were established by considering the ratio of the intensities, $I_{hkl}/I_{hk\bar{l}}$, thereby reducing errors arising from absorption effects.

The x coordinate was obtained by considering those reflections $hk0$ for which $I_{hk0} = 0$. The determination of u and z then involved essentially a trial-and-error procedure. However, using reasonable K–F distances, these parameters could be determined with a minimum of effort. The final values are: $u = 0{\cdot}700 \pm 0{\cdot}004$, $x = 0{\cdot}156 \pm 0{\cdot}003$, and $z = 0{\cdot}244 \pm 0{\cdot}004$. A comparison between observed and calculated structure factors is given in Table 1. Absorption and temperature corrections are not included.

Results

The resulting structure shows each titanium atom to be linked to six fluorine atoms at the corners of a distorted octahedron. The interionic distance is Ti–6F = 1·91 Å. With the value of 1·33 Å for the F^- radius (Zachariasen, 1950) we obtain 0·58 Å for the Ti^{+4} radius, which is in excellent agreement with the value 0·60 Å reported by Zachariasen (1950). Each potassium atom is bonded to twelve fluorine atoms, of which six are at a distance of 2·87 Å, three at 2·75 Å, and three at 3·08 Å, the average distance being 2·89 Å. This distance may be compared with the value of 2·85 Å for K^+–F^- deduced from the ionic radii of Zachariasen. The agreement is very satisfactory.

This structure is one of several now reported which are of the K_2GeF_6 type (Hoard & Vincent, 1939).

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A Neutron-Diffraction Study of Magnesium Aluminium Oxide

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The neutron-diffraction pattern of spinel, $MgAl_2O_4$, demonstrates that the cationic arrangement corresponds closely with the so-called 'normal' structure, the scattering amplitudes of Mg and Al being sufficiently different to distinguish this from the 'inverse' structure. The oxygen parameter u is 0·387.

Introduction

Many metal oxides of the type XY_2O_4 have the 'spinel' structure, so-called after the mineral spinel $MgAl_2O_4$, which was first investigated with X-rays by Bragg (1915) and by Nishikawa (1915). The structure may be considered to consist of an arrangement of close-packed oxygen ions with two types of interstices for the metal ions. The unit cell, which contains eight molecules, includes eight metal positions (A sites) tetrahedrally co-ordinated by oxygen and sixteen (B sites) octahedrally co-ordinated. In the simplest arrangement of the cations the eight X ions occupy the A sites and the sixteen Y ions the B sites. This arrangement is usually termed 'normal' in contrast to the so-called 'inverse' structure in which the A sites are occupied by eight of the Y ions with the B sites filled by the X ions and remaining Y ions distributed at random. It was shown by Barth & Posnjak (1932), who first drew this distinction, that X-ray intensity measurements could distinguish the two cases if the scattering powers of the X and Y ions were sufficiently different. For spinel itself, magnesium aluminium oxide, the scattering factors for Mg^{++} and Al^{+++} are too nearly equal for any decision to be made. In the case of neutron diffraction, however, the scattering cross-section of a magnesium nucleus is sufficiently greater than that of aluminium to suggest that a distinction should be possible. Before describing an experimental investigation of this point it is recalled, as emphasized by Verwey & Heilmann (1947), that the 'normal' and 'inverse' arrangements are merely the two extremes of a continuous range of distributions which satisfy the spinel symmetry.

Experimental measurements

In the absence of a suitable single crystal of pure $MgAl_2O_4$ the measurements were made by powder-diffraction methods using a sample prepared in the laboratory of the Royal College of Science by Mrs A. E. Carter. A mixture of partly hydrated Al_2O_3 and $MgCO_3$ was fired at 1400° C. for 15 hr., followed by grinding and refiring. The X-ray powder photograph of the product showed spinel lines only. The neutron-diffraction spectrum was measured at a wavelength of 1·08 Å with the spectrometer described by Bacon, Smith & Whitehead (1950), the spinel powder being packed into a cylindrical aluminium can, $\frac{5}{8}$ in. in diameter and $1\frac{1}{4}$ in. long, which was bathed in a neutron beam of slightly greater dimensions. The most significant portion of the diffraction pattern is illustrated in Fig. 1, which shows the (111), (220) and unresolved (311+222) reflexions. The intensity of the (111) reflexion, which is the one expected to show the largest difference between the 'normal' and 'inverse' structures, amounts only to 5 neutrons/min. on a background of 50 neutrons/min. at the tail of the undeviated neutron beam which rises to a peak count of about 500,000 neutrons/min. at $\theta = 0°$. In order to measure the intensity of this line as accurately as possible a summation was made, at intervals of 0·1° of θ, of the ordinates on 16 independent automatic pen recordings of the pattern. The points marked on Fig. 1 are the mean values given by this summation. In addition to the low-angles lines shown in this figure the intensities of the fairly strong reflexions (400), (511+333) and (440+531) were found as the mean of direct area measurements on ten individual records.

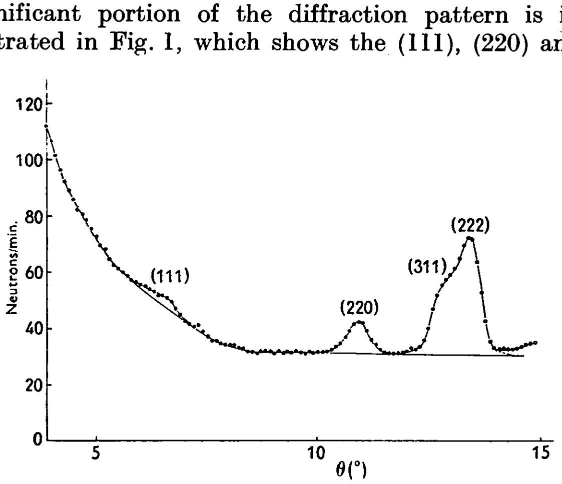

Fig. 1. Low-angle portion of neutron-diffraction pattern.

The experimental intensities were placed on an absolute basis by comparison with those measured for a similar type of powdered diamond sample, in the manner described by Shull & Wollan (1951), assuming the coherent scattering amplitude for carbon to be $0{\cdot}64\times10^{-12}$ cm. A small correction of the (111), (220) intensities was made to allow for the effect of about 0·3% of radiation at $\lambda = 0{\cdot}54$ Å, this being one half of the fundamental wavelength of the 'monochromatic' beam.

Analysis of results

Calculation of the expected neutron intensities for the 'normal' and 'inverse' structures was made over the range from 0·375 to 0·40 of the parameter u which defines the position of the oxygen ions, as listed by Wyckoff (1931).

During these calculations attention was attracted to the surprisingly large difference for magnesium in the values of the total cross-section ($\sigma = 4{\cdot}2$ barns) and the coherent cross-section ($S = 2{\cdot}4$ barns) given by Shull & Wollan (1951). Recently Squires (1952) has made a direct measurement of the disordered scattering cross-section s, which equals $\sigma - S$, and has concluded that $s = 0{\cdot}11$ barn. Moreover, Rainwater, Havens, Dunning & Wu (1948) give $\sigma = 3{\cdot}4\pm0{\cdot}1$ barns for the total cross-section of a free magnesium nucleus, and this value has been confirmed by Egelstaff (1952), leading to $3{\cdot}7\pm0{\cdot}1$ barns for the bound cross-section. Using Squires's value for s, this gives $S = 3{\cdot}6\pm0{\cdot}1$ barns and a coherent scattering amplitude $\bar{a}$ of $0{\cdot}53\pm0{\cdot}01\times10^{-12}$ cm. in contrast to Shull & Wollan's value of $0{\cdot}44\times10^{-12}$ cm. Further measurements of diffraction intensities by the writer, using various materials such as cast magnesium, MgO and Mg_2Sn, all support the higher value. The mean value of $\bar{a}$ found from these diffraction data, $0{\cdot}52\times10^{-12}$ cm., is thought to be accurate to 0·01 cm. and was used in calculating the spinel intensities.

The results of the intensity calculations (corrected for absorption but not for thermal vibrations) are shown in Fig. 2 for the most important reflexions. The intensities are shown as a function of u, the oxygen parameter, for both 'normal' and 'inverse' structures.

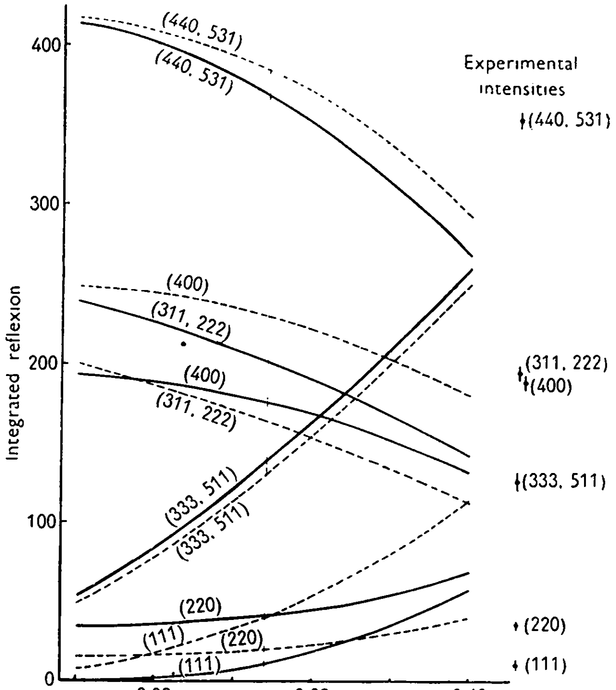

Fig. 2. Variation of integrated reflexions with oxygen parameter, u.
Full line: calculated intensities for 'normal' structure.
Broken line: calculated intensities for 'inverse' structure.

At the right hand side of the figure are shown the experimental intensities, in the same absolute units, together with the estimated errors. Besides showing marked differences for the two structures certain of the intensities are very sensitive to the value of u. The ratio of the intensities of the pairs of lines (440+531) and (511+333) is particularly sensitive to u, as shown in Fig. 3. This ratio provides a very accurate method of determining u, particularly as the two sets of lines have very similar values of $\sin \theta/\lambda$, equal to 0·31 and $0{\cdot}34 \times 10^8$ cm.$^{-1}$ respectively, making the ratio practically independent of correction for thermal vibrations—for calculating which no value of the Debye temperature seems to have been reported. Comparison of the experimental intensities in Fig. 2, especially for (111) and (220), leads to the conclusion that the structure has the 'normal' cation arrangement, and in conjunction with Fig. 3 it is concluded that $u = 0{\cdot}387$ with a probable error of little more than $\pm 0{\cdot}001$. This value of the parameter is consistent with that of $0{\cdot}390 \pm 0{\cdot}006$ given by Barth & Posnjak (1932) from X-ray measurements.

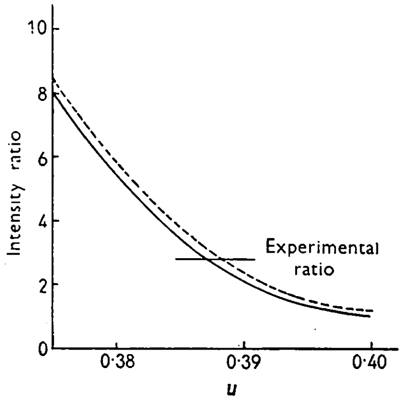

Fig. 3. Calculated variation of the intensity ratio of the reflexions (440, 531) and (511, 333) with oxygen parameter, u. Full line: 'normal' structure. Broken line: 'inverse' structure.

Discussion

The intensity data are summarised in Table 1 which lists the experimental and calculated values of the most significant intensities and ratios.

Any corrections for thermal vibrations will be negligible in the case of the intensities of the (111) and (220) reflexions and for the intensity ratios given at the foot of the table. Some falling off of the absolute intensities of (511+333) and (440+531) would be expected. Approximately, the experimental values for these reflexions are 7% below those calculated; this would be accounted for if the Debye temperature were of the order of 700° K.

Table 1. *Intensity data for* $MgAl_2O_4$

Reflexion	Calculated intensity for *normal* structure, $u = 0{\cdot}387$	Experimental intensity (absolute units)	Calculated intensity for *inverse* structure, $u = 0{\cdot}387$
111	11	11 ± 3	41
220	41	36 ± 4	21
311 222	202	194 ± 5	163
400	176	188 ± 5	230
511 333	138	126 ± 8	130
440 531	369	352 ± 6	384
Ratio $\frac{311+222}{220}$	4·9	5·4	7·8
Ratio $\frac{311+222}{111}$	18·3	17·5	4·0
Ratio $\frac{220}{111}$	3·7	3·3	0·5
Ratio $\frac{311+222}{400}$	1·15	1·03	0·71

It is clear that the data given in Table 1 are overwhelmingly in favour of the 'normal' structure. In particular, it is remarked that if the structure were 'inverse' then the area under the (111) peak in Fig. 1 would be nearly four times greater than that shown, and that for (220) would be almost halved. However, detailed consideration of the results in Table 1 suggests that the idealized 'normal' structure is not completely achieved and effectively there is a small movement towards the 'inverse' form, but no claim is made that the results are sufficiently accurate to prove this point.

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