

## THE CELL-EDGE OF JACOBSITE<sup>1</sup>

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### ABSTRACT

Jacobsite from Weabonga, N.S.W., of composition  $\text{Mn}_{0.980}\text{Mg}_{0.008}\text{Fe}_{2.009}\text{O}_{4.000}$  corresponds closely to the ideal composition. A precise determination of the cubic cell-edge by extrapolation gave  $8.5050 \pm 0.0005$  Å. The great variation among cell-edge determinations of artificial preparations is discussed. It may arise from oxygen present in excess of stoichiometric formula requirements, shown to be absent from the mineral studied, or from variations in the distribution of the cations in the spinel structure of jacobsite. The smaller cell edge relative to normal type spinel structures does not necessarily indicate for jacobsite the presence of the inverse spinel structure.

Very few measurements of the cell-edge of naturally occurring jacobsite, the rare manganese iron spinel, have been published. Two concurring measurements of 8.44 Å,<sup>2</sup> have been made on material containing 9.26% MgO from Jacobsberg by Johannsen (1928) and Wickman (1947). The cell edge of the material of composition  $\text{MnFe}_2\text{O}_4$  is known however only for the artificial compound, and the measurements by different workers range from 8.48 Å to 8.59 Å.

A new occurrence of jacobsite shown by chemical analysis to be exceedingly close to the ideal stoichiometric composition  $\text{MnFe}_2\text{O}_4$  has recently been described from Weabonga, N.S.W., by Stillwell & Edwards (1951). Through the courtesy of Drs. Stillwell & Edwards a portion of their analysed sample was obtained for the present *x*-ray investigation.

Sharp *x*-ray powder patterns were obtained of this Weabonga jacobsite on 57.3 mm. diameter and 114.59 mm. diameter powder cameras of the design described by Parrish & Cisney (1948), in which errors due to film shrinkage and inexact knowledge of the radius of the camera are eliminated. The patterns first obtained showed that all but a very small amount of grinding produced particles too fine to give sharp back diffraction rings.

A portion of the sample was also examined on a North American Philips Norelco Geiger Counter *X*-ray Spectrometer. Sharp peaks were obtained, in excellent agreement with the powder patterns. As the Norelco unit utilizes a much larger sample than the powder camera this indicated any possible inhomogeneity in composition of the jacobsite, such as zoning, was sufficiently small to have no determinable effect on the lattice spacings. The powder patterns, which were made on a minute

<sup>1</sup> Extracted from a thesis for the Ph.D. degree, University of Toronto.

<sup>2</sup> Throughout this paper measurements are given in angstrom units, converted where necessary from the original values in the references cited. In the absence of a statement of the wavelength used, particularly before 1943, the measurements although usually specified as being in Å were presumed to be in kX.

amount of material, may thus be safely taken as representative of jacobsite of the composition found by analysis.

The interplanar spacings and indexing of all but the weakest lines of the  $x$ -ray powder pattern for higher diffraction angles on the large camera are given in Table 1, together with the lattice parameter calculated from each spacing. The table shows in the back diffraction region a slight but definite increase of the cell-edge calculated from the lines of the powder pattern with increasing angle of diffraction. As is well known, this arises from systematic offsetting of the diffraction lines, and the error in the lattice parameter measurement can be greatly lowered by extrapolation back to  $\theta=90^\circ$ . The parameter values calculated from the high angle lines of the pattern were extrapolated against each of the functions  $\cos^2 \theta$  (Bradley & Jay, 1932),  $\cot \theta \cos^2 \theta$  (Buerger, 1942), and

$$\frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} - \frac{\cos^2 \theta}{\theta} \right) \text{ (Nelson \& Riley, 1945).}$$

In each case a straight line was obtained within the limits of measurement error. However plotting against  $\cos^2 \theta$  gave the best linear extra-

TABLE 1. JACOBSITE, WEABONGA, N.S.W. STRONGER LINES AT HIGHER DIFFRACTION ANGLES OF THE X-RAY POWDER PATTERN ON THE 114.6 MM DIAMETER CAMERA. Fe TARGET, Mn FILTER

$d(\text{meas})$	$hkl$	$a$
1.634	(333), (531)	8.490
1.501 <sub>5</sub>	(440)	8.494
1.295 <sub>3</sub>	(533)	8.494
1.281 <sub>0</sub>	(622)	8.4972
1.226 <sub>7</sub>	(444)	8.4990
1.1062 $\alpha_1$	(553), (731)	8.4970
1.0629 $\alpha_1$	(800)	8.5032
.98202 $\alpha_1$	(555), (751)	8.5045
.98205 $\alpha_2$	(555), (751)	8.5048

polation, and was used for the final extrapolation (fig. 1). The parameter obtained by this extrapolation was  $8.505_0 \pm 0.0005$  A, and those from the other extrapolations were in agreement, within this estimated error. The measurements were made for the specimen at  $27^\circ\text{C}$ ., and the wavelengths of the  $x$ -rays from the iron target were taken as  $K_{\alpha_1} = 1.93597$  A,  $K_{\alpha_2} = 1.93991$  A,  $K_{\alpha} = 1.9373$  A.

The complete  $x$ -ray powder pattern of jacobsite from the 57.3 mm diameter powder camera is given in Table 2. This is in excellent agreement with that from the larger camera, although the figures show a greater scatter, as is to be expected.

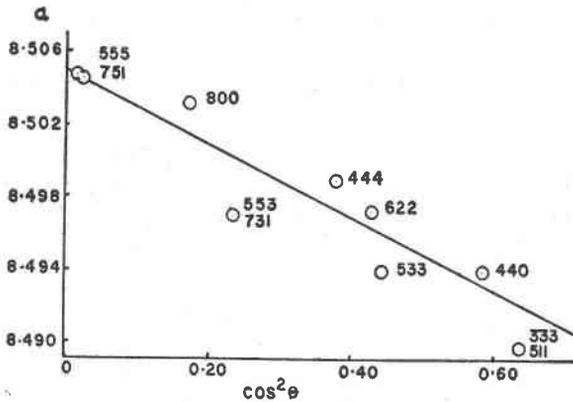


FIG. 1. Extrapolation against  $\cos^2 \theta$  of the lattice parameter.

Comparison of the cell-edge obtained for naturally occurring  $\text{MnFe}_2\text{O}_4$  with that given by other investigators on artificial preparations is difficult because of striking variation among the latter. The following measurements<sup>1</sup> have been collected from the literature, with errors as estimated by the respective authors—

$8.505_0 \pm 0.0005$ A	naturally occurring, this paper.
$8.442 \pm 0.002$ A	Clarke, Ally & Badger (1931).
or $8.474 \pm 0.002$ A	Clarke, Ally & Badger (1931).
$8.482 \pm (0.004)$ A	calculated from Mason (1947).
$8.532 \pm 0.005$ A	Passerini (1930).
$8.589 \pm 0.002$ A	Holgersson (1927).

The cell-edge from Mason was obtained by interpolation between measurements on artificial preparations with Mn:Fe atomic ratios of 30:60 and 20:70. The values given by Holgersson and Passerini may not be quite as precise as indicated, for at the time when these measurements were made the nature of the systematic errors was not fully known. The measurement of Clarke, Ally, & Badger, which is that given in the 7th edition of Dana's *System of Mineralogy* (1944) needs further consideration. In their original paper the value of  $8.457 \pm 0.002$  A is given. This figure was obtained by averaging all values calculated from lines with  $\theta$  in the range  $6^\circ$  to  $25^\circ$  recorded on their film, which was measured with a scale reading directly in lattice spacings. The accuracy they claim is therefore probably far greater than that actually obtained. The two values listed above were obtained by conversion, firstly to A units from the wavelength 0.712 "A" stated for the Mo radiation used, secondly

<sup>1</sup> See footnote at commencement of this paper.

TABLE 2. JACOBSITE, WEABONGA, N.S.W.: X-RAY POWDER DATA  
 Fe target, Mn filter;  $a=8.505_0$  Å

<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)
4	4.94	111	4.910	$\frac{1}{2}$	1.435	531	1.438
4*	3.11	—	—	$\frac{1}{4}$	1.339	620	1.345
4	3.01	220	3.007	2	1.296	533	1.296
10	2.558	311	2.564	$\frac{3}{2}$	1.278	622	1.282
$\frac{1}{4}$	2.449	222	2.455	1	1.225	444	1.227
1*	2.410	—	—	$\frac{1}{4}$	1.191	551, 711	1.191
6	2.123	400	2.126	$\frac{1}{2}$	1.134	642	1.136
1	1.739	422	1.736	4	1.107 <sub>5</sub>	553, 731	1.1073
6	1.636	333, 511	1.637	2	1.062 <sub>4</sub>	800	1.0631
$\frac{1}{4}$ *	1.549	—	—	3 $\alpha_1$	0.9820	555, 751	0.9820
6	1.501	440	1.503	1 $\alpha_2$	0.9820	555, 751	0.9820

\* Extraneous lines, absent from another pattern of the same specimen.

from the wavelength 0.70783 kX then known for MoK in which the scale may well have been calibrated.

Nevertheless there remains to be accounted for a distinct range of 8.48 Å–8.59 Å in values of the parameter obtained by different workers. Two possibilities present themselves for consideration in this respect; firstly variation of chemical composition, as known for some spinels, by the presence of oxygen in excess of the stoichiometric formula requirements; secondly by variation in arrangement of the cations in the atomic structure, which is also well known for some members of the spinel group.

In the normal structure of an  $AB_2O_4$  spinel (Bragg, 1915), the unit cell with 32 O contains 8 *A* cations occupying the equiposition 8(*a*), in tetrahedral coordination with the oxygen, and 16 *B* cations in the 16(*d*) equipositions, in octahedral coordination with the oxygen. In some spinels (Barth & Posnjak, 1932) the cations occupy the same two equipositions, but 8 *B* cations fill the 8(*a*) positions, and 8*A* + 8*B* cations are distributed at random through the 16 (*d*) positions.

Furthermore, the spinel structure has been long known as capable of existing with a deficiency of metal constituents below the stoichiometric requirements of the formula  $AB_2O_4$ . With this there is a commensurate replacement of the *A* or lower valency cation by the *B* or higher valency cation to maintain over-all electrostatic neutrality, and a corresponding decrease in the cell dimensions. Thus magnetite when oxidized at up to 300° C. may vary continuously in composition from  $Fe_3O_4$  to  $Fe_{8/3}O_4$ , retaining the same structure, but with a uniform decrease in the cell edge from 8.40 Å to 8.32 Å (Hägg, 1935), and a similar change is known when  $Al_2O_3$  is "dissolved" in  $MgAl_2O_4$  (Hägg & Söderholm, 1935). It may

be noted that the structural formula for these composition variations may be expressed as  $B_2(B_x A_{1-3x/2})O_4$  with  $x$ , between 0 and  $\frac{2}{3}$  for the above examples, indicating the amount of vacant cation positions in the lattice.

The artificial preparations of  $MnFe_2O_4$  on which the cell dimensions quoted above were measured, were all made by heating at up to  $1300^\circ C$ . in air preparations containing Mn and Fe in the atomic ratio 1:2. In none of these preparations was a check made on the Mn+Fe:O ratio after heating. Therefore addition of oxygen beyond the formula requirements may well have occurred, with a corresponding increase in charge of some of the cations. The product would give an  $x$ -ray powder pattern of the spinel type but with a slightly lower cell dimension than that of composition  $MnFe_2O_4$ .

The presence of such defects in the lattice may be determined from the chemical analysis. The atomic ratio of total cations to oxygen will be 3:4 for a structure without vacant cation positions, and a structure with the vacant positions will have a lower cation:oxygen ratio. The analysis of the Weabonga jacobsite (Stillwell & Edwards, *op. cit.*) was recalculated in atomic ratios relative to O=4.000, and gave the formula  $Mn_{0.980}Mg_{0.006}Fe_{2.009}O_{4.000}$ . The ratio of total cations to oxygen was 2.995:4.000, or, within the limits of error of analysis, 3:4. The lattice parameter for this material therefore represents that of  $MnFe_2O_4$  without appreciable vacant cation positions. Similar calculations were made for five other analyses of naturally occurring jacobsite. In each the cation:oxygen ratio was very close to 3:4, being so within the probable limits of error of the chemical analysis.

Finally it remains to consider the influence of the structure type on the cell dimensions of the spinel. Verwey & Heilmann (1947) have recently pointed out that, in going from the spinel series (aluminates) to the chromite series (chromites) to the magnetite series (ferrites) there is a regular increase in cell dimensions. For spinels having the normal structure the increase is about 0.23 Å and 0.12 Å respectively. In contrast, the ferrites  $CuFe_2O_4$ ,  $MgFe_2O_4$ , and  $FeFe_2O_4$ , shown to have the inverse structure by Barth & Posnjak (1932), Verwey & Heilmann (1947) and Verwey, Haayman, & Romeijn (1947) respectively, have a much smaller increase in cell dimension above that of the corresponding chromites and aluminates.

For the latter two ferrites the increase is about 0.06 Å above the corresponding chromites. In the series  $MnAl_2O_4$ — $MnCr_2O_4$ — $MnFe_2O_4$  the increases 0.23 Å and 0.06 Å respectively were therefore taken by Verwey & Heilmann to indicate the inverse structure for  $MnFe_2O_4$ .

As the scattering powers to  $x$ -rays of Mn and Fe are closely similar,

TABLE 3. LATTICE DIMENSION DIFFERENCES IN THE SPINELS

$B$ $r(B^{3+})$	Al 0.57		Cr 0.64		Fe 0.67	Structure of the ferrite
$A$						
Zn	8.08	0.23	8.31	0.12	8.43	normal
Cd	—	—	8.58	0.12	8.70	normal
Cu	8.08	(0.24	—	0.06)	8.38	inverse
Mg	8.08	0.24	8.32	0.05	8.37	inverse
Fe	8.13	0.22	8.35	0.05	8.40	inverse
Mn	8.27	0.23	8.50	0.01	8.51	?
				(0.06	8.56)	Holgersson.

Modified from Verwey & Hilemann (1947).

the intensities of the  $x$ -ray diffraction beams do not enable a distinction between the two when present together in the one crystal structure, and such indirect reasoning was necessary to determine which of the cation positions each occupied in the jacobsite structure.

In  $\text{MnFe}_2\text{O}_4$  the inverse structure would contain  $\text{Fe}^{3+}$  in  $8(a)$  and  $\text{Mn}^{2+} + \text{Fe}^{2+}$  occupying  $16(d)$ . An alternative possibility is an arrangement with the small  $\text{Mn}^{4+}$  in  $8(a)$ , and  $\text{Fe}^{2+}$  in  $16(d)$ . In this arrangement, corresponding to  $\text{Mn}^{4+}\text{Fe}_2^{2+}\text{O}_4$ , the equipositions  $8(a)$  are occupied by ions of lower radius than in an inverse  $\text{Fe}^{3+}(\text{Mn}^{2+}\text{Fe}^{3+})\text{O}_4$  structure. These positions of tetrahedral coordination, which in the latter arrangement contain  $\text{Fe}^{3+}$  of radius about 0.70 Å, are occupied by  $\text{Mn}^{4+}$  of radius about 0.55 Å. The  $16(d)$  equipositions are occupied by  $\text{Fe}^{2+}$  of radius about 0.83 Å, in place of  $\text{Mn}^{2+} + \text{Fe}^{3+}$  with a maximum radius of 0.90 Å. Therefore this alternative structure would give an increase of cell dimension over the normal  $\text{MnCr}_2\text{O}_4$  structure equally small if not smaller than that for the inverse  $\text{Mn}^{2+}\text{Fe}_2^{3+}\text{O}_4$  structure.

This second possibility is actually a normal type structure, and the two cannot be readily distinguished on the basis of cell size. A third possible arrangement of cations is with 8  $\text{Mn}^{3+}$  filling the  $8(a)$  positions, and 8  $\text{Fe}^{2+} + 8 \text{Fe}^{3+}$  occupying the  $16(d)$  sites at random. However as, according to Verwey & de Boer (1936), the  $\text{Mn}^{4+}$  ion is relatively stable, and the  $\text{Mn}^{2+}$  ion much more stable than the  $\text{Mn}^{3+}$  ion, it is unlikely that the  $\text{Mn}^{3+}$  ionic state would exist in the presence of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

At elevated temperatures where the thermal vibrations in the lattice are relatively large, a more general random distribution of the cations in jacobsite, or a partial change from one to the other of the possibilities

given above may occur. If this were the case, small variations in the lattice dimensions may occur in  $\text{MnFe}_2\text{O}_4$  after heating, varying with the heating and rate of cooling or quenching of the material. A similar change in cation arrangement at high temperatures has been deduced for  $\text{Fe}_2\text{AlO}_4$  by Verwey, Haymen, and Romeijn (1947) as the reason for variation in the electrical conductivity with heat treatment.

In conclusion, the cell-edge values for artificial  $\text{MnFe}_2\text{O}_4$  cannot be taken as representative of a spinel of composition corresponding to this formula until the cation: oxygen ratio of the preparations is shown by analysis to be 3:4. The variation among the reported cell-edge values may well be due to the formation of defect structures by varying oxygen content in excess of formula requirements, acquired at elevated temperatures. The Weabonga jacobsite, of cell-edge reported above, is however substantially free from such structural defects. Nevertheless, the different cation arrangements which are geometrically possible cannot be distinguished by either intensities of the coherent  $x$ -ray diffractions, or by consideration of the cell size, and a variation between these arrangements may well occur. Such a change offers a second explanation of variations in cell dimensions observed in the artificial preparations by different workers, and may be the reason for the high value of 8.589 Å measured by Holgersson.

A portion of the analysed Weabonga jacobsite was kindly made available by Drs. Stillwell and Edwards for the  $x$ -ray examination. The study was carried out at the University of Toronto while holding a Studentship of the Science and Industry Endowment Fund and the Commonwealth Scientific and Industrial Research Organization of Australia.

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