constants. The $YAlO_3$ described in I was extremely pure; the largest impurity was $< 0{\cdot}03\%$ Pb. Analyses were also made of the $EuAlO_3$ and $NdAlO_3$. The former seemed to contain a substantial amount of lead ($> 1\%$) and the latter had a minor (0·1–3·0%) Sm impurity. Although we feel that most of the lead was occluded, it is not impossible that very small amounts did dissolve in the $EuAlO_3$ (since we have no proof of the contrary) and it is very probable that all the Sm is dissolved in the $NdAlO_3$. This, however, does not detract significantly from the results described herein, particularly since the trend of lattice-constant variation is the same as that shown in the orthoferrites and in the other series studied. Also, checks of the sort made for $LaAlO_3$ described above give confirmatory evidence that the Pb is not interfering significantly.

An interesting experiment related to this work was carried out on $BaTiO_3$ to see whether weak superstructure reflections have gone unnoticed in the past. As described above, the superstructure reflections of the rhombohedral aluminates are very few and very weak (e.g. see Table 1). It would not be impossible to overlook the two lines on the $LaAlO_3$ powder photograph, for example, or the few on the oscillation photographs used to align the $PrAlO_3$ crystal. It could also happen that none of the superstructure reflections would be strong enough to show on a powder photograph of normal exposure. For this reason, a $BaTiO_3$ crystal was photographed on a Buerger precession camera as follows: settings were made for the first layer assuming the repeat distance to be twice the known one; that is, settings were made for the '½th layer' with the tetragonal *c* axis as the precession axis. Mo *K* radiation filtered with Zr was used; exposure time was 72 hr. No reflections were observed.

The authors wish to thank J. P. Remeika for supplying the crystals for this investigation, E. A. Wood for the optical examinations, and P. W. Anderson and M. A. Gilleo for discussions relative to this work.

The spectroscopic analyses made by W. Hartmann, the IBM calculations of *d* spacings carried out by Miss D. P. Booth and the drawings made by H. S. Seubert are gratefully acknowledged.

References

Geller, S. (1956). *J. Chem. Phys.* **24**, 1236.
Geller, S. & Wood, E. A. (1956). *Acta Cryst.* **9**, 563.
Hendershot, O. P. (1937). *Rev. Sci. Instrum.* **8**, 436.
Keith, M. L. & Roy, R. (1954). *Amer. Min.* **39**, 1.
Megaw, H. (1954). *Acta Cryst.* **7**, 187.
Naráy-Szabó, St. v. (1947). *Publ. Univ. Tech. Sci., Budapest*, **1**, 30.
Remeika, J. P. (1956). *J. Amer. Chem. Soc.* **78**, 4259.
Ruggiero, A. & Ferro, R. (1955). *Gazz. chim. ital.* **85**, 892.
Wood, E. A. (1951). *Amer. Min.* **36**, 768.

Acta Cryst. (1956). **9**, 1025

The Structure of Tetragonal Copper Ferrite

By E. Prince* and R. G. Treuting

Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.

(*Received* 7 *May* 1956 *and in revised form* 19 *June* 1956)

Copper ferrite, $CuFe_2O_4$, is a tetragonally distorted inverse spinel. Since neutron diffraction measurements have shown no evidence for cation ordering on the octahedral sites, the structure parameters have been determined assuming the space group D_{4h}^{19}–$I4_1/amd$. The oxygen octahedra are elongated parallel to the *c* axis, but the FeO_4 tetrahedra are undistorted, and have the same dimensions found in cubic inverse ferrites. The magnetic structure is consistent with the Néel model of ferrimagnetism.

Introduction

Weil, Bertaut & Bochirol (1950) have shown that copper ferrite, $CuFe_2O_4$, has a structure which is a distortion of the spinel structure. They found that if a sample was heated to a temperature above 760° C. and then rapidly quenched to room temperature, the structure was cubic, but was neither the normal spinel structure, with divalent ions in the tetrahedral '*A*' sites and trivalent ions in the octahedral '*B*' sites, nor the inverse spinel structure, with trivalent ions in the *A* sites, and the *B* sites occupied by divalent ions and trivalent ions at random. It was rather a disordered structure, with both kinds of ion in both kinds of site. By treatment at temperatures below 760° C. these authors produced samples whose crystal structure was tetragonal, with a *c*/*a* ratio, as referred to a face-centered cell, increasing with decreasing temperatures, and reaching 1·06 at 20° C. They also found that the increase in the *c*/*a* ratio was accom-

---

[*] Guest scientist at Brookhaven National Laboratory, Upton, New York, U.S.A.

panied by an increase in the degree of inversion, approaching the completely inverse structure at room temperature. They suggested that the copper and iron ions in the *B* sites might also be ordered according to the scheme proposed by Verwey, Haaymann & Romeyn (1947) for the low-temperature phase of magnetite, which has orthorhombic symmetry (Abrahams & Calhoun, 1953, 1955). The purpose of the present paper is to re-examine the symmetry and structure of copper ferrite in the light of additional X-ray diffraction and neutron diffraction observations.

X-ray observations

Some samples of copper ferrite had been made by calcining a mixture of $CuCO_3$, Fe_2O_3 and a small quantity of $MnCO_3$ at a temperature of 900° C. to produce the composition $Cu_1Fe_{1\cdot 9}Mn_{0\cdot 02}O_{4\pm}$. The first sample to be examined by X-ray diffraction had also been reground, pressed, and sintered by firing in air at 1100° C. for 20 hr., then furnace cooled at an initial rate of about 300° C. per hour. This had the analysis $Cu_{1\cdot 0}Fe_{2\cdot 1}Mn_{0\cdot 02}O_{4\pm}$ (Van Uitert, 1956). The X-ray powder pattern of this sample, taken on a G. E. XRD-3 diffractometer, using Cr *K* radiation and a vanadium filter, was complex and not readily analyzed at first. However, another sample which had been calcined at 900° C. but not sintered was tetragonal with a *c*/*a* ratio, again referred to the face-centered cell, of 1·05. Comparison of this pattern with the first showed the latter to be a mixture of the cubic and tetragonal phases, with the parameters

$$a_0 \text{ (cubic)} = 8{\cdot}38_3 \text{ Å} ,$$
$$a_0 \text{ (tetragonal)} = 8{\cdot}30_6 \text{ Å}, \; c/a = 1{\cdot}03 .$$

The observed spacings for the lines in both patterns are shown in Table 1, with the indices from the cubic and face-centered tetragonal cells. These values are not corrected for the systematic errors of the diffractometer.

It may be observed that the present specimen calcined at 900° C. and cooled in air has values of *a* and *c*/*a* corresponding to the equilibrium structure given by Weil *et al.* for 500° C. and shows some slight evidence of a cubic phase. Although the lines are diffused, with no resolution of the *Kα* doublet, there was no difficulty in indexing the patterns on the basis of the given tetragonal cell. It remains quite possible that material is present representing a continuous range of structures from that at 500° C. to the cubic. On the other hand, although the specimen fired at 1130° C. was furnace cooled and would have passed through the temperature range below 800° C. very slowly, it has two distinct phases present in comparable quantity. These are the cubic phase and a tetragonal one of a_0 and *c*/*a* corresponding to the Weil *et al.* equilibrium structure at about 730° C. Not only is the presence of the cubic structure harder to account for in view of the slow cooling rate, but the clear distinction of the phases does not seem consistent with the continuous range of *c*/*a* ratios described by Weil *et al.*

Table 1. *X-ray reflections from* $CuFe_2O_4$ *samples*

Observed spacings* (Å)		Reflections	
As sintered 1130° C.	As reacted 900° C.	Cubic	Tetragonal
4·83	4·83	111	111
2·97	2·98	—	202
2·96	—	220	—
2·93	2·91	—	220
2·56	2·58	—	113
2·52	—	311	—
2·50	2·50	—	311
2·41	2·42	222	222
2·134	2·15	—	004
2·091	—	400	—
2·073	2·06	—	400
—	1·935	—	313
1·920	—	331	—
—	—	—	331
1·725	1·736	—	224
1·709	—	422	—
1·703	1·696	—	422
1·639	1·654	—	115
1·612	1·612	511, 333	333
1·597	1·588	—	511
1·487	1·492	—	404
1·481	—	440	—
1·465	1·457	—	440
1·429	—	—	315
1·416	—	531	—
1·413	—	—	513
—	—	—	531
—	—	—	206
—	—	620	—
—	1·305	—	620
—	1·291	—	335
—	—	533	—
1·274	1·270	—	533
1·263	—	622	—
1·254	1·246	—	622
1·210	1·209	444	444

* Uncorrected for systematic errors.

It is apparent from the table that all orders of 111 reflections are common to the cubic and tetragonal structures (to an extent giving good resolution of the *Kα* doublet in the actual patterns). This is an indication that the actual symmetry of the distorted structure is either truly tetragonal or face-centered orthorhombic. The distortion is not analogous to that found in low-temperature magnetite (Abrahams & Calhoun, 1953, 1955), which corresponds to a body-centered orthorhombic structure. It would be surprising if a body-centered orthorhombic ordering system, such as that proposed for magnetite (Verwey *et al.*, 1947), produced a distortion of the type observed in copper ferrite. There are, however, at least two possible ways of ordering the *B* sites of an inverse spinel that have tetragonal symmetry. One of these belongs to the space group D_4^3–$P4_122$ or its enantiomorph D_4^7–$P4_322$, while the other belongs to the space group D_{2d}^5–$P\bar{4}m2$. These structures, as compared with the magnetite structure, are shown in Fig. 1.

Weil *et al.* (1950) found no evidence for cation ordering in their X-ray observations. It is possible, however, that the difference in scattering power for X-rays of iron and copper is not sufficient, even when the wavelength is carefully chosen, to make such effects observable. It is also possible, as Bertaut (1951) himself has suggested, that only short-range order is present. On the other hand, Goodenough & Loeb (1955) have suggested that the iron and copper in the B sites are not ordered at all, but that the tetragonal distortion is due to the tendency of the Cu^{++} ion to form square covalent bonds when it is placed in sixfold coordination. In order to test all of these ideas, it seemed desirable to examine copper ferrite by means of neutron diffraction, which allows use of the moderate difference in nuclear scattering powers and the large difference in magnetic scattering powers of the Cu^{++} and Fe^{+++} ions. In addition, the comparatively large nuclear scattering power of oxygen allows more accurate determination of the oxygen parameters.

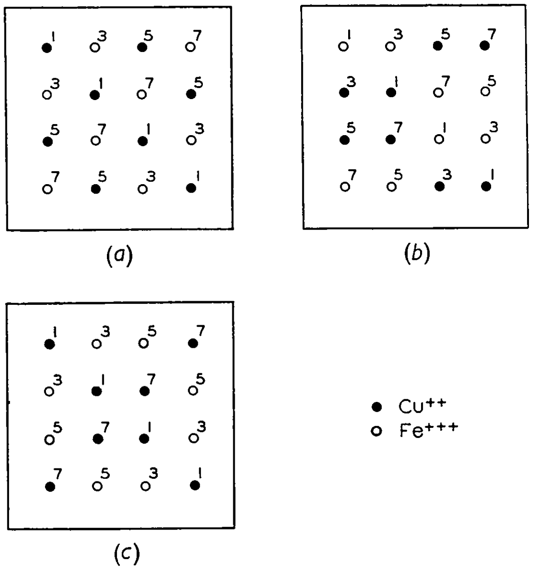

Fig. 1. Arrangement of B-site atoms in various possible ordering schemes for inverse spinels. Elevations in multiples of $c/8$.
(a) *Imma* (magnetite structure); (b) $P4_122$; (c) $P\bar{4}m2$.

Neutron diffraction observations

A specimen of copper ferrite suitable for neutron diffraction observation, a cylinder 2·5 cm. in diameter and 5 cm. long, was made for this purpose from another lot of powder in the proportion $Cu_{1\cdot0}$:$Fe_{1\cdot85}$ calcined at 910° C. These compositions are customarily made copper-rich to compensate for the loss of copper during the reaction treatment. From X-ray diffraction, this material had a c/a ratio of 1·06, and the value of a_0 was close to that found by Weil *et al.* (1950) at room temperature,

$$a_0 = 8{\cdot}22 \text{ Å} .$$

The small differences from the previous sample for X-ray analysis are ascribable to minor differences in the sample preparations and treatments, which probably result in some difference in the degree of inversion; they are not considered to affect the conclusions significantly. A neutron diffraction pattern ($\lambda = 1{\cdot}00$ Å) of this sample at room temperature confirmed the lattice parameters and showed all the lines to be expected from a tetragonal pseudo-spinel, and none extra that would be indicative of cation ordering. The intensities indicated virtually complete inversion. We shall, therefore, assume that the structure can be described by the space group D_{4h}^{19}–$I4_1/amd$. For convenience, we shall convert indices and parameters to the conventional, body-centered unit cell, taking the origin at a center of symmetry. In this space group there are two oxygen parameters, but all cations are in fixed special positions.

Since copper ferrite is ferrimagnetic at room temperature, the intensities consist of nuclear and magnetic contributions. Nuclear scattering factors have been tabulated by Bacon & Lonsdale (1953). The magnetic scattering factor, D, can be calculated from the relation $D = 0{\cdot}539Sf$, where S is the spin of the ion, and f is a form factor. Corliss, Hastings & Brockman (1953) have given a form factor for the Fe^{+++} ion which appears to be a satisfactory approximation to other ions also. It has been assumed in these calculations that the average spin on the A sites is $\frac{5}{2}$, that on the B sites is $\frac{3}{2}$, and the moments on the A sites are aligned antiparallel to those on the B sites, in accordance with the model proposed by Néel (1948). This is in substantial agreement with the observed net magnetization at 1·3° K. of 1·13 Bohr magnetons per molecule. This moment is not consistent with the suggestion of Goodenough & Loeb (1955) that the spin of the Cu^{++} ion should not contribute to the magnetic

Table 2. *Observed and calculated neutron intensities for tetragonal copper ferrite*

Reflections		Intensities			
		Calculated			
F.c. cell	B.c. cell	Nuclear	Magnetic	Total	Observed
111	101	0·3	66	66·3	66·5
202	112	21·3	13	49	49
220	200	10·7	4		
113	103	48	0	48	46·5
311	211	66	0	66	64
222	202	5·1	9	14·1	16
004	004	30	7	37	34
400	220	51·5	6	57·5	58
313	213	0·1	13	17	13·4
331	301	0·2	4		
224	204	7·1	2	46	44·5
422	312	14·2	3		
115	105	20·2	0		
333	303	8·5	0	60·5	58
511	321	52	0		
404	224	150	0	220	220
440	400	70	0		

moment. The best agreement between observed and calculated intensities is obtained on assuming that the moments are aligned perpendicular to the c axis. Oxygen parameters were determined by trial and error. Neutron diffraction data are very sensitive to variations in oxygen parameters; in this case the limits of error are probably less than $\pm 0{\cdot}002$. Table 2 shows a comparison of the final observed and calculated intensities. Atomic parameters are listed in Table 3.

Table 3. *Structure parameters for* $CuFe_2O_4$

Space group D_{4h}^{19}–$I4_1/amd$. Origin at center of symmetry

Atom	x	y	z
Fe (A sites)	0	$\frac{3}{4}$	$\frac{1}{8}$
Fe, Cu (B sites)	0	0	$\frac{1}{2}$
O	0	0·016	0·250

Discussion of the structure

An important feature of the structure is that the oxygen octahedra around the B sites are elongated parallel to the c axis and contracted in the ab plane. An even more striking feature of the structure, however, is that FeO_4 tetrahedra are completely undistorted, within the small limits of error, in spite of the considerable distortion of the structure, and have the same oxygen–oxygen distance, 3·08 Å, that is found in the cubic inverse ferrites of magnesium (Corliss *et al.*, 1953), nickel (Hastings & Corliss, 1953) and cobalt (Prince, 1956). The iron–oxygen distance is 1·89 Å, which is 0·10 Å less than the sum of the Goldschmidt ionic radii. This suggests that the FeO_4 tetrahedra may be bound together by bonds which are at least partially covalent. The environment of the B sites supports the suggestion of Goodenough & Loeb (1955) that the tetragonal distortion is due to the tendency of the Cu^{++} ion to form square covalent bonds. However, it is not obvious how the constancy of the Fe–O distances around the A sites, independent of the nature of the B ions and of the distortion of the structure, can be reconciled with their assertion that the formation of covalent bonds on one kind of site should weaken the tendency to form them on the other kind of site.

Although there is no direct evidence for cation ordering in the B sites, we cannot rule out the possibility of either short-range order or a structure such as would be produced by twinning on a microcrystalline scale. This latter effect could occur very easily, particularly as all oxygen sites and B sites lie in planes perpendicular to the c axis. A stacking fault which would convert the right-hand screw axis of $P4_122$ to the left-hand screw axis of $P4_322$ would add very little to the total internal energy of the crystal. We may conclude that the true symmetry of the low-temperature form of copper ferrite is probably tetragonal, and that any ordering present should conform to this tetragonal symmetry.

The authors are indebted to Mrs J. F. Breidt and R. T. Walsh for technical assistance. L. G. Van Uitert and F. J. Schnettler provided the samples, and these two as well as several others, notably R. D. Heidenreich and S. Geller, contributed many useful suggestions. We are grateful to R. M. Bozorth, D. Walsh, and A. J. Williams for measuring the magnetic moment of the sample used for neutron diffraction. We thank Brookhaven National Laboratory for the provision of neutron diffraction facilities.

References

Abrahams, S. C. & Calhoun, B. A. (1953). *Acta Cryst.* **6**, 105.

Abrahams, S. C. & Calhoun, B. A. (1955). *Acta Cryst.* **8**, 257.

Bacon, G. E. & Lonsdale, K. (1953). *Rep. Progr. Phys.* **16**, 1.

Bertaut, E. F. (1951). *J. Phys. Radium*, **12**, 252.

Corliss, L. M., Hastings, J. M. & Brockman, F. G. (1953). *Phys. Rev.* **90**, 1013.

Goodenough, J. B. & Loeb, A. L. (1955). *Phys. Rev.* **98**, 391.

Hastings, J. M. & Corliss, L. M. (1953). *Rev. Mod. Phys.* **25**, 114.

Néel, L. (1948). *Ann. Phys., Lpz.* **3**, 139.

Prince, E. (1956). *Phys. Rev.* **102**, 674.

Van Uitert, L. G. (1956). To be published.

Verwey, J. W., Haaymann, P. W. & Romeyn, F. C. (1947). *J. Chem. Phys.* **15**, 181.

Weil, L., Bertaut, E. F. & Bochirol, L. (1950). *J. Phys. Radium*, **11**, 208.