cite, is still apparent when the symmetry is cubic, the potassium ion has presumably moved across to the normal caesium-ion position in pollucite. If this reasoning is correct, then rubidium analcite, and thallium^{I} analcite if stable, may also show a similar high-temperature transition.

The importance of the degree of hydration of the mineral must be stressed. Although the potassium, rubidium, thallium, ammonium and caesium forms of analcite may not be completely anhydrous, they do not contain interstitial water to anything like the same extent as the sodium and silver forms, which may be written M_2O, Al_2O_3, $4SiO_2$, $2H_2O$. This is due to the fact that the water molecules normally occupy the positions (0·125, 0·125, 0·125), which are, of course, the caesium positions in pollucite. Presumably the repulsion forces due to the potassium, rubidium, thallium^{I} and ammonium ions in the anhydrous forms make these positions untenable. Since the potassium and ammonium ions are only slightly too large for them to fit into the normal sodium positions in analcite, it seems possible that a very strongly sorbed gas might convert these into a cubic form. There appears to be no experimental evidence in favour of this suggestion.*

References

Barrer, R. M. (1950). *J. Chem. Soc.* p. 2342.
Barrer, R. M., Baynham, J. W. & McCallum, N. (1953). *J. Chem. Soc.* p. 4035.
Náray-Szabó, S. von (1938). *Z. Kristallogr.* **99**, 277.
Taylor, W. H. (1930). *Z. Kristallogr.* **74**, 1.
Taylor, W. H. (1934). *Proc. Roy. Soc.* A, **145**, 80.
Taylor, W. H. (1938). *Z. Kristallogr.* **99**, 283.
Wyart, J. (1938). *Bull. Soc. franç. Minér.* **61**, 228.

---

* *Note added in proof*, 13 *March* 1954.—Barrer, Baynham & McCallum (1953) have recently reported the synthesis of a *hydrated* form of leucite which is cubic.

Acta Cryst. (1954). **7**, 359

The (*hki*0) Reflexions of Graphite

By G. E. Bacon

Atomic Energy Research Establishment, Harwell, England

(*Received* 22 *January* 1954)

Some quantitative data are presented for the shape and position of the *hki*0 reflexions of graphite, in the intermediate region between a random-layer structure and a true three-dimensional structure. With increasing perfection the reflexion rapidly becomes symmetrical but the displacement of the peak decreases more slowly.

In an earlier note (Bacon & Franklin, 1951) it was pointed out that the variation of the *a* dimension for fairly well crystallized graphites (Bacon, 1950) could be explained by an extension of Warren's (1941) treatment of the two-dimensional reflexions of random-layer structures. This study has now been carried further, giving a quantitative picture of the transition, with increasing crystalline perfection, from the displaced and asymmetrical two-dimensional reflexion band to the normal centred and symmetrical three-dimensional peak. A numerical error in the earlier note has emerged, although this does not affect the qualitative conclusions of the latter.

Following, for example, Wilson's (1949) treatment of diffraction using the reciprocal lattice, the intensity distribution in the neighbourhood of the (*hk*) reflexions may be derived from a consideration of Fig. 1, which illustrates the intersection of the *hk* spike in reciprocal space by the powder reflecting sphere. The changes of reflecting density across and along the spike, i.e. horizontally and vertically, are indicated at (i) and (ii). The intensity diffracted at any angle θ, corresponding to the radius *s*, is obtained by carrying out a summation over the area which appears in section as the path QPQ'. To a very close approximation for the purpose of this summation the sphere may be replaced by a cylinder with the same centre, *O*, and with its axis

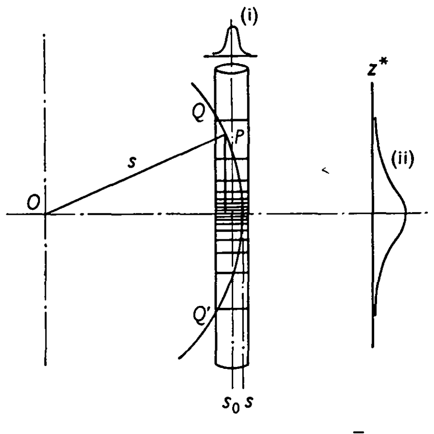

Fig. 1. Calculation of the contour of the $11\bar{2}0$ reflexion from the reciprocal-lattice diagram for an *hk* spike.

perpendicular to the paper. The summation over the area of intersection of spike and sphere is then equivalent to a line summation along QPQ', if the distribution shown at (i) is a distribution of scattering density across the spike when projected on to the plane of the paper. The form of such a projected density distribution has been given by Brindley & Méring (1951) for reciprocal-lattice spikes of various cross-sections. The value of their $T(X)$ for hexagonal particles has been used for the case of graphite. The vertical variation of density which appears at (ii) is that given by the formula of Hendricks & Teller (1942):

$$I = \frac{1-U^2}{1+U^2-2U\cos\varphi}\,, \tag{1}$$

where $U \equiv 1-p$, p being the probability of layer displacement, and $\varphi \equiv \pi l$. Here l is the z index, not necessarily integral, and equals z^*c, where c is the vertical dimension of the graphite unit cell and z^* is the vertical distance in reciprocal space. The numerical error in the previous note, mentioned above, led to the deduction of too small a rate of decrease of intensity with increase of z^*, resulting in an over-simplification of the problem.

Numerical summations along QPQ', made in the above manner, have been carried out for the $11\bar{2}0$ reflexion for graphites of various degrees of crystalline perfection and various values of layer diameter L. The crystalline perfection is represented by the quantity p, which is the probability of layer displacement (see Franklin, 1951) and which thus ranges from $p = 0$ for a perfect three-dimensional structure to $p = 1$ for a random-layer, two-dimensional structure. Typical line shapes, for a layer of dimension 700 Å, are shown in Fig. 2. For $p = 1$ the shape is that of the two-dimensional band, as derived by Warren's analysis, where the abscissa a_w is Warren's parameter a defined by

$$a_w = \frac{2\sqrt{\pi}\,.\,L}{\lambda}(\sin\theta-\sin\theta_0)\,, \tag{2}$$

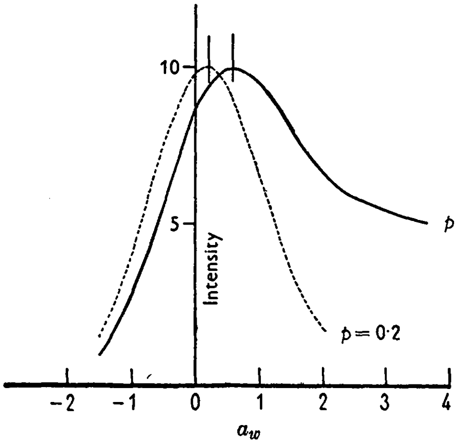

Fig. 2. The contours of the $11\bar{2}0$ reflexion from layers of diameter 700 Å for $p = 0{\cdot}2$ and $p = 1{\cdot}0$ respectively.

in which θ_0 is the Bragg angle for a true three-dimensional reflexion and θ is the angle at which the intensity is being determined. It will be noted that the curve for $p = 0{\cdot}2$, which corresponds to a typical artificial graphite, still retains a displacement away from θ_0, i.e. from $a_w = 0$, but is practically symmetrical about its maximum. The displacement varies with the value of p, as shown in Fig. 3, which gives the numerical results obtained for layer dimensions of 300 and 700 Å respectively. This figure also shows the corresponding values of Δa, the apparent error in the a dimension of the graphite unit cell, which can be deduced by equation (2) from the peak displacement Δa_w.

The width and asymmetry of the reflexion, also, vary with p, and these variations are shown, for a layer of 700 Å, in Fig. 4. The line width is that, in units of a_w, between the two points of half-intensity either side of the peak, and the asymmetry is represented by the ratio of the two components of this width to the right and left of the peak. As p falls below unity, i.e. as the three-dimensional perfection develops, the (*hki*0) reflexion quickly becomes narrower and symmetrical. For p values below 0·3 the reflexion may be regarded as symmetrical and the layer dimension will be scarely

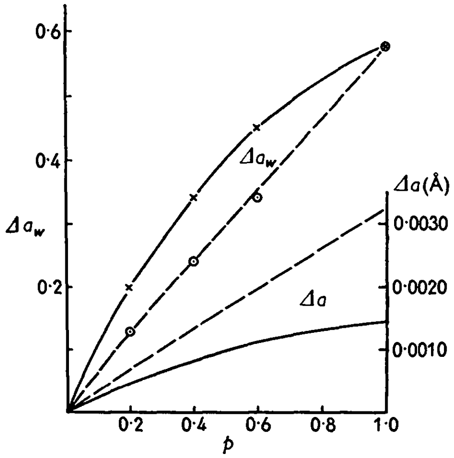

Fig. 3. Variation of peak displacement, Δa_w, and apparent error in a dimension, Δa, with the value of p. Full line: $L = 700$ Å; broken line: $L = 300$ Å.

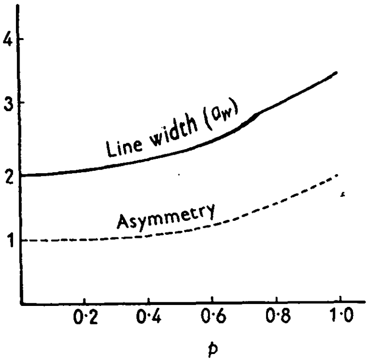

Fig. 4. The dependence of line width and line asymmetry on p, for a layer diameter of 700 Å.

in error if determined by the ordinary line-width formula

$$\beta = \frac{\lambda}{L\cos\theta} \tag{3}$$

for the angular width of a three-dimensional reflexion. On the other hand, for $p = 1$ the width is almost doubled, being given, as Warren has shown, by

$$\beta = \frac{1{\cdot}84\,\lambda}{L\cos\theta}\,. \tag{4}$$

The extent to which the above conclusions can be confirmed experimentally, with graphites whose a dimension can be measured precisely, is limited by the accuracy with which the observed line widths can be corrected for geometrical broadening in order to deduce the value of L. For a graphite with $p = 0{\cdot}2$ the layer dimension L was found by Jones's (1937) method, using Cr $K\alpha$ radiation, to be between 560 and 790 Å, the two values being those given respectively by Jones's curves (*a*) and (*b*). From the curve given in Fig. 3 for the approximate mean L value of 700 Å it is seen that the displacement of the line peak will be such as to give an error in the a dimension of the graphite unit cell of 0·0005 Å. The measured error, obtained by comparing the a value of this sample with that of a very perfect graphite, was 0·0007±0·0002 Å.

With more highly crystalline graphites, having p values 0·11 and 0·05, values of Δa from the $11\bar{2}0$ reflexion were found to be 0·0004±0·0001 and 0·00010±0·00005 Å respectively. There is a corresponding increase of L which becomes increasingly difficult to determine owing to the predominant influence of geometrical broadening on the line widths. Precise correlation with the results of the foregoing analysis is therefore not possible, although agreement within the accuracy of the data is indeed obtained.

This paper is published by permission of the Director of the Atomic Energy Research Establishment.

References

Bacon, G. E. (1950). *Acta Cryst.* **3**, 137.
Bacon, G. E. & Franklin, R. E. (1951). *Acta Cryst.* **4**, 561.
Brindley, G. W. & Méring, J. (1951). *Acta Cryst.* **4**, 441.
Franklin, R. E. (1951). *Acta Cryst.* **4**, 253.
Hendricks, S. & Teller, E. (1942). *J. Chem. Phys.* **10**, 147.
Jones, F. W. (1937). *Proc. Roy. Soc.* A, **166**, 16.
Warren, B. E. (1941). *Phys. Rev.* **59**, 693.
Wilson, A. J. C. (1949). *X-ray Optics*. London: Methuen.

Acta Cryst. (1954). **7**, 361

An X-ray Examination of the Spinel-type Mixed Oxide, $MgFeAlO_4$

By G. E. Bacon

Atomic Energy Research Establishment, Harwell, Didcot, England

and A. J. E. Welch

Department of Inorganic and Physical Chemistry, Imperial College, London S.W. 7, England

(*Received* 17 *November* 1953)

The use of X-ray powder diffraction methods for determining the oxygen parameter and cation distribution in $MgFeAlO_4$ is described, with particular reference to the effect of K-electron dispersion on atomic scattering factors.

Introduction

In a neutron diffraction study of $MgFeAlO_4$ Bacon & Roberts (1953) have established the distribution of the cations amongst the tetrahedrally and octahedrally coordinated sites of the spinel-type structure. In the course of this work they found that the previously reported different conclusions of Nicks (1951) from X-ray work could not be justified. As stated by Bacon & Roberts, the X-ray intensities do, in fact, support their own conclusions and it is the purpose of the present paper to present this evidence in detail. The data are of interest as an example of the accuracy of intensity measurement by X-ray powder methods and, more particularly, the effect of K electron dispersion on atomic scattering factors.

Experimental

Independent measurements of the diffraction pattern of $MgFeAlO_4$, and subsequent photometry for intensity determination, have been carried out by each of us, using Co $K\alpha$ radiation in each case. Comparison of our two sets of intensities is given for the main