

## *On the composition of delafossite*

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*Summary.* Oxides of the Cu-Fe-O system prepared by solid-state reaction methods have been investigated by X-ray, Mössbauer effect, and analytical chemical techniques. In agreement with most previous investigations of this system, it is found that CuFeO<sub>2</sub> exists as a stable compound, and that the mineral delafossite has essentially this composition. These results are in disagreement with those of Buist, Gadalla, and White who propose that delafossite has an approximate composition Cu<sub>6</sub>Fe<sub>3</sub>O<sub>7</sub>, instead of CuFeO<sub>2</sub>. In fact, a compound of composition Cu<sub>6</sub>Fe<sub>3</sub>O<sub>7</sub> could not be prepared. The Mössbauer isomer shift provides confirmation that the iron in CuFeO<sub>2</sub> is trivalent.

CONTRARY to previous findings,<sup>2</sup> Buist, Gadalla, and White (1966) (see also Gadalla and White, 1966) came to the conclusion that the compound CuFeO<sub>2</sub>, commonly considered to be the same as the mineral delafossite, does not exist. Instead, they postulated the existence of a new compound of the approximate composition Cu<sub>6</sub>Fe<sub>3</sub>O<sub>7</sub> ( $\equiv 3\text{Cu}_2\text{O}\cdot\text{Fe}_3\text{O}_4$ ). The latter composition was derived from the measured weight loss during heating on a thermobalance and the initial composition of mixtures of CuO and Fe<sub>2</sub>O<sub>3</sub>. No chemical analysis of the resulting compound was given. From X-ray powder diffraction patterns Buist *et al.* (1966) obtained *d*-spacings for the new compound that are in good agreement with those calculated from the rhombohedral unit cell containing one CuFeO<sub>2</sub>, suggested by Soller and Thompson (1935) [ $a_r = 5.96 \text{ \AA}$ ,  $\alpha = 29^\circ 26'$ , Cu at (0, 0, 0), Fe at ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) and 2 oxygens at  $\pm(0\cdot111, 0\cdot111, 0\cdot111)$ ].

Recently we (Muir and Wiedersich, 1967) have studied CuFeO<sub>2</sub> and the mineral delafossite using the Mössbauer effect (ME) without

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<sup>2</sup> Soller and Thompson (1935), Delorme and Bertaut (1953), Kushima and Amanuma (1955), Théry and Collongues (1962), Schmal and Müller (1964), and Yund and Kullerud (1964).

discovering any evidence that would indicate that prior conclusions<sup>1, 2</sup> regarding the composition of natural delafossite and  $\text{CuFeO}_2$  were incorrect. Therefore, we have examined the phases present in oxides with Cu to Fe ratios of 2:1 and 1:1. Only a compound at or near the composition  $\text{CuFeO}_2$  can be produced. A single phase at or near the composition  $\text{Cu}_6\text{Fe}_3\text{O}_7$ , as suggested by Buist, Gadalla, and White (1966), was not obtained.

### *Experimental techniques*

*Materials preparation.* Samples were prepared by solid state ceramic techniques. The starting materials were reagent grade  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and  $\text{Fe}_2\text{O}_3$  powders.  $\text{Fe}_3\text{O}_4$  was prepared by reduction of the  $\text{Fe}_2\text{O}_3$  with high purity iron metal powder, added in appropriate proportion, in sealed silica capsules. The  $\text{Cu}_2\text{O}$  was annealed at  $850^\circ\text{C}$  in 0.05 mm Hg oxygen pressure for 24 hours to achieve proper stoichiometry prior to use (Starr, 1936).  $\text{CuO}$  was dried in vacuum at  $110^\circ\text{C}$  and  $\text{Fe}_2\text{O}_3$  in air at  $250^\circ\text{C}$ . Batches of about 10 g were prepared by mixing appropriate proportions of the components by weight ( $\pm 0.01$  g). They were ground together and mixed for 2 to 4 hours in polyethylene ball-mill containers using tungsten carbide balls. The mixtures were pressed dry at 80 000 to 100 000 lb/in<sup>2</sup> in tungsten carbide dies.

It is well known that platinum is not suitable as a crucible material for melting copper- or iron-containing oxides. In preliminary work for the previous study (Muir and Wiedersich, 1967), it was found that platinum was not even suitable for solid-state reactions of copper-iron oxide mixtures. Platinum preferentially extracts Cu from the pellets, apparently by forming a platinum-copper alloy. High purity, high density  $\text{Al}_2\text{O}_3$  crucibles (Morganite triangle RR and McDanel 997 Alumina) did not react with the samples to any extent as long as no melting occurred. Therefore, all samples were fired in  $\text{Al}_2\text{O}_3$  crucibles. Liquid  $\text{CuFeO}_2$  wets  $\text{Al}_2\text{O}_3$  completely and penetrates slightly into the crucible material. With the exception of sample 4, the samples were quenched in air after firing. Sample 4 was sealed in an evacuated silica capsule, which was broken under water after firing.

The compositions and treatments of the materials are given in Table I. The notation 'in argon' indicates that the sample was fired in flowing high purity argon. Sample 1 is the material used in the previous

<sup>1</sup> See footnote <sup>2</sup>, p. 643.

<sup>2</sup> Friedel (1873), Rogers (1913), and Pabst (1946). See also the following paper by Hey.

investigation. The preparation for samples 2 and 3 paralleled that of Buist *et al.* (1966) with the exception that  $\text{Al}_2\text{O}_3$  crucibles were substituted for platinum lined crucibles. Samples 4 and 5 were prepared as additional attempts to obtain the compound  $\text{Cu}_6\text{Fe}_3\text{O}_7$ .

TABLE I. Sample preparation and results of analysis

|    | Initial composition                            | Treatment conditions           | Phases identified by                                |   | Chemical analysis |                       |
|----|--|--------------------------------|---|---|-------------------|-----------------------|
|    |  |                                | X-ray   | ME*   | Fe/Cu $\pm 0.05$  | Spectrographic wt. %† |
| 1  | $\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$  | 1000–1200° C<br>24 h. in argon | $\text{CuFeO}_2$                                    | $\text{CuFeO}_2$<br>( $\text{Fe}_3\text{O}_4$ ) | 1.10              | Al 0.01<br>Zn 0.17    |
| 2‡ | $2\text{CuO} + \text{Fe}_2\text{O}_3$          | 1025° C<br>48 h in argon       | $\text{CuFeO}_2$<br>( $\text{Cu}_2\text{O}$ )       | $\text{CuFeO}_2$                                | 1.02              | Al 0.01               |
| 3§ | $4\text{CuO} + \text{Fe}_2\text{O}_3$          | 1060° C<br>24 h in air         | $\text{CuFeO}_2$<br>$\text{Cu}_2\text{O}$<br>spinel | $\text{CuFeO}_2$<br>spinel                      | 0.61              | Al 2.7<br>Si 0.24     |
| 4  | $3\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_4$ | 1025° C<br>24 h sealed         | $\text{CuFeO}_2$<br>$\text{Cu}_2\text{O}$           | $\text{CuFeO}_2$                                | 0.55              | Al none<br>Si 0.24    |
| 5  | $3\text{Cu}_2\text{O} + \text{Fe}_3\text{O}_4$ | 1025° C<br>24 h in argon       | $\text{CuFeO}_2$<br>$\text{Cu}_2\text{O}$           | $\text{CuFeO}_2$                                | 0.55              | Al 0.01               |

\* Mössbauer effect determines only Fe containing phases.

† Semi-quantitative spectrographic analysis for Al and other metals exceeding 0.1 wt. %.

‡ Treatment conditions repeated after intermediate grinding and repressing.

§ Temperature of sample lowered to 1025° C before air quench. The sample partially melted. Results are shown for the unmelted part of the sample.

|| Barely detectable amount.

*X-ray analysis.* A multiple Guinier-DeWolff camera was used to obtain X-ray patterns with low background intensity. It was equipped with a quartz monochromator. The equivalent Debye-Scherrer diameter of 229.2 mm provided high resolution. One-hour exposures were taken with  $\text{Cu-K}\alpha$  radiation.

*Mössbauer effect analysis.* All samples were studied by ME spectroscopy, using a multichannel-analyser-loudspeaker-drive system operating in the 'baseline' mode. The speaker was driven sinusoidally at its resonance frequency ( $\sim 57$  cycles/sec). A xenon nitrogen proportional counter was used to detect the 14.4 KeV radiation emitted by the  $\sim 20$  mc  $\text{Co}^{57}$  in Pd source (commercially obtained). All measurements were taken with the source and absorber at room temperature. The isomer shifts (both in the text and on the figure scales) are referred to a metallic iron absorber at room temperature, which was also used for calibrating (Preston, Hanna, and Heberle, 1962) the spectrometer. Positive velocity corresponds to motion of the source towards the

absorber. For these measurements the specimen investigated was ground into an extremely fine powder, which was pressed and held in a uniform layer ( $\sim 35 \text{ mg/cm}^2$ ) in a sample holder with thin Lucite<sup>1</sup> windows.

*Chemical analysis.* To check against possible loss of metal from the reacting systems, analytical chemical techniques were employed to determine the Fe and Cu content of the samples, from which molar Fe/Cu ratios were calculated. The total of Fe and Cu was measured by EDTA compleximetric titration and Cu was measured by potentiometric titration with EDTA using a mercury indicator electrode after electrolytic separation from the Fe. The Fe was determined by difference or by titration with ceric sulphate.<sup>2</sup> Semiquantitative spectrographic analyses were also made on the samples to check for impurities, especially the possible pick-up of aluminium from the crucibles.

### Results

All samples were examined by X-ray diffraction and ME spectroscopy. The latter method can be used for identification of phases containing the isotope used, here Fe<sup>57</sup>. Some X-ray diffraction patterns are shown in fig. 1 together with the patterns for the pure phases for comparison. Fig. 2 gives examples of ME spectra. The results, including those from chemical analysis, are summarized in table I. Table II gives the ME parameters (isomer shift and quadrupole interaction) obtained for the CuFeO<sub>2</sub> phase.

*Sample 1* appears to be entirely CuFeO<sub>2</sub> according to the X-ray result; however, it contains a very minor amount of Fe<sub>3</sub>O<sub>4</sub> according to the ME spectrum (see fig. 2*a* of Muir and Wiedersich, 1967). The major phase gives a characteristic quadrupole split doublet (essentially identical to that of sample 2 shown here in fig. 2*a*). Similar ME results have also been obtained by Apostolov (1966). The atomic ratio Fe/Cu by chemical analysis is  $1.10 \pm 0.05$ , slightly larger than unity, which is accounted for by the presence of the minor amount of Fe<sub>3</sub>O<sub>4</sub>.

*Sample 2* consisted of CuFeO<sub>2</sub> according to the X-ray pattern (fig. 1*a*) as well as to the ME spectrum (fig. 2*a*). CuO reacts very slowly with Fe<sub>2</sub>O<sub>3</sub>. Small amounts of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O are retained usually after the first firing. Even after the second firing, a minute amount of Cu<sub>2</sub>O is still retained as indicated by the presence of the strongest X-ray line

<sup>1</sup> Polymethyl methacrylate, similar to Perspex.

<sup>2</sup> The authors are especially grateful to Mr. D. H. Hern who performed the chemical analyses. The outlined procedure was satisfactory, while several procedures in the literature that did not involve separations gave unreliable results.

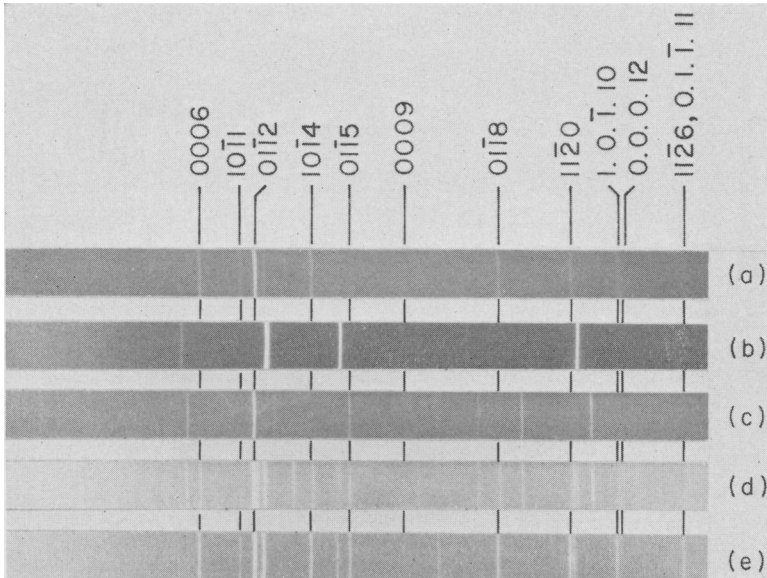


FIG. 1. X-ray diffraction patterns. (a) Sample 2,  $\text{CuFeO}_2$ ; diffraction lines are identified in hexagonal notation. (b)  $\text{Cu}_2\text{O}$ . (c)  $\text{Fe}_3\text{O}_4$ ; the cubic copper-iron spinels have the same pattern except for the scaling resulting from slightly different lattice parameters. (d) Sample 3, containing  $\text{CuFeO}_2$ ,  $\text{Cu}_2\text{O}$ , and spinel. (e) Sample 4, containing  $\text{CuFeO}_2$  and  $\text{Cu}_2\text{O}$ .

TABLE II. Room temperature Mössbauer parameters for  $\text{CuFeO}_2$  phase

| Sample    | IS* (mm/sec)   | $\epsilon$ (mm/sec)† |
|-----------|----------------|----------------------|
| 1‡        | +0.401 ± 0.015 | 0.319 ± 0.015        |
| 2         | +0.393 ± 0.015 | 0.315 ± 0.015        |
| 3         | +0.390 ± 0.015 | 0.322 ± 0.020        |
| 4         | +0.391 ± 0.015 | 0.318 ± 0.015        |
| 5         | +0.395 ± 0.015 | 0.320 ± 0.015        |
| mineral‡§ | +0.394 ± 0.015 | 0.328 ± 0.015        |
| mineral   | +0.397 ± 0.015 | 0.341 ± 0.015        |

\* Isomer shift relative to metallic iron at room temperature.

† Quadrupole interaction, one-half of the doublet separation.

‡ Data from Muir and Wiedersich (1967).

§ Delafossite from Bisbee, Arizona.

|| Delafossite from Nizhnii Tagil (the type locality), B.M. 1914, 42.

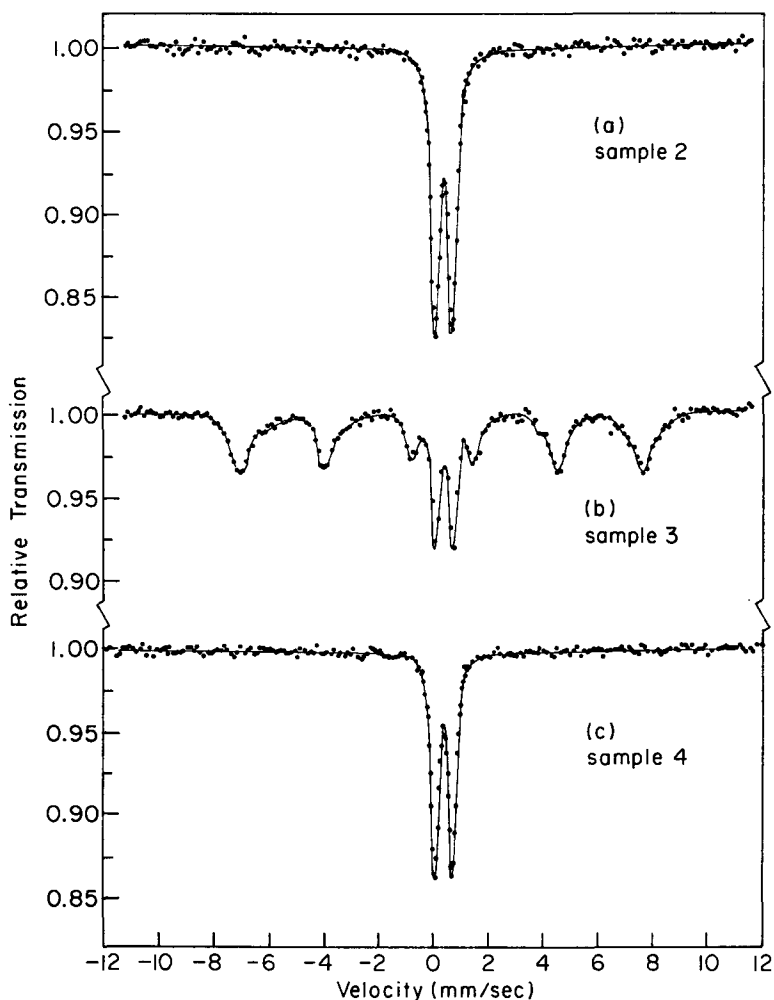


FIG. 2. Mössbauer spectra. (a) Sample 2,  $\text{CuFeO}_2$ . (b) Sample 3; the iron is contained in  $\text{CuFeO}_2$  and a copper-iron spinel. (c) Sample 4; all iron is in the  $\text{CuFeO}_2$  phase.

of  $\text{Cu}_2\text{O}$ , which is just visible. Chemical analysis gave a Fe/Cu ratio of  $1.02 \pm 0.05$  in good agreement with the expected ratio of unity for the compound  $\text{CuFeO}_2$ . If the Cu-Fe-O phase diagram proposed by Gadalla and White (1966) were correct, one would expect sample 2 to consist of ' $\text{Cu}_6\text{Fe}_3\text{O}_7$ ' and a (magnetically ordered) spinel phase, contrary to the present observations.

*Samples 3, 4, and 5.* Several attempts were made to obtain the compound  $\text{Cu}_6\text{Fe}_3\text{O}_7$  proposed by Buist *et al.* (1966). Sample 3, prepared following their method, melted partially during firing and wetted almost the entire surface of the alumina crucible. The unmelted part of the material contained  $\text{Cu}_2\text{O}$ ,  $\text{CuFeO}_2$ , and a spinel according to the X-ray diffraction pattern (fig. 1*d*). The ME spectrum revealed  $\text{CuFeO}_2$  and a magnetically ordered phase similar to that of copper-iron spinels observed previously.<sup>1</sup> From chemical analysis the Fe/Cu ratio was  $0.61 \pm 0.05$ . Especially noteworthy is the appreciable pick-up of aluminium. Similar results have been obtained for the melted part of this material.

The starting mixture for samples 4 and 5 would not require the loss of oxygen to form  $\text{Cu}_6\text{Fe}_3\text{O}_7$ . These samples were fired in a closed system and in flowing argon, respectively. Both treatments gave the same results. The X-ray pattern exhibited the lines of  $\text{Cu}_2\text{O}$  and  $\text{CuFeO}_2$  (fig. 1*e*). The ME spectra, see fig. 2*c*, revealed that all the iron is in the  $\text{CuFeO}_2$  phase. Chemical analysis gave for both samples a Fe/Cu ratio of  $0.55 \pm 0.05$  as compared to the expected ratio of 0.50.

The ME isomer shift (see table II) clearly indicates that all the iron is trivalent, as previously inferred by Pabst (1946) and by Delorme and Bertaut (1953). If the composition proposed by Buist *et al.* (1966) for this phase ( $3\text{Cu}_2\text{O} \cdot \text{Fe}_3\text{O}_4$ ) were correct, one would expect to find evidence for the presence of divalent iron.

### Conclusions

The existence of the compound  $\text{CuFeO}_2$  has been reconfirmed. In view of the agreement of the ME (see Table II), chemical (Hey, 1968), and X-ray results<sup>2</sup> for natural delafossite with those for  $\text{CuFeO}_2$ ,<sup>3</sup> there seems to be no doubt that the mineral is essentially  $\text{CuFeO}_2$ . We were unable to obtain a compound of the composition  $\text{Cu}_6\text{Fe}_3\text{O}_7$  postulated by Buist, Gadalla, and White using either the procedure indicated by these authors or different methods that could yield this compound. In all attempts more than one phase was found. The probable cause of the

<sup>1</sup> A preliminary report of the ME spectroscopy of Cu-Fe oxides has been presented (A. H. Muir, Jr. and H. Wiedersich, *Bull. Amer. Phys. Soc.*, vol. 11, p. 49 (1966)).

<sup>2</sup> The *d*-spacings for the  $\text{CuFeO}_2$  phase are essentially the same as those obtained by Pabst (1946) for natural delafossite.

<sup>3</sup> In table II, it appears that  $\epsilon$  for the minerals is somewhat larger than for the synthetic samples. This can be caused by the impurities present in the mineral samples, since we have found that relatively minor amounts of impurities and very slight structure parameter changes can significantly alter  $\epsilon$  in other compounds.

discrepancies may have been the use of platinum crucible liners by Buist *et al.*, who experienced difficulties with the crucible material. Platinum can easily extract copper from copper-bearing oxides at elevated temperatures.<sup>1</sup> Thus, this process may have reduced the copper content of their final product sufficiently below that of the original charge so as to invalidate their assumptions about the composition of the samples.

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<sup>1</sup> When, as part of another series of measurements, an equimolar mixture of  $\text{CuFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  was fired in a platinum boat at  $1200^\circ\text{C}$  in argon, the resulting product had about half the copper to iron ratio of the charge, showing a preferential extraction of copper. Moreover, spectrographic analysis showed that this material had picked up  $\sim 1\%$  (by weight) Pt. The ME spectrum was very similar to the  $\text{Fe}_3\text{O}_4$  spectrum and unlike the spectra of other samples of the same nominal composition that were not fired in Pt boats.