in error if determined by the ordinary line-width formula

$$\beta = \frac{\lambda}{L \cos \theta} \quad (3)$$

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

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

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.

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

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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

Table 1. *X-ray intensity data for* $Mg(FeAl)O_4$ *at* 20° C. *with* Co $K\alpha$ *radiation*

Reflexion	θ (°)	Experimental intensities I_1 0·42 mm.	Experimental intensities I_2 0·30 mm.	Corrected values of I_1 Absorption	Corrected values of I_1 Temperature	Calculated value; structure d; $u = 0{\cdot}385$
111	11	1·1	1·2	1·4	1·3	1·2
220	18	3·3	3·7	3·5	3·5	3·7
311	21	10	10	10	10	10
400	26	3·8	4·0	3·4	3·7	3·9
422	32	1·3	1·1	1·0	1·1	1·0
511, 333	34	5·0	4·3	3·6	4·0	3·9
440	37·5	7·8	6·6	4·7	5·5	6·0

Table 2. *Calculated X-ray intensities for various postulated cationic arrangements* (*a*), (*b*), (*c*) *and* (*d*)

Values are shown (i) without, and (ii) with correction for K electron dispersion. In all cases $u = \frac{3}{8}$.

Structure	(*a*)		(*b*)		(*c*)		(*d*)	
A sites	Mg		Fe		Al		$Al_{0·5}$, $Fe_{0·5}$	
B sites	Al, Fe		Mg, Al		Fe, Mg		$MgAl_{0·5}$, $Fe_{0·5}$	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
111	2·0	2·7	0·2	1·0	2·0	3·2	0·2	0·1
220	1·9	1·5	4·7	5·9	2·0	1·6	3·2	3·4
311	10	10	10	10	10	10	10	10
400	5·3	5·2	2·4	1·1	5·2	4·9	3·6	2·7
422	0·7	0·5	1·3	1·8	0·8	0·6	1·0	1·1
511, 333	2·8	3·2	2·8	3·8	2·9	3·3	2·8	3·3
440	6·3	5·6	5·5	4·7	6·2	5·5	5·8	5·0

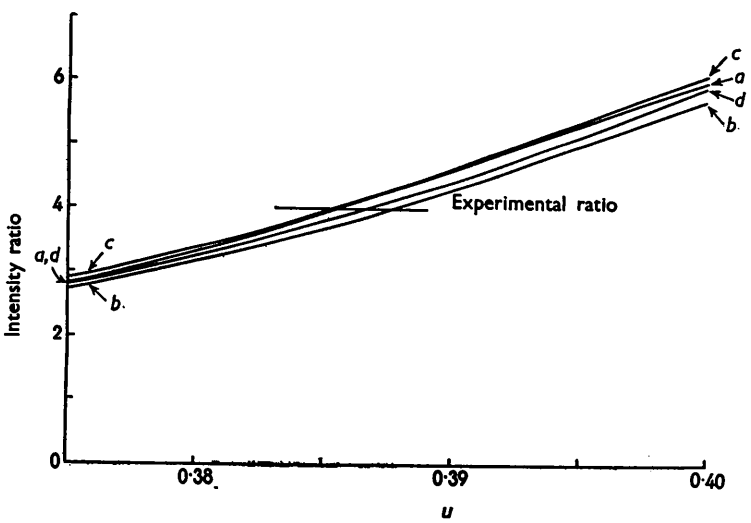

Fig. 1. Variation of intensity of (511, 333) relative to (311), with oxygen parameter u for cationic arrangements *a*, *b*, *c* and *d*.

lines of the pattern in Table 1, expressed in terms of the intensity of the 311 line. Both measurements were made using standard 19 cm. diameter powder cameras, and the specimen diameters in the two cases were 0·43 mm. and 0·30 mm. respectively. The apparent increase of relative intensity with increase of θ for the thicker specimen is due to the effect of absorption. For this specimen an absorption correction was calculated, using a measured value of specimen density from which was deduced a linear absorption coefficient equal to 136 $cm.^{-1}$. The corrected intensity values are included in Table 1, together with the result of a further correction for thermal vibrations, using a Debye temperature $\Theta = 500°$ K., as suggested by Bacon & Roberts. The last column of the table shows for comparison the calculated intensities for the particular cationic arrangement and oxygen parameter now to be deduced.

Deduction of structure

In calculating the expected intensities for various structures the effect on the scattering factor of dispersion of the Co $K\alpha$ radiation by the K electrons of

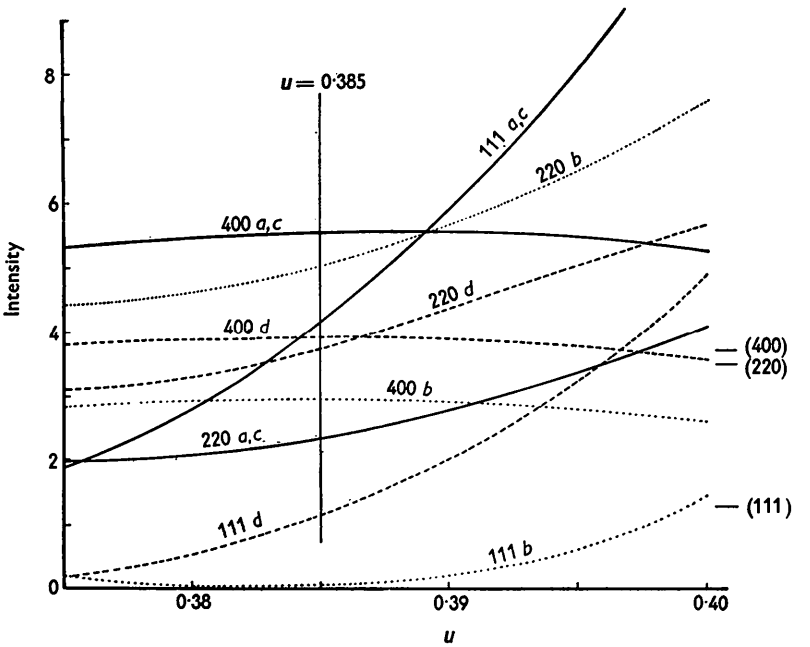

Fig. 2. Variation of calculated reflexion intensities with oxygen parameter u for cationic arrangements a, b, c and d (to avoid confusion a single curve has been drawn for the closely similar intensities of a and c). The experimental intensities are indicated at the right-hand edge of the diagram.

the iron atoms is of importance. The wavelengths of the incident radiation and the K absorption edge of the scattering element are 1·791 and 1·743 Å respectively, and it is found from the discussion and tables given by James (1948) that the correction to the scattering factor for iron amounts to −3·9 electron units. This correction has a marked effect on the calculated line intensities, particularly those for lines such as the (111) which depend markedly on the *difference* between the mean scattering factors of atoms on tetrahedral and octahedral sites. Its importance is shown in Table 2, which lists the line intensities both with and without the dispersion correction, for the four structures a, b, c, and d considered by Bacon & Roberts (following Nicks), for the simplest case in which the oxygen parameter is taken to be $\frac{3}{8}$.

The actual value of the oxygen parameter is most readily determined by calculating the variation of the intensity ratio of the lines (511, 333) and (311) for the various structures, this being a ratio which is not very dependent on the cation distribution among the sites. The effect is illustrated in Fig. 1, from which it is evident that the X-ray data are consistent with the neutron diffraction value of $u = 0{\cdot}385 \pm 0{\cdot}002$, the parameter being susceptible to higher accuracy of determination with neutrons owing to the more significant scattering contribution of oxygen.

Finally, Fig. 2 shows the calculated intensity variation with the parameter u for the lines 111, 220 and 400 for the structures a, b, c and d. Comparison with the experimental intensities indicated at the right-hand side of the figure decides in favour of structure d. With X-rays it is not possible to proceed further and choose between the suggested variants d_1, d_2, d', d'' which can be distinguished by neutrons (Bacon & Roberts, 1953).

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