations and used to calculate a section of the potential distribution in the MgO lattice. The practical possibilities of the use of fine-structure data in the structure analysis of small crystals are discussed.

1. Introduction

The potential distribution within a crystal may be represented by a Fourier series of the form

$$V(x, y, z) = \sum_h \sum_k \sum_l V_{hkl} \exp \{2\pi i(hx + ky + lz)\}.$$

Since the potential, like the electron density, has a well-defined maximum at each atomic position, crystal structure analyses may be performed by summing the Fourier series for the potential distribution instead of that for the electron-density distribution. The magnitudes of the Fourier coefficients, V_{hkl} , may be obtained from the intensities of the electron diffraction spots given by suitable crystals (Cowley, Rees & Spink, 1951) in the same way as the magnitudes of the Fourier coefficients of the electron-density distribution function can be determined by X-ray diffraction. Recently, however, it has been shown that the magnitudes of the V_{hkl} coefficients may be derived without reference to the intensities of reflexions. They may be deduced from measurements of the linear dimensions of the fine-structure detail in diffraction spots given by small crystals of regular habit.

The observation of the fine-structure detail in electron diffraction patterns became possible with the advent of high-resolution instruments. Hillier & Baker (1945) and Sturkey & Frevel (1945) observed a splitting of the rings given by small cube-shaped particles of MgO and CdO. This the latter authors attributed to a refraction effect resulting from the inner potential, V_0 . Cowley & Rees (1946, 1947) and Honjo (1947) showed that individual cubic crystals give reflexions consisting of groups of spots, often in the form of six-pointed stars. Cowley & Rees also showed that the individual refraction components of these stars are frequently doubled as if two values of the inner potential were simultaneously effective. Sturkey (1948) suggested that the appearance of the two values for the inner potential is, in fact, predictable from the dynamic theory of electron diffraction. He showed

that when a crystal is oriented to give the hkl reflexion, the effective inner potential is $V_0 \pm V_{hkl}$, where V_{hkl} is the Fourier coefficient of the potential distribution in the crystal.

The complete dynamical theory of the diffraction of electrons by a finite polyhedral crystal, with the usual assumptions of no absorption and only two strong beams, has been worked out by Kato & Uyeda (1951), Kato (1949, 1952*a*, *b*) and, more recently, Molière & Niehrs (1954). These authors applied their results to the case of cubic MgO crystals and showed that the predictions of the theory are in essential agreement with experimental observations such as those of Honjo & Mihama (1954) and Altenhein & Molière (1954). Procedures for deriving the Fourier coefficients of the potential distribution, V_{hkl} , from the separation of the component spots have been described by Honjo & Mihama (1954) and by Molière & Niehrs (1955). The details of the fine structure may be explained in terms of a combination of refraction effects and a dynamic 'shape transform', resembling, but differing in important respects from, the kinematic shape transform. The kinematic shape transform may be considered as the Fourier transform of a function which is unity within the boundaries of a crystal and zero elsewhere. As a two-dimensional example, Fig. 1(*a*) shows the form of the shape transform of a crystal

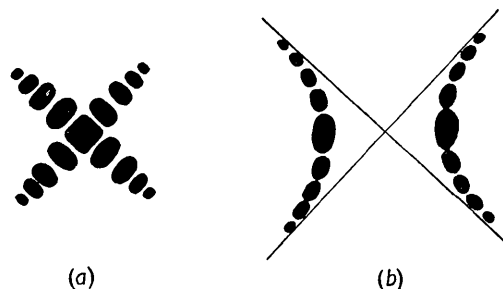


Fig. 1. Sketch illustrating the form of (*a*) the kinematic shape transform and (*b*) the effective dynamic 'shape transform', for a crystal of square cross-section.

of square cross-section (Rees, 1953). The region of scattering power around a reciprocal-lattice point takes the form of a primary maximum surrounded by secondary maxima lying on 'spikes' in directions perpendicular to the crystal faces. Rees & Spink (1950) have observed shape transforms of this type in electron diffraction spots given by zinc oxide smoke particles. In the dynamic theory the region of scattering power about a reciprocal-lattice point is described by what may be called, by analogy, the dynamic shape transform. For a crystal of square cross-section this may take the form shown in Fig. 1(b). The maxima lie along the two branches of a hyperbola with the crystal face normals as asymptotes. This effective shape transform is no longer independent of the crystal structure and the diffraction conditions. The separation of the two branches of the hyperbola depends on the potential coefficients, V_{hkl} , the wave-length of the electrons, and the orientation of the crystal relative to the incident beam.

The dynamic shape transform becomes indistinguishable from the kinematic in the limiting cases of very small V_{hkl} or very small crystal size. For the latter case, Kato (1952b) has calculated the order of magnitude of the crystal size for which the branches of the hyperbola are so blurred that they cannot be distinguished.

During the last five or six years, the present authors have made observations on the MgO fine structure which have paralleled those of the authors quoted above. We have made extensive tests of the predictions of the dynamic theory as to the form of the effective shape transform and have derived the values of V_{hkl} for as many of the reflexions as possible. We have used these values to calculate the potential distribution in one plane of the MgO unit cell.

For the purpose of structure analysis, the derivation of V_{hkl} values from fine-structure measurements may have some advantage over more conventional methods since, at least in principle, measurement of distances can be made more accurate than intensity measurement. In practice the source of data must be governed largely by the morphology of the crystals. For good fine-structure effects the crystals must be of regular habit with sharp edges and dimensions greater than about 500 Å (Kato, 1952b), whereas for single-crystal intensity data the crystals are ideally in the form of thin plates less than about 500 Å thick and of the order of a micron in diameter (Cowley, 1953).

It may be noted that, except in special cases which we do not consider here, when interaction between two or more strong diffracted beams takes place, no information on the phase of the V_{hkl} coefficients can be obtained from fine-structure detail. The distances measured give information on the amplitudes only.

In the present paper our aim is to confirm that the dynamic theory of the fine structure of diffraction spots provides a valid basis for the derivation of structure amplitudes, and to examine the practical

possibilities of the use of fine-structure data in the structure analysis of small crystals.

2. Interpretation of spot group configuration

The individual spots in the spot groups given by small cube-shaped crystals lie on three straight lines each containing four spots, as in Fig. 2(a). The crystal

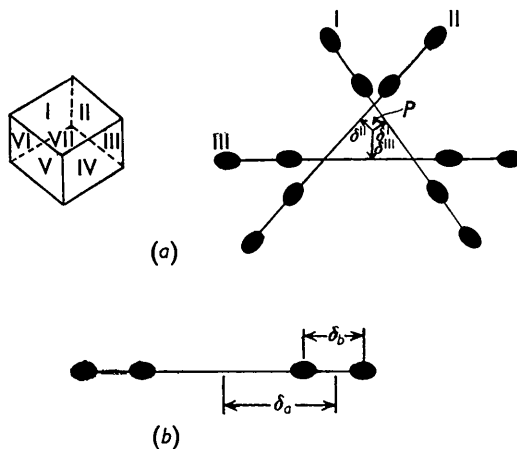


Fig. 2. The fine structure of a diffraction spot given by a cubic crystal. (a) The correlation of spots with crystal regions. (b) The parameters defining spot separations.

may be considered as divided, by planes parallel to the beam direction, into regions corresponding to the possible combinations of entrance and exit faces. Except in the case of very small crystals, these regions may be considered to diffract independently. Each line of spots corresponds to the diffraction in regions of the crystal adjacent to two parallel crystal edges, such as the regions I and IV in Fig. 2(a). In addition, a spot may appear at one of the vertices of the triangle formed by the intersection of the three lines as a result of diffraction in the central region, VII, where the entrance and exit faces of the crystal are parallel. If the crystal is large compared with the mean free path for inelastic scattering of electrons in the crystal, the spot from VII will be extinguished by absorption, and the diffracting regions will be limited to thin strips along the crystal edges. However, the spot positions will not be affected.

The point P , the orthocentre of the triangle formed by the three lines, is the undeflected diffraction spot position. If the Bragg condition for the diffraction is exactly satisfied, the dimensions of the triangle are reduced to zero, and the spot group is centrosymmetric about this point.

In each line of four spots, the separations may be characterized by two parameters δ_a and δ_b , as in Fig. 2(b). The vector displacement δ_a is that given by refraction when the beam passes through two non-parallel crystal faces, and is given by

$$\delta_a = \frac{V_0}{2E} \left(\frac{\mathbf{n}_1}{\cos \varphi_1} + \frac{\mathbf{n}_2}{\cos \varphi_2} \right), \quad (1)$$

where \mathbf{n}_1 and \mathbf{n}_2 are the face normals, φ_1 and φ_2 are the angles made by the beam with these normals, E is the accelerating voltage of the electron beam and V_0 is the mean potential within the crystal. The opposite pair of non-parallel faces gives the deflection $-\delta_a$.

The separation of the spots δ_b arises from the shape transform of the crystal region or its dynamic equivalent. The shape transform given by the kinematic theory takes the form of 'spikes' of scattering power parallel to the face normals. The intersection of the Ewald sphere with a pair of spikes gives a pair of spots with separation proportional to the distance of the Ewald sphere from the reciprocal-lattice point.

In the dynamic theory, as worked out by Kato (1949), the effective 'shape transform' of each region of the crystal takes the form of the two branches of a hyperbola with the normals to the crystal faces as asymptotes, as illustrated in Fig. 3. The vector displacements of the two spots from the refraction spot

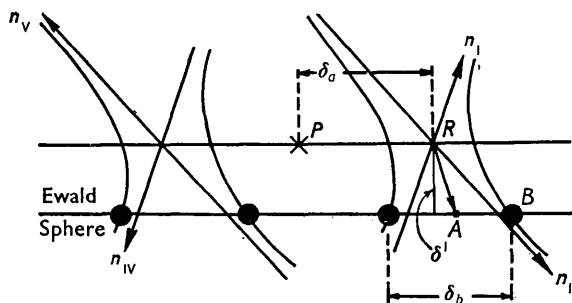


Fig. 3. The intersection of the Ewald sphere with the effective 'shape transform' of the dynamic theory.

position R , are given by

$$\left. \begin{aligned} \delta'_b &= \frac{V_{hkl}}{2E} \left\{ \frac{\mathbf{n}_1}{\cos \varphi_1} [\sqrt{(W^2+1)} - W] \right. \\ &\quad \left. + \frac{\mathbf{n}_2}{\cos \varphi_2} [\sqrt{(W^2+1)} + W] \right\}, \\ \delta''_b &= -\frac{V_{hkl}}{2E} \left\{ \frac{\mathbf{n}_1}{\cos \varphi_1} [\sqrt{(W^2+1)} + W] \right. \\ &\quad \left. + \frac{\mathbf{n}_2}{\cos \varphi_2} [\sqrt{(W^2+1)} - W] \right\}, \end{aligned} \right\} \quad (2)$$

where $W = -2\pi\zeta/\lambda v_{hkl}$ is a convenient variable proportional to the distance ζ of the Ewald sphere from the reciprocal-lattice point, known as the 'excitation error', and $v_{hkl} = V_{hkl} \cdot 8\pi^2 m e / h^2$.

Rearrangement of these equations shows that the vector displacements are made up of hyperbolic and linear components, shown as AB and RA respectively in Fig. 3; thus

$$\delta'_b = \frac{V_{hkl}}{2E} \left\{ \sqrt{(W^2+1)} \left(\frac{\mathbf{n}_1}{\cos \varphi_1} + \frac{\mathbf{n}_2}{\cos \varphi_2} \right) + W \left(\frac{\mathbf{n}_2}{\cos \varphi_2} - \frac{\mathbf{n}_1}{\cos \varphi_1} \right) \right\}. \quad (3)$$

The linear component is the same for all four spots on a line, and so corresponds to a shift of the line as a whole relative to the point P . The separation $\delta_b = |\delta'_b - \delta''_b|$ of the two spots from one shape transform is then given as

$$\delta_b = \frac{V_{hkl}}{E} \sqrt{(W^2+1)} \left| \frac{\mathbf{n}_1}{\cos \varphi_1} + \frac{\mathbf{n}_2}{\cos \varphi_2} \right| = \frac{2V_{hkl}}{V_0} \delta_a \sqrt{(W^2+1)}. \quad (4)$$

Hence the plot of δ_b/δ_a against W is a hyperbola with asymptotes $\delta_b/\delta_a = \pm W \cdot 2V_{hkl}/V_0$. At the Bragg angle, $W = 0$ and $\delta_b/\delta_a = 2V_{hkl}/V_0$. The spot group can then be explained in terms of two values for the apparent inner potential, $V_0 \pm V_{hkl}$.

3. Experimental procedures

Patterns from MgO smoke, collected on a fine wire mesh above magnesium burning in air, have been obtained, using the high-resolution electron diffraction camera described by Cowley & Rees (1953) with accelerating voltages of 40–45 kV.

In order to test the predictions of the dynamic theory as to the hyperbolic shape-transform, it is desirable to record the changes in the configuration of a spot group as the Ewald sphere is swept through the vicinity of a reciprocal-lattice point. Since difficulties of manipulation and observation precluded the setting-up of a particular crystal in a known orientation, it was necessary to make observations on stars in ring patterns, given by crystals fortuitously in suitable orientations, and to deduce the orientations of the crystals from the geometry of the stars.

A large number of series of exposures was made of portions of spotty ring patterns, the specimen being rotated through angles of about 0.2° about an axis perpendicular to the beam between successive exposures of a series. Each series consisted of up to twenty exposures of $\frac{1}{2}$ in. strips on a 10×4 in. photographic plate. For individual spot groups the rotation of the specimen corresponded to changes in excitation error, or W , proportional to the sine of the angle between the axis of tilt and the line joining the spot group to the central spot.

In some series of exposures individual spot groups could be followed through their entire observable range of W . For the best of these the variation of δ_b with W was determined.

The position of a spot group on a diffraction ring gives the orientation of the crystal concerned, except for an azimuthal angle. The azimuthal angle can be

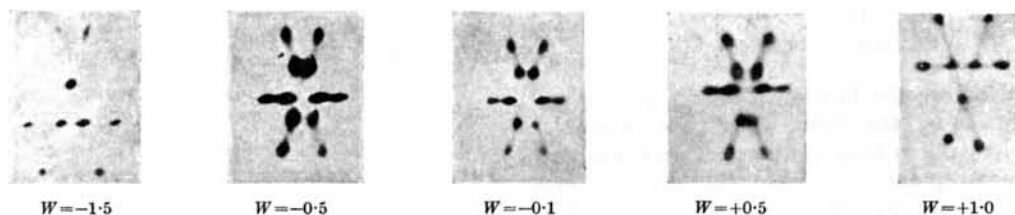


Fig. 4. The changes in configuration of a (220) spot group as the Ewald sphere is swept through the vicinity of a reciprocal-lattice point.

determined from the angles between the three lines of spots forming the group. Hence φ_1 , φ_2 , \mathbf{n}_1 and \mathbf{n}_2 can be derived.

The increments in W between exposures were initially calculated from the rotation of the specimen. This method, however, did not give consistent or reproducible results, presumably because the orientations of the individual crystals were affected by local variations in electrostatic fields or by vibration of the specimen holder. The value of W for each spot group was therefore calculated from the dimensions of the triangle formed by the three lines of spots. The displacements δ^l etc. in Fig. 2(a) are the components, perpendicular to the lines of spots (see Fig. 3), of the linear terms in equation (3). Neither this calculation nor that of the orientation involves any assumption as to the validity or otherwise of the dynamic theory.

If we assume the equations (1) and (4) derived from the dynamic theory to hold, values of V_{hkl} and V_0 may be calculated from the dimensions of the spot groups. From equation (4) it can be seen that V_{hkl} can be calculated most simply and accurately for the case $W = 0$. Where possible, the $W = 0$ orientation was chosen from a series of exposures such as described above. This allowed greater accuracy than the alternative method of choosing the most symmetrical spot groups from a number of unrelated exposures.

Difficulties arise in the case of $h00$ reflexions. For these the electron beam is very nearly parallel to two faces of the cube-shaped crystals, so that only one line of four spots can be observed. The $W = 0$ condition can be recognized only as corresponding to a minimum value of the ratio δ_b/δ_a , and the value of V_0 found from other rings is assumed.

4. Results

Our first step was to test the predictions of the dynamic theory as to the hyperbolic form of the effective shape transform. For a number of spot groups the series of exposures taken with small rotations of the specimen between exposures were sufficiently complete to allow the dependence of the configuration of the group on W to be determined over the complete range of W for which the intensity was appreciable. Of these spot groups several lay on each of the (111), (200), (220) and (222) rings. Incomplete series of exposures corresponding to a limited range of W values have been

obtained for spot groups on other rings. A selection of exposures from a (220) spot-group series is shown in Fig. 4. From such a series it is possible to derive the effective shape transform for each crystal region by plotting the measured values of the spot separation, δ_b , against the value of W derived from the dimensions of the triangle formed by the three lines of spots in the spot group. This has been done, for example, for a (220) star in Fig. 5. For each experimental point

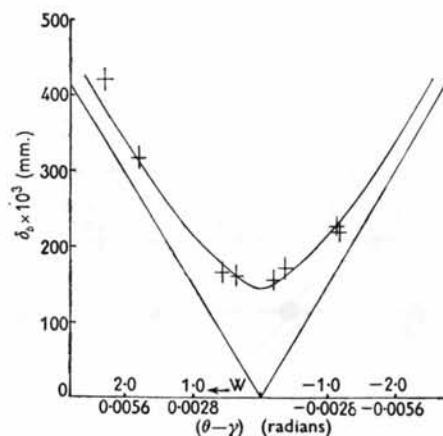


Fig. 5. Experimental values and theoretical curve for the spot separation, δ_b , as a function of W or the angular deviation from the Bragg angle, $(\theta - \gamma)$.

the estimated possible errors in the estimation of δ_b and W are indicated. The continuous hyperbola represents the effective shape transform of the dynamic theory, calculated from equation (4). The pair of straight lines which form the asymptotes of the hyperbola represent the kinematic shape transform. The experimental points are seen to deviate from the hyperbola by less than the estimated error except for one or two for large W values. The conclusion, confirmed by plotting similar graphs for other reflexions, is that the dynamic theory in the approximate form here considered gives an effective shape transform, qualitatively of the correct form and quantitatively at least as accurate as the experimental determinations.

Values of V_0 were calculated from measurements made on a large number of stars, mainly on the (220) and (111) rings, using equation (1). No evidence was found for any significant variation of the value of V_0 with the indices of the diffraction spots.

The values of V_{hkl} were found, by the methods outlined in the preceding section, for all reflexions for which the individual spots could be resolved, i.e., in the present case, all reflexions for which $V_{hkl} > 1$ volt. These include all reflexions with h, k and l even out to the (440), but only the (111) with h, k and l odd. The limited accuracy with which the angles and distances in the individual stars could be measured gave rise to some scatter in the V_{hkl} values. A further cause of error was the assumption that the two-beam approximation to the dynamic theory was valid for all orientations of the crystal. Experience in electron diffraction suggests that for most crystal orientations more than one diffracted beam will have appreciable intensity. The effective value of V_{hkl} will then be modified. The accuracy with which the orientation of the crystal can be deduced from the geometry of the spot group is not sufficient to allow any useful estimation of the magnitude of this effect. However, these contributions from other reflexions will usually be small, and positive or negative with equal frequency. It may therefore be assumed that their effect will average out if a sufficiently large number of independent measurements are made for each V_{hkl} .

Table 1. *Experimental and theoretical values of V_{hkl} for MgO*
(Values in volts)

hkl	Honjo & Mihama (1954)	Molière & Niehrs (1955)	Present authors	Theoretical
000	15.5	15.3 ± 0.2	14.4 ± 0.3	~12
111	1.7	1.25 ± 0.15	1.2 ± 0.2	1.29
200	7.0	7.55 ± 0.2	8.0 ± 0.4	7.58
220	5.5	5.09 ± 0.13	5.3 ± 0.2	5.02
222	4.2	3.5 ± 0.3	3.5 ± 0.2	3.80
400	—	2.6 ± 0.6	2.7 ± 0.4	3.09
420	—	2.4 ± 0.3	2.2 ± 0.15	2.57
422	—	2.0 ± 0.7	1.5 ± 0.2	2.20
440	—	2.1 ± 0.4	1.2 ± 0.2	1.65
442	—	2.0 ± 0.6	—	1.48

In Table 1 our experimental values of V_{hkl} , with indications of their estimated accuracy, are compared with the experimental values of Honjo & Mihama (1954) and of Molière & Niehrs (1955), and theoretical values calculated using the atomic scattering factors (for X-rays) given by Viervoll & Ögrim (1949). Magnesium oxide has a face-centred cubic, rocksalt-type structure with $a = 4.203$ Å. The structure factors are therefore $4(\epsilon_{Mg} + \epsilon_O)$ for h, k and l all even, and $4(\epsilon_{Mg} - \epsilon_O)$ for h, k and l all odd, $\epsilon(\theta)$ being the atomic scattering factor for electrons. The theoretical values have been multiplied by a temperature factor of the form $\exp[-B(\sin^2 \theta)/\lambda^2]$. From the Debye temperature of 660° C. for MgO found by Brill, Hermann & Peters (1948) the value of B was found to be 0.44 Å².

Our value for the inner potential, V_0 , is seen to be appreciably lower than that of the other authors quoted, but still considerably higher than the theo-

retical value of about 12 V. Molière & Niehrs (1955) have quoted theoretical values in this region, and also an unpublished experimental determination of the inner potential of MgO by R. B. Kehoe, who used the 'reflexion' method and obtained a value of 12.7 ± 0.6 V. when he used a decharger as against 15.3 ± 1.2 V. without a decharger. Molière & Niehrs concluded that the difference between their value of over 15 V. and the theoretical value could probably be attributed to the formation of an electrostatic double layer arising from the presence of unidentified structural defects in the surface layers. Our lower experimental value of 14.4 V. could then be considered to correspond to a different set of surface conditions brought about by a slightly different impurity content or by differing conditions of preparation of the crystals. However, definite conclusions on this subject must await further experimental evidence.

Our experimental values for V_{hkl} agree with those of Molière & Niehrs within the limits of the estimated errors except for one or two of the outermost reflexions. Comparison with the theoretical values shows approximate agreement, but the experimental values are seen to decrease more rapidly at higher angles. The effect is that of a higher effective temperature factor than the value of $B = 0.44$ Å² used in the calculation of the theoretical values. A value for B of about 1.0 Å² gives better agreement for the higher-angle reflexions, but increases the differences for the inner reflexions. It does not seem possible that the temperature of the MgO crystals should have been raised by the rather weak electron beams employed by an amount sufficient to increase the temperature factor appreciably. There is, of course, considerable uncertainty in the values of the theoretical structure factors both because the atomic scattering factors for electrons are obtained from formulae known to be approximations, and because of the undetermined effect of the ionization of the atoms. The effect of ionization should be more pronounced for lower angles of scattering and so may lead to discrepancies in the V_{hkl} values for the inner reflexions. It should make little difference, however, to the structure factors for the outer reflexions.

The high value for the effective temperature factor remains unexplained. A more complete investigation of this effect must await the attainment of higher resolving power in the electron diffraction camera.

5. Fourier sections

The number of V_{hkl} values which has been measured is sufficient to give an approximate picture of the potential distribution in the crystal lattice. For example, Fig. 6(a) is a contour map of the potential distribution in the $z = 0$ plane of the MgO unit cell, obtained by performing the summation

$$\sum_h \sum_k \sum_l V_{hkl} \cos 2\pi(hx + ky).$$

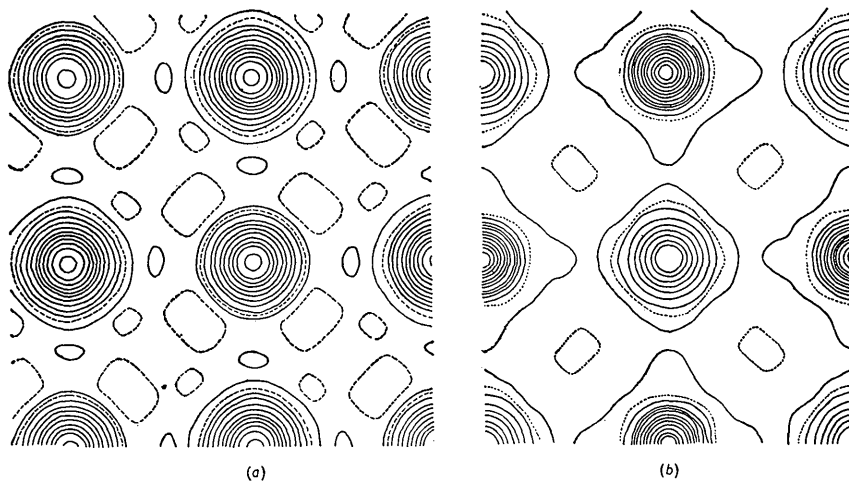


Fig. 6. (a) The $z = 0$ section of the potential distribution in MgO obtained from experimental values of V_{hkl} . (b) The $z = 0$ section of the potential distribution in MgO as for (a), with the estimated contributions of small V_{hkl} values added.

Since only the magnitudes and not the phases of the V_{hkl} coefficients could be obtained from the fine-structure measurements, phases derived from the known structure of MgO were introduced. In this map, the peaks representing the Mg and O atoms are of approximately equal height. This is so because of the omission of all terms with h , k and l odd except the (111). The difference in height of the Mg and O peaks is proportional to the sum of these odd-index terms, whereas the terms for which h , k and l are all even contribute equally to all peaks. A better representation of the potential distribution would be obtained by adding in terms for h , k and l odd. This has been done, assuming the values of V_{hkl} calculated from the theoretical scattering factors, modified by the experimentally determined temperature factor. The $z = 0$ section in Fig. 6(b) was obtained using the V_{hk} for h , k and l values out to $h^2 + k^2 + l^2 = 40$, the V_{hkl} values less than 1 V. being calculated in this way. The peaks corresponding to Mg and O are seen to be more clearly differentiated, the peak heights being very nearly in the ratio 3:2.

6. Discussion

In order to obtain potential maps of MgO of the quality of Fig. 6(b) purely from experimental data, it would be necessary to increase the resolving power of the electron diffraction camera by a factor of three or four. This presents no great difficulty from a constructional point of view, in that lenses of shorter focal length could be used to decrease the effective source diameter. However, in practice, the improvement in resolution is limited by the available intensity. Thus, in order to measure a value of V_{hkl} smaller by a factor s than that now possible, the effective source diameter would be reduced by a factor s and consequently the intensity incident on the crystal would be

reduced by a factor s^2 . The diffracted intensity of the spot, relative to the incident beam would also be less by a factor of s^2 . Hence the exposure time required to record the spot group for measurement would have to be increased by a factor of s^4 . At present the exposure times required to allow measurements of the weaker spot groups are of the order of minutes. It is doubtful whether the stabilities of the specimen and electron beam are sufficient to make much longer exposure times practicable. The principal requirement for the measurement of smaller V_{hkl} values appears to be an electron source of much greater brightness than that now used.

Magnesium oxide is not, however, a particularly suitable substance for the measurement of a large number of potential coefficients. The atomic scattering factors for electrons, and hence the magnitudes of the V_{hkl} , increase almost linearly with the atomic number. Hence a substance containing heavier atoms would give more intense reflexions and larger spot separations. The number of terms in the Fourier summations which could be obtained with existing techniques might then be much greater.

The problems associated with getting a complete set of V_{hkl} values from one crystal appear to be almost insuperable. Apart from the difficulties of observing and manipulating the crystal, the problem arises of making visible the very weak diffracted beams so that the presence of suitable spot groups could be recognized. For the present, then, the spotty ring patterns from polycrystalline material must be used. While this has few disadvantages for crystals of simple structure and high symmetry, such as MgO, ambiguities may arise when the crystal symmetry is lower. It may be difficult, for example, to identify the particular reflexion giving rise to a spot group when several non-equivalent lattice planes have the same, or very nearly the same, d value. For non-cubic crystal habits, the

derivation of the crystal orientation from the angles between the lines of spots in the spot groups may be arduous.

It may be noted that, if spot groups can be obtained for which the Bragg condition is exactly satisfied, the values of V_{hkl} , relative to V_0 , can be derived from equation (4) in the absence of any information as to the habit or orientation of the crystals concerned. In order to obtain the V_{hkl} values on an absolute basis, however, it is necessary to know the angles between the crystal faces and the orientation of the crystal for at least one reflexion. The potential distribution within the crystal lattice may then be determined on an absolute basis except that, until a satisfactory explanation for the discrepancy between the calculated and observed V_0 values and for the variations in the observed V_0 values is found, the potential must be considered uncertain to the extent of a small additive constant.

References

- ALTENHEIN, H. J. & MOLIÈRE, K. (1954). *Z. Phys.* **139**, 103.
 ALTENHEIN, H. J., MOLIÈRE, K. & NIEHRS, H. (1952). *Naturwissenschaften*, **39**, 447.

- BRILL, R., HERMANN, C. & PETERS, CL. (1948). *Z. anorg. Chem.* **257**, 151.
 COWLEY, J. M. (1953). *Acta Cryst.* **6**, 516.
 COWLEY, J. M. & REES, A. L. G. (1946). *Nature, Lond.* **158**, 550.
 COWLEY, J. M. & REES, A. L. G. (1947). *Proc. Phys. Soc.* **59**, 287.
 COWLEY, J. M. & REES, A. L. G. (1953). *J. Sci. Instrum.* **30**, 33.
 COWLEY, J. M., REES, A. L. G. & SPINK, J. A. (1951). *Proc. Phys. Soc. A*, **64**, 609.
 HILLIER, J. & BAKER, R. F. (1945). *Phys. Rev.* **68**, 98.
 HONJO, G. (1947). *J. Phys. Soc., Japan*, **2**, 133.
 HONJO, G. & MIHAMA, K. (1954). *J. Phys. Soc., Japan*, **9**, 184.
 KATO, N. (1949). *Proc. Japan Acad.* **25**, 41.
 KATO, N. (1952a). *J. Phys. Soc., Japan*, **7**, 397.
 KATO, N. (1952b). *J. Phys. Soc., Japan*, **7**, 406.
 KATO, N. & UYEDA, R. (1951). *Acta Cryst.* **4**, 227.
 MOLIÈRE, K. & NIEHRS, H. (1954). *Z. Phys.* **137**, 445.
 MOLIÈRE, K. & NIEHRS, H. (1955). *Z. Phys.* **140**, 581.
 REES, A. L. G. (1953). *J. Proc. Roy. Soc. N. S. W.* **86**, 38.
 REES, A. L. G. & SPINK, J. A. (1950). *Acta Cryst.* **3**, 316.
 STURKEY, L. (1948). *Phys. Rev.* **73**, 183.
 STURKEY, L. & FREVEL, L. K. (1945). *Phys. Rev.* **68**, 56.
 VIERVOLL, H. & ÖGRIM, O. (1949). *Acta Cryst.* **2**, 277.

Acta Cryst. (1957). **10**, 25

Magnetic Anisotropy and Crystal Structure of Barium Chlorate Monohydrate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

BY A. MOOKHERJI

Physics Laboratory, Agra College, Agra, India

(Received 23 November 1955 and in revised form 20 July 1956)

The magnetic anisotropy of single crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ has been measured, and the result has been correlated with the fine-structure study of the crystal by X-ray methods.

Introduction

Raman & Krishnan (1927) have correlated magnetic birefringence, optical and magnetic properties of ions in crystals. Chinchalkar (1932) observed that the magnetic birefringence of the chlorate ion is negative. Representing the gram molecular diamagnetic susceptibility along the directions normal to the plane of the oxygen triangle of the ClO_3 ions by K_{\parallel} and that along directions in the plane of oxygens by K_{\perp} , one finds that K_{\perp} is greater than K_{\parallel} , since $R_c - R_o = -2.12$ for the ClO_3 ion in KClO_3 crystals (*International Critical Tables*, 1926). (R_c is the gram molecular refractivity for the direction normal to the plane of the oxygens, and R_o is that in the plane of the oxygens.)

In the following we correlate our magnetic anisotropy results with the fine-structure analysis of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ by X-ray methods (Karth, 1952).

Experimental and results

The magnetic anisotropy was measured by the method of Krishnan & Banerji (1935). The absolute susceptibility in a convenient direction was measured with a Dutta balance (1944). In order to get information

Table 1. *Measured susceptibilities*

χ_3 is the gram molecular susceptibility along the b crystallographic axis of the monoclinic crystals; the algebraically greater of the two values in the symmetry plane (010) is denoted by χ_1 and the smaller by χ_2 ; φ is the angle which the χ_1 direction makes with the c crystallographic axis, taken positive from c towards a through the obtuse β .

Crystal	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$	φ (°)	$\bar{\chi} =$
	(c.g.s.e.m.u.)	(c.g.s.e.m.u.)		$\frac{1}{3}(\chi_1 + \chi_2 + \chi_3)$ (c.g.s.e.m.u.)
KClO_3	5.41×10^{-6}	5.66×10^{-6}	59.2	-48.7×10^{-6}
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	5.54	0.57	60.9	-104.3