

The structure of Co_3Mo is not related to those of $\sigma\text{-Co}_2\text{Mo}_3$ and $\mu\text{-Co}_7\text{Mo}_6$. Mo-Mo contacts, which are the most significant feature in the last two structures (Forsyth & Alte da Veiga, 1962, 1963), do not occur in Co_3Mo . On the other hand, all Co-Mo distances are short in Co_3Mo , but not in the other two structures.

I wish to thank Professor Sir Nevill Mott, F.R.S., and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. I am indebted to Dr P. Jane Brown for helpful discussions, and to Dr M. V. Wilkes and Mr E. N. Mutch for providing time on the EDSAC computer. I also wish to thank the Calouste Gulbenkian Foundation, Lisbon, for the award of a Research Studentship.

References

- BABICH, M. M., KISLYAKOVA, E. N., & UMANSKIY, J. S. (1939). *Z. Tekh. Fiz. SSSR*, **9**, 533.
- DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
- FARQUHAR, M. C. M. & LIPSON, H. (1946). *Proc. Phys. Soc.* **58**, 200.
- FORSYTH, J. B. & ALTE DA VEIGA, L. (1962). *Acta Cryst.* **15**, 543.
- FORSYTH, J. B. & ALTE DA VEIGA, L. (1963). *Acta Cryst.* **16**, 509.
- FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
- HANSEN, M. (1958). *Constitution of Binary Alloys*. New York: McGraw-Hill.
- LIPSON, H. & COCHRAN, W. (1953). *The Crystalline State*, Vol. III. London: Bell.
- PEARSON, W. B. (1958). *Handbook of Lattice Spacings and Structures of Metals and Alloys*. New York: Pergamon Press.
- QUINN, T. J. & HUME-ROTHERY, W. (1963). *J. Less-Common Metals*, **5**, 314.
- RAHLFS, P. (1937). *Metallwirtschaft*, **16**, 343.
- SYKES, W. P. & GRAFF, H. F. (1935). *Trans. Amer. Soc. Met.* **23**, 249.
- VEIGA, L. ALTE DA (1963). Dissertation for the Ph. D. Degree, University of Cambridge.

Acta Cryst. (1965). **18**, 859

A Neutron and X-ray Diffraction Study of Ulvöspinel, Fe_2TiO_4

BY R. H. FORSTER AND E. O. HALL

Department of Metallurgy, Newcastle University College, Newcastle, N.S.W., Australia

(Received 23 July 1964)

Powdered specimens of ulvöspinel, Fe_2TiO_4 , having lattice parameters of 8.521 ± 0.003 Å and 8.538 ± 0.003 Å respectively, were studied by neutron and X-ray diffraction techniques. It was confirmed that the titanium ions, Ti^{4+} , prefer to occupy the octahedral (*B*) sites rather than the tetrahedral (*A*) sites. However, the ordering was not complete and the degree of inversion was $y = 0.92$. Estimates of the oxygen parameter yielded $u = 0.386 \pm 0.001$.

Introduction

The discovery of natural ulvöspinel by Morgensen (1946) led to a realization that this mineral may be of some significance particularly from petrological and ore dressing standpoints. A number of studies of the properties of ulvöspinel have been undertaken mainly because of its relation to rock magnetism.

Since the first synthetic specimen of ulvöspinel was prepared (Barth & Posnjak, 1932), it has been generally accepted that it is isomorphous with magnetite, that is, it has the well known spinel structure. However, the exact positions of the cations are difficult to determine accurately by X-ray diffraction because the similarity in scattering power of the iron and titanium atoms results in only small intensity differences for different cation arrangements. Moreover, the intensities are also affected by a change in the oxygen parameter. An accurate structure analysis

should be possible by neutron diffraction because the effective scattering cross-sections for neutrons of iron and titanium ions are widely different.

This paper describes a detailed structural study of two synthetic ulvöspinel specimens.

Previous work

Ulvöspinel has a spinel structure (space group *Fd3m*) similar to magnetite (Barth & Posnjak, 1932) except that eight iron ions have been replaced by eight titanium ions in the unit cell, which contains eight molecules. If the titanium ions are considered to be tetravalent, then the addition of eight titanium ions to the magnetite structure is accompanied by the removal of eight Fe^{3+} ions and the conversion of eight Fe^{3+} ions to eight Fe^{2+} ions, so that a constant total valence of the cations is maintained. This question of the valency of the titanium ions in Fe_2TiO_4 has been

investigated experimentally by a number of workers (see *e.g.* Gorter, 1957; Basta, 1959; MacChesney & Muan, 1959), the results confirming that the titanium ions are in fact tetravalent.

In an ideal spinel structure the ions are arranged in perfect close packing. A deviation from perfect close packing of the anions is usually observed and this can be described by a single parameter, u , whose difference from the ideal value of 0.375 gives a measure of the deviation.

The twenty-four cations present in the unit cell of a spinel may occupy either of two types of site. There are eight cation sites which are each surrounded by four oxygen ions and are called tetrahedral or *A* sites, and there are sixteen cation sites which are each surrounded by six oxygen ions (octahedral or *B* sites).

Barth & Posnjak (1932) in their X-ray diffraction study of synthetic ulvöspinel considered two possible cation arrangements:

- (i) The titanium ions occupy *A* sites (a 'normal' spinel);
- (ii) The titanium ions are all located in *B* sites (an 'inverse' spinel).

The structure was deduced to be that of an inverse spinel. However, there is little difference between the calculated intensities for the normal and inverse cation arrangements and the experimental errors involved make it difficult to decide which model fits better the observed results. The results of Barth & Posnjak indicate that the structure is more likely to be inverse than normal but do not indicate complete inversion. Thus there is the possibility that the titanium ions may be distributed among the *A* sites and the *B* sites.

Werwey & Heilmann (1947) noted that in a number of binary spinels a certain order of preference for the tetrahedral sites seems to exist. This depends in the first place on the charge and size of the ions, and Verwey, de Boer & van Santen (1948) calculated the lattice energy of a purely ionic crystal as a function of the charge distribution and the oxygen parameter. The calculations revealed that large ions with high valency (such as Ti^{4+}) should have a preference for octahedral sites. Ions with part-filled $3d$ shells like Fe^{2+} and Fe^{3+} should have no specific preference for either coordination according to Romeijn (1953) and Gorter (1957). Verhoogen (1956) also considers that Ti^{4+} ions have a preference for octahedral sites but maintains that Fe^{3+} ions prefer to occupy tetrahedral sites.

Many of the suggestions put forward regarding the distribution of the cations in Fe_2TiO_4 have been based on magnetic measurements. From measurements of the specific intensity of saturation magnetization quoted by Akimoto (1954), Nicholls (1955) claims that a structure having Ti^{4+} ions in *B* sites alone gives reasonable agreement with the observed magnetic properties.

At room temperature Fe_2TiO_4 appears to be paramagnetic (Nagata, 1953) but measurements of the Curie points of a number of compositions in the

Fe_2TiO_4 - Fe_3O_4 solid solution series carried out by Akimoto, Katsura & Yoshida (1957) can be extrapolated and indicate that Fe_2TiO_4 has a Curie point of about -150°C . If ulvöspinel has an inverse structure with all the titanium ions in the octahedral positions, then it should be antiferromagnetic below -150°C , since in the Néel model of antiferromagnetism (see *e.g.* Néel, 1955) the titanium ions have no participating magnetic moment and the moments of the Fe^{2+} ions in the tetrahedral sites completely cancel the moments of the Fe^{2+} ions in the octahedral sites, since there are equal numbers of Fe^{2+} ions in these sites and they are aligned antiparallel (Stacey, 1963).

However, Akimoto *et al.* (1957) determined the thermomagnetic curve for a specimen of chemical composition 0.96 Fe_2TiO_4 -0.04 Fe_3O_4 and noticed that it became ferromagnetic below -100°C . This suggests that pure Fe_2TiO_4 may become ferromagnetic at temperatures below -150°C because some titanium ions occupy tetrahedral sites, thereby disturbing the compensation of magnetic moments between tetrahedral and octahedral sites (Akimoto, 1962). Such a disordering of cations from their theoretical distribution is quite probable when specimens are prepared by quenching from temperatures of the order of $1,100^\circ\text{C}$ as was done by Akimoto *et al.* Under equilibrium conditions Stacey (1963) considers that the ordering of the titanium ions in the *B* sites is substantially complete at the Curie temperature.

Experimental results

Preparation of specimens

The two synthetic specimens of ulvöspinel used in the diffraction experiments were prepared by the usual sintering method. The desired proportions of titanium dioxide TiO_2 , ferric oxide Fe_2O_3 , and iron powder were mixed thoroughly, pressed into pellets, and sealed in a silica capsule evacuated to about 10^{-5} mmHg. Specimen *A* was heated in a furnace at 1100°C for 24 hours and then furnace cooled while specimen *B* was heated at 1000°C for 48 hours and then allowed to cool in air.

Preliminary X-ray powder photographs were made with iron-filtered cobalt radiation with a Philips diffraction apparatus and a 114.83 mm. diameter camera. The powder photographs revealed that specimen *A* was contaminated with FeO while a trace of ilmenite could be seen in specimen *B*. The values of the lattice parameters obtained were:

$$\text{Specimen } A \ 8.521 \pm 0.003 \text{ \AA}$$

$$\text{Specimen } B \ 8.538 \pm 0.003 \text{ \AA}$$

The value obtained for specimen *B* agrees with the value $a = 8.538 \pm 0.001 \text{ \AA}$ obtained by Lindsley (1962) for a synthetic specimen. However, Pouillard (1950) and Akimoto, Katsura & Yoshida (1957) report a value of $a = 8.534 \text{ \AA}$. The value obtained for specimen *A* appears to be rather low but Ernst (1943) obtained

the value $a=8.49 \pm 0.01 \text{ \AA}$ for a synthetic specimen, while Vincent (1960) examined a natural specimen of ulvöspinel and determined the lattice parameter to be $a=8.491 \text{ \AA}$.

Since X-ray data for ulvöspinel have not yet been included in the ASTM X-ray Powder Data File, the d values and relative intensities obtained in the investigation of specimen *B* are given in Table 1.

Table 1. X-ray diffraction of ulvöspinel Fe_2TiO_4 (specimen *B*) $\text{Co K}\alpha$ radiation

d	I/I_{311}	hkl
4.93	0.11	111
3.019	0.32	220
2.574	1.00	311
2.465	0.05	222
2.135	0.22	400
1.743	0.16	422
1.643	0.36	333, 511
1.509	0.44	440
1.350	0.04	620
1.302	0.10	533
1.287	0.02	622
1.232	0.06	444
1.1409	0.10	642
1.1116	0.30	553, 731
1.0673	0.10	800
1.0062	0.05	660, 822
0.9859	0.10	555, 751
0.9546	0.05	840

The intensity measurements for the low Bragg angle reflexions up to the 440 line were determined accurately

from point count measurements. The rest of the intensities were estimated visually from the powder photograph.

Neutron diffraction

The neutron diffractometry experiments were carried out at the Australian Atomic Energy Research Establishment at Lucas Heights. A neutron beam from the Commission's reactor, HIFAR, was reflected from a copper single-crystal monochromator giving a beam with $\lambda=1.105 \text{ \AA}$, which then passed through the powdered specimens in $\frac{1}{2}$ -inch diameter vanadium cans. The diffracted rays were recorded by means of a boron trifluoride detector. The counter was moved in 3 minutes of arc (2θ) steps, and the monitored count was printed out at each step.

The histograms for the two specimens are reproduced in Fig. 1. A salient feature of these histograms is the absence of any 111 reflexion. However, the background radiation was rather high at the low Bragg angles and this would have made it difficult to discern any small intensity due to the 111 reflexion not being exactly zero. Table 2 summarizes the results of the intensity measurements of the diffraction lines.

The theoretical intensity ratios were calculated over the range of oxygen parameter $u=0.3600$ to $u=0.4100$ with an IBM 1620 computer. The experimental results were analysed by determining the oxygen parameter required to give the observed intensity ratio for a

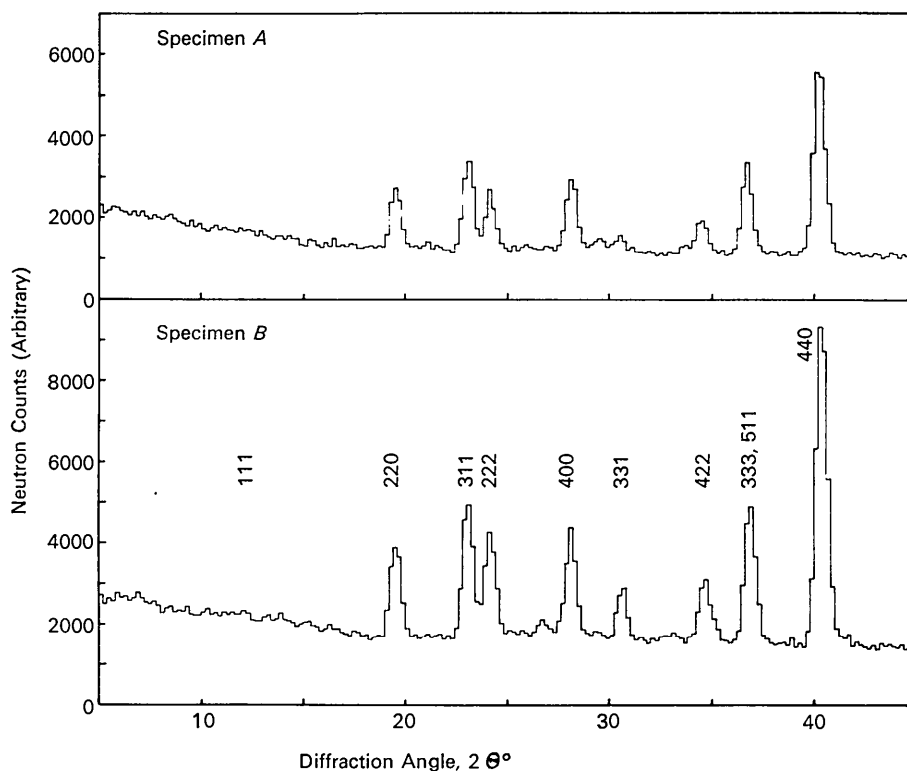


Fig. 1. Neutron diffraction histograms of two specimens of ulvöspinel.

Table 2. Neutron diffraction of *Ulvöspinel*, Fe_2TiO_4

Reflexion <i>hkl</i>	$I_{hkl}/(I_{311} + I_{222})$	
	Specimen A	Specimen B
111	0	0
220	0.374	0.369
400	0.485	0.462
331	0.134	0.140
422	0.216	0.224
333, 511	0.559	0.567
440	1.445	1.398

particular degree of inversion, y . For each reflexion a curve can be drawn showing the relationship between the oxygen parameter u and degree of inversion y which must exist if the observed value of $I_{hkl}/(I_{311} + I_{222})$ is to be obtained. The point of nearest intersection of these curves determines the parameters y and u quite accurately. This method of analysis has been employed by Corliss, Hastings & Brockman (1953) and others. Fig. 2(a) and (b) shows the results obtained for the two specimens of ulvöspinel.

From Fig. 2(a) it can be seen that specimen A had a degree of inversion of $y = 0.91 \pm 0.01$ and an oxygen parameter $u = 0.386 \pm 0.001$. The presence of some FeO in the specimen does not appear to have had any marked effect on the results as they compare quite favourably with those for specimen B which [from Fig. 2(b)] are $y = 0.92 \pm 0.01$ and $u = 0.386 \pm 0.001$. Barth & Posnjak (1932) obtained an oxygen parameter $u = 0.390 \pm 0.01$.

X-ray diffraction

The X-ray diffraction experiments were carried out with a horizontal diffractometer constructed on a Philips X-ray unit. Iron-filtered cobalt radiation was used and the diffracted rays were detected by a proportional counting tube. Since the accuracy in determining the degree of inversion is not very high when X-ray diffraction is used, the results of this section were utilized to obtain another independent value of the oxygen parameter, while assuming the degree of inversion to be that obtained earlier from the neutron diffraction experiments. The X-ray diffraction intensities obtained from both the specimens are given in Table 3.

Table 3. X-ray diffraction of *ulvöspinel*, Fe_2TiO_4

Reflexion <i>hkl</i>	$I_{hkl}/(I_{311} + I_{222})$	
	Specimen A	Specimen B
111	0.106	0.100
220	0.294	0.303
400	0.212	0.201
331	0	0
422	0.148	0.156
333, 511	0.343	0.388
440	0.430	0.424

The ratio $I_{hkl}/(I_{311} + I_{222})$ was calculated over the range of oxygen parameter from $u = 0.3600$ to $u = 0.4100$ with an IBM 1620 computer. These calculated values have been compared with the observed values in Fig. 3(a) and (b), by plotting as ordinate the ratio of the calculated value of the intensity ratio (I_{calc})

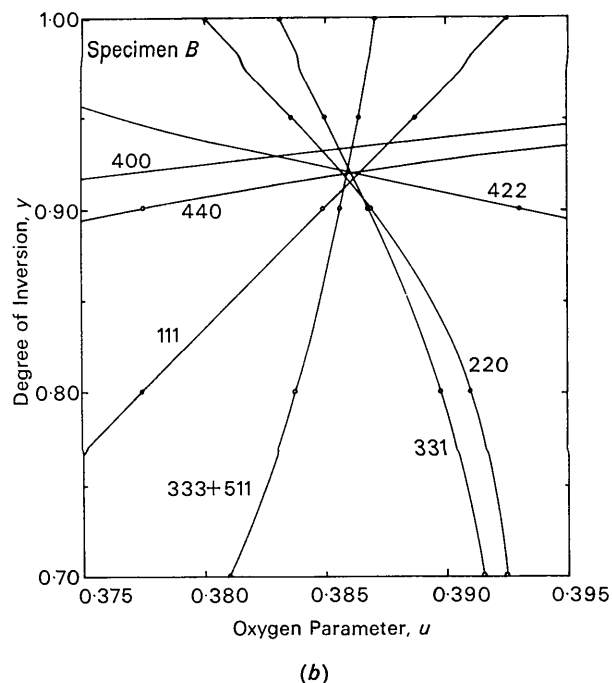
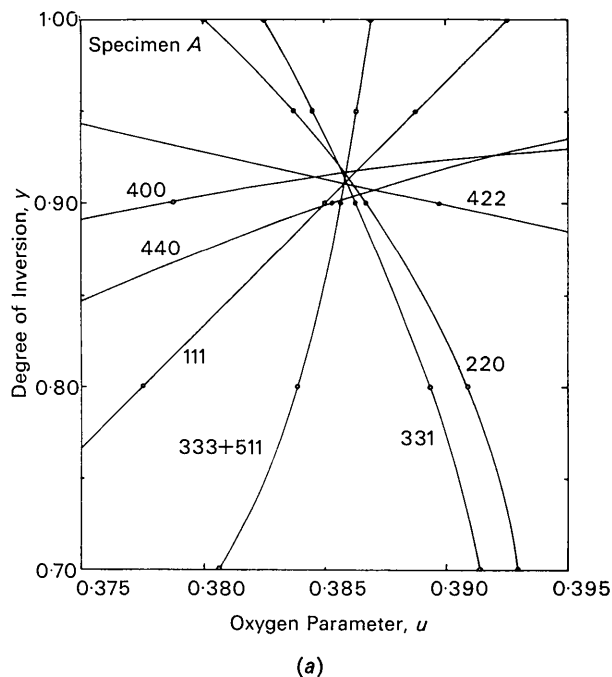


Fig. 2. (a) and (b) Dependence of the oxygen parameter on the degree of inversion of ulvöspinel as determined from neutron diffraction.

divided by the observed value of the intensity ratio (I_{obs}) for various values of the oxygen parameter u . A solution was sought with $I_{\text{calc}}/I_{\text{obs}} = 1.0$ for all lines with a unique value of the oxygen parameter u .

It can be seen from Fig. 3 that the 422, 111 and 331 reflexions will allow one to determine the oxygen parameter most accurately since these lines have the greatest slope. The error in an oxygen parameter estimated from the other lines would be greater. However, the intensities of 422, 111 and 331 reflexions are all relatively small compared with the 311 reflexion, and so the observed intensity ratios for these lines are not as accurate as the ratios for the other lines. Because of these factors, the oxygen parameter which was estimated from the X-ray diffraction results was not as

accurate as that obtained from the neutron diffraction results.

A further point concerns the 331 reflexion. As far as could be ascertained, the intensity of this reflexion was zero for both specimens. However, it is quite possible that the intensity was not exactly zero but below the limit of detection. A curve was constructed for the 331 intensity ratio by taking $I_{\text{obs}} = 0.0001$. The possible error associated with this curve is quite large as can be seen from the 331 intensity curve which was constructed assuming $I_{\text{obs}} = 0.0015$, a value which would still have been undetected.

The region of intersection of the curves in Fig. 3(a) for specimen *A* is rather large. This may be attributed to the presence of FeO in the sample. In particular, the 200 reflexion of FeO almost coincides with the 400 reflexion of Fe_2TiO_4 and this explains the high intensity obtained for the 400 reflexion.

The oxygen parameter for specimen *A* was estimated to be $u = 0.385 \pm 0.003$. However, a better correlation between the observed and calculated intensity ratios was obtained with the results from specimen *B* and this is indicated by the oxygen parameter of $u = 0.386 \pm 0.002$ which agrees quite well with the value obtained from the neutron diffraction experiments.

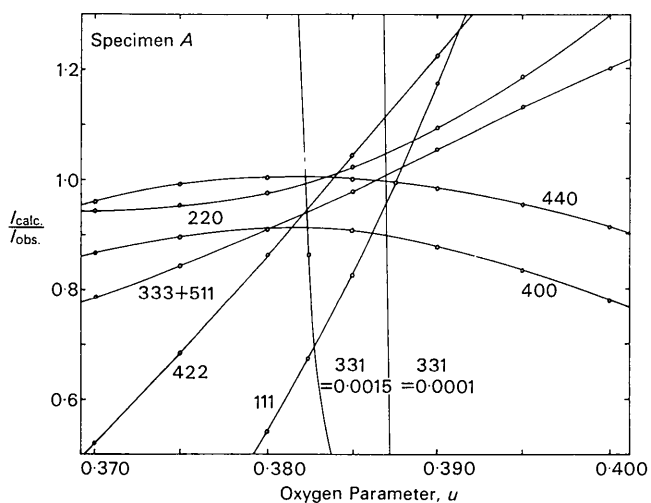
Conclusion

The neutron and X-ray diffraction investigations of ulvöspinel confirmed that the titanium ions have a preference for the octahedral sites. However, in the two specimens examined it was found that the ordering was not complete and some titanium ions were present in the tetrahedral sites. The neutron diffraction study clearly indicated a degree of inversion of $y = 0.92$ while the oxygen parameter was estimated to be 0.386 ± 0.001 . The X-ray diffraction results confirmed these values.

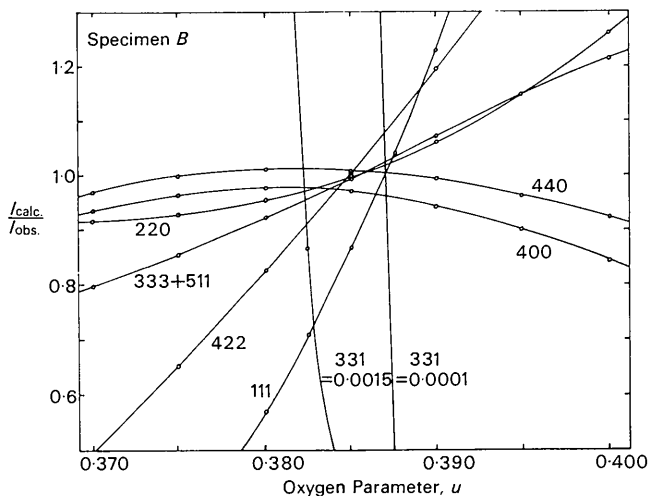
The authors wish to express their thanks to Mr T. E. Sabine, of the Australian Atomic Energy Commission, for assistance with the neutron diffraction experiments, and to the Australian Institute of Nuclear Science and Engineering for a grant-in-aid in support of this work.

References

- AKIMOTO, S. (1954). *J. Geomagn. Geoelect.*, Kyoto, **6**, 1.
 AKIMOTO, S. (1962). *J. Phys. Soc. Japan*, Suppl. B-1, **17**, 706.
 AKIMOTO, S., KATSURA, T. & YOSHIDA, M. (1957). *J. Geomagn. Geoelect.*, Kyoto, **9**, 165.
 BARTH, T. F. W. & POSNJAK, E. (1932). *Z. Kristallogr.* **82**, 325.
 BASTA, E. Z. (1959). *Econ. Geol.* **54**, 698.
 CORLISS, L. M., HASTINGS, J. M. & BROCKMAN, F. G. (1953). *Phys. Rev.* **90**, 1013.
 ERNST, T. (1943). *Z. angew. Miner.* **4**, 394.
 GORTER, E. W. (1957). *Advanc. Phys.* **6**, 336.



(a)



(b)

Fig. 3. (a) and (b) Dependence of the oxygen parameter on the ratio of the calculated intensity ratio $I_{\text{calc}} = I_{hkl}/(I_{311} + I_{222})_{\text{calc}}$ to the observed intensity ratio $I_{\text{obs}} = I_{hkl}/(I_{311} + I_{222})_{\text{obs}}$ for X-ray diffraction of ulvöspinel.

- LINDSLEY, D. H. (1962). *Carnegie Institution of Washington, Annual Report of the Director of the Geophysical Laboratory* (1961–1962). p. 100.
- MACCHESNEY, J. B. & MUAN, A. (1959). *Amer. Min.* **44**, 926.
- MORGENSEN, F. (1946). *Geol. Fören. Stockh. Förh.* **68**, 578.
- NAGATA, T. (1953). *Nature, Lond.* **172**, 850.
- NÉEL, L. (1955). *Advanc. Phys.* **4**, 191.
- NICHOLLS, G. D. (1955). *Advanc. Phys.* **4**, 113.
- POUILLARD, E. (1950). *Ann. Chim.* **5**, 164.
- ROMEIJN, F. C. (1953). *Philips Res. Rep.* **8**, 1301.
- STACEY, F. D. (1963). *Advanc. Phys.* **12**, 45.
- VERHOOGEN, J. (1956). *J. Geophys. Res.* **61**, 201.
- VERWEY, E. J. W., DE BOER, J. H. & VAN SANTEN, J. H. (1948). *J. Chem. Phys.* **16**, 1091.
- VERWEY, E. J. W. & HEILMANN, E. L. (1947). *J. Chem. Phys.* **15**, 174.
- VINCENT, E. A. (1960). *Neues Jb. Miner.* **94**, 993.

Acta Cryst. (1965). **18**, 862

On Miller-Bravais Indices and four-dimensional Vectors

BY F. C. FRANK

H. H. Wills Physics Laboratory, University of Bristol, England

(Received 29 June 1964)

The Miller-Bravais and Weber symbols for planes and directions in hexagonal crystals can be interpreted as four-dimensional vectors, which are confined to a particular three-dimensional section of 4-space by the rule that the first three indices sum to zero. This is useful for the calculation of distances and angles in hexagonal crystals. The direction symbolized by $[uv\bar{t}w]$ is that of the cartesian 4-vector $[u, v, t, \lambda w]$ and the normal to the plane $(hkil)$ is the cartesian vector $[h, k, i, l/\lambda]$, where $\lambda = (2/3)^{1/2} (c/a)$. The angle between two of these 4-vectors is given by the usual formula $\cos \alpha = (\mathbf{r}_1 \cdot \mathbf{r}_2) / r_1 r_2$, and other useful vector equations apply to these 4-vectors just as for the 3-vectors associated with Miller indices. Seeming inconsistencies in the naming of axes for the reciprocal lattice of a hexagonal structure are eliminated by regarding the direct lattice as the projection on to three dimensions and the reciprocal lattice as the three-dimensional section of four-dimensional lattices reciprocal to each other.

Introduction

The impetus to write this note came from discovering that a research student could work for some years with hexagonal crystals and still need a stereogram or a model to ascertain whether the direction $[10\bar{1}3]$, for example, was parallel to the plane $(2\bar{1}\bar{1}1)$, and that though the author could tell him how, he could not easily explain why. In fact, though all who have to do with hexagonal crystals employ the Miller-Bravais notation, few exploit its capabilities to the full, the reason being that most students receive only an *ad hoc* exposition of the system in relation to its use in descriptive crystallography, which makes no attempt to relate it to any more general system of mathematics.

Three dimensions for the representation of two

It is a fairly familiar device (not always explained in these terms) to use a three-dimensional coordinate system for a two-dimensional figure where that figure has threefold or sixfold symmetry, exploiting the redundant dimension to obtain a much more symmetrical algebraic representation, while still retaining the advantages of cartesian coordinates. Thus the equations for the sides of a regular hexagon, centred on the origin, when expressed in two-dimensional cartesian coordinates (x, y) :

$$\begin{aligned} hx + ky &= \pm d & (1a, 1b) \\ -\frac{1}{2}(h + \sqrt{3}k)x + \frac{1}{2}(\sqrt{3}h - k)y &= \pm d & (1c, 1d) \\ -\frac{1}{2}(h - \sqrt{3}k)x - \frac{1}{2}(\sqrt{3}h + k)y &= \pm d & (1e, 1f) \end{aligned}$$

by no means reveal the symmetry instantaneously to the eye: whereas if we consider the figure to be described on the plane

$$x + y + z = 0 \quad (2)$$

of a three-dimensional cartesian system the equations:

$$\begin{aligned} hx + ky + iz &= \pm d & (3a, 3b) \\ kx + iy + hz &= \pm d & (3c, 3d) \\ ix + hy + kz &= \pm d & (3e, 3f) \end{aligned}$$

are simpler and more immediately revealing.

By themselves, of course, equations (3a...f) define planes in the three-dimensional space (x, y, z) : but it is only the intersections of these planes with the (111) plane through the origin defined by (2) which we regard as significant. The normal from the origin to any one of the six planes (3a...f), say to the plane defined by (3a), is simply expressed by the equations:

$$x/h = y/k = z/i, \quad (4)$$

or, in equivalent terms, its direction is the vector with components $[h, k, i]$. We here employ square and round brackets for directions and planes respectively in accordance with crystallographic conventions. The