NOTES ON THE STRUCTURE OF DELAFOSSITE

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Abstract

From a consideration of interionic radii and coordination it is shown that delafossite, $CuFeO_2$, is probably to be considered cuprous metaferrite. That is, the copper is present as cuprous ions and the iron as ferric ions.

Eight years ago I reported to the society[1] on a comparison of spacing measurements derived from powder patterns of delafossite with spacings calculated for the structure of artificial $CuFeO_2$ which had been briefly described by Soller and Thompson. It was concluded that delafossite probably has the same structure as Soller and Thompson's artificial material.[2]

The density calculated from this structure, 5.52 (using the same value of Avogadro's number used by Siegbahn, since it is assumed that Soller and Thompson used Siegbahn wave-lengths), greatly exceeds the value 5.07, then current in the literature, or the highest values I had then been able to obtain from the material used. A few years ago the late Dr. Berman reported to me that the value 5.41 had been obtained on an 8 mg. crystalline sample and this value is now incorporated in the seventh edition of Dana's *System of Mineralogy* and credited to Frondel.

Table 1 shows the spacing measurements and intensity observations on powder patterns of delafossite from various sources compared with theoretical spacings corresponding to the lattice of Soller and Thompson. The discrepancies between the several sets of spacings, especially between the records taken from other publications and those obtained during this work, give an indication of the sort of departures that are often met in *x*-ray identification work. These are probably not due to variations in the delafossite. The smaller differences are near the limits of accuracy of measurement, or may be due to differences in the manner of handling the data, but the absence of any line near 1.253 and the presence of a line at 1.080 reported by Harcourt are somewhat disturbing. It seems unjustified to attribute the 1.080 line to contamination when there is no suggestion of other such lines in the range of the larger spacings where they would be more likely. It seems probable that Harcourt's report on a delafossite pattern leaves something to be desired in the way of careful observation and reporting.

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[1] Crystal structure and density of delafossite (abstract only), *Am. Mineral.*, **23**, 175–176 (1938).

[2] It had earlier been assumed by Ramdohr (*Zentralbl. f. Mineral.*, **A**, 289–303 (1937)) that such is the case.

TABLE 1. INTERPLANAR SPACINGS OF DELAFOSSITE

		Calculated spacings†	Observed spacings and intensities							
			Bisbee Pabst#		Kimberley Pabst#		Waldo*		Bisbee Harcourt**	
hkīl	$h_r k_r l_r$	*d*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
0006	222	2.85	2.87	.45	2.85	.40	2.84	m	2.84	1.0
$01\bar{1}2$	110	2.49	2.52	1.20	2.51	1.15	2.49	s	2.51	5.0
$10\bar{1}4$	211	2.235	2.246	.50	2.230	.45	2.22	m	2.23	1.0
$01\bar{1}8$	332	1.656	1.670	.45	1.666	.40	1.650	m	1.66	1.0
$11\bar{2}0$	$10\bar{1}$	1.512	1.516	.35	1.511	.35	1.507	m	1.515	1.0
$10\bar{1}.10$	433	1.432	1.436	.35	1.436	.35	1.428	m	1.435	0.5
000.12	444	1.424								
$11\bar{2}6$	321	1.337	1.349	.25	1.339	.25	1.332	m	1.340	1.0
$01\bar{1}.11$	443	1.337								
$20\bar{2}2$	200	1.296	1.293	.15	1.295	.15	1.289	w	1.295	0.5
$02\bar{2}4$	220	1.253	1.251	.10	1.253	.05	1.247	w		
$20\bar{2}8$	422	1.117	1.116	.10	1.118	.10	1.113	vw		
									1.080	0.2
$02\bar{2}.10$	442	1.039	1.040	.20	1.039	.15	1.036	w		
$11\bar{2}.12$	543	1.037								
$12\bar{3}2$	$21\bar{1}$	.985	.983		.984		.988	vw		
$21\bar{3}4$	310	.966	—		.966		.962	ew		
							.949	ew		
$12\bar{3}8$	431	.899	.898		.896		.898	vw		
$30\bar{3}0$	$2\bar{1}\bar{1}$	.873	—		.876		—	—		
					.860		.853	vw		
					.830		—			
					—		.813	ew		
					.807		.804	vw		

† For a cell of dimensions $a_r=5.96$, $\alpha=29°26'$; $a_h=3.03$, $c_h=17.09$.

Mo radiation. Intensities recorded in heights of peaks on photometer curves in centimeters. Diffraction patterns obtained through the courtesy of Mr. W. H. Dore, Division of Plant Nutrition, University of California.

* A. W. Waldo, Identification of the copper ore minerals by means of *x*-ray diffraction patterns: *Am. Mineral.*, **20**, 575–597 (1935). Radiation not indicated, s—strong, m—medium, w—weak, vw—very weak, ew—exceptionally weak.

** G. A. Harcourt, Tables for the identification of ore minerals by *x*-ray powder patterns: *Am. Mineral.* **27**, 63–113 (1942). Radiation not indicated.

The technique of *x*-ray identification of crystalline materials, after many years of slow growth has been making more rapid progress in recent years. Unfortunately such failings as that just indicated are likely to be a hindrance. More crystallographic indexing of films and more checks against the literature of crystal structure wherever possible by those who use and especially by those who publish powder data for identification purposes seem to be called for. There are, of course, many cases where such indexing or checking is not feasible, but it has often been omitted for no better reason than that the authors found it too tedious.

Delafossite was first reported from America by Professor Rogers when he described crystals from Bisbee in 1913.[3] At that time Professor Rogers considered the chemical constitution of the mineral and tried to determine the valence of the copper and iron. After several chemical experiments which were not fully decisive it was concluded that "delafossite is probably cuprous metaferrite, $Cu'Fe'''O_2$."

Various methods not available thirty years ago might now be used to discriminate between $Cu''Fe''O_2$ and $Cu'Fe'''O_2$. The method most appropriate to the present case depends on determination of interionic distances in the crystal lattice.

TABLE 2. SUMMARY OF INTENSITY CALCULATIONS FOR DELAFOSSITE WITH Cu IN 0, 0, 0 Fe IN $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ AND O IN u, u, u AND $\bar{u}, \bar{u}, \bar{u}$, AND INTENSITY OBSERVATIONS WITH Mo RADIATION

		Calculated							Observed*	
		u1/9#		1/9		1/10	0.23	7/18	Bisbee	Kimberley
hkil	$h_rk_rl_r$		Δ		Δ					
0003	111	9		10		2	4	51	—	—
0006	222	161	13	174	32	142	150	174	.45	.40
$10\bar{1}1$	100	43		36		40	5	10	—	—
$01\bar{1}2$	110	510	19	529	29	558	264	529	1.20	1.15
$10\bar{1}4$	211	187	9	196	17	213	505	196	.50	.45
$01\bar{1}5$	221	8		7		9	12	24	—	—
0009	333	7		7		5	6	2	—	—
$10\bar{1}7$	322	2		2		0	3	0	—	—
$01\bar{1}8$	332	192	1	193	33	160	176	193	.45	.40
			$\Sigma\|\Delta\|42$		$\Sigma\|\Delta\|111$					
$11\bar{2}0$	$10\bar{1}$			156		156	156	156	.35	.35
$11\bar{2}3$	210			1		0	0		—	—
$10\bar{1}\cdot 10$	433			116 } 138		127 } 159	74 } 103		.35	.35
$000\cdot 12$	444			22		32	29			
$11\bar{2}6$	321			108 } 109		92 } 96	96 } 97		.25	.25
$01\bar{1}\cdot 11$	443			1		4	1			
$02\bar{2}1$	$11\bar{1}$			2		4	1		—	—
$20\bar{2}2$	200			58		65	45		.15	.15
$02\bar{2}4$	220			36		38	75		.10	.05

Calculated with ionic f_0 values. All other intensities calculated with atomic f_0 values. See text.

* Observed intensities measured by heights of peaks on photometric curve in centimeters.

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[3] Delafossite, a cuprous metaferrite from Bisbee, Arizona: *Am. Jour. Sci.*, **35,** 290–294 (1913).

Before proceeding with this it seemed best to check the observed intensities of delafossite powder patterns against intensities calculated from the structure. Table 2 gives all pertinent data. It is seen that the observed intensities of lines on two patterns agree well with the intensities corresponding to the structure given by Soller and Thompson[4] with one $CuFeO_2$ in a rhombohedral cell ($a_r = 5.96$, $\alpha = 29°26'$; $a_h = 3.03$, $c_h = 17.09$) Cu in 0, 0, 0 Fe in 1/2, 1/2, 1/2 and O in 1/9, 1/9, 1/9 and 8/9, 8/9, 8/9. It is to be noted, however, that the lines observed all have $h+k+l=2n$. The intensities of these lines would be the same if any parameters are altered by 1/2, 1/2, 1/2. Hence there is no difference in the intensity of these lines for O in 1/9 (8/9) etc. i.e., 2/18 (16/18) etc., or in 11/18 (7/18) etc. The intensities of lines for which $h+k+l \neq 2n$ are affected by such a parameter change, but no such lines are observed in powder patterns.

Most of the intensity calculations recorded in Table 2 have been made with f_0 values for the neutral atoms as given in the *International Tables for the Determination of Crystal Structures*, vol. **II**, pp. 571 and 572. It may seem that it would have been better to use the scattering factors for the appropriate ions, especially since one of the objects of this work is to check on the valence state of the metals in the structure. Unfortunately tables are lacking for copper or iron ionic scattering factors. The difference in calculated intensities would be slight except for the first line or two, since the scattering power of O and O^{-2}, which differ by 25% at zero scattering angle, differ by only 4.7% at the angle for 222 of delafossite and even less for other lines. For iron and copper the proportional difference in the scattering factors would be much less. Nevertheless, a calculation with improvised ionic scattering factors for Cu^{+1} and Fe^{+3} and the accepted values for O^{-2} has been made for the first ten lines to show that no discrimination as to valence state of the ions is possible on this basis. Comparing the calculated intensities in the first three columns of Table 2 one can conclude that the effect on the intensities of diffracted beams due to change of internuclear distances attending valence change outweighs the effect due to change in scattering power.

Figure 1 shows the variation in intensities of the first ten possible powder lines with variation in the oxygen parameter from 0 to $\frac{1}{2}$. It is seen that Soller and Thompson's choice of parameter is well justified, if we take into account that reducing it below 1/9 is excluded by atomic radii, but that 7/18 gives equally satisfactory agreement of observed and calculated intensities. Our diagram shows also that observation of 100

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[4] Soller, Walter, and Thompson, A. J., The crystal structure of cuprous ferrite: *Phys. Rev.*, **47**, 644 (1935).

and/or 111 or, best of all, a pattern on which the odd orders of *hhh* could be compared would make possible a choice.

Accepting for the moment the oxygen parameter of 1/9 we may draw a picture of the structure and also determine interatomic distances and coordinations. Figure 2 shows such a structure in clinographic projection and 2*a* shows a section through it on a symmetry plane.

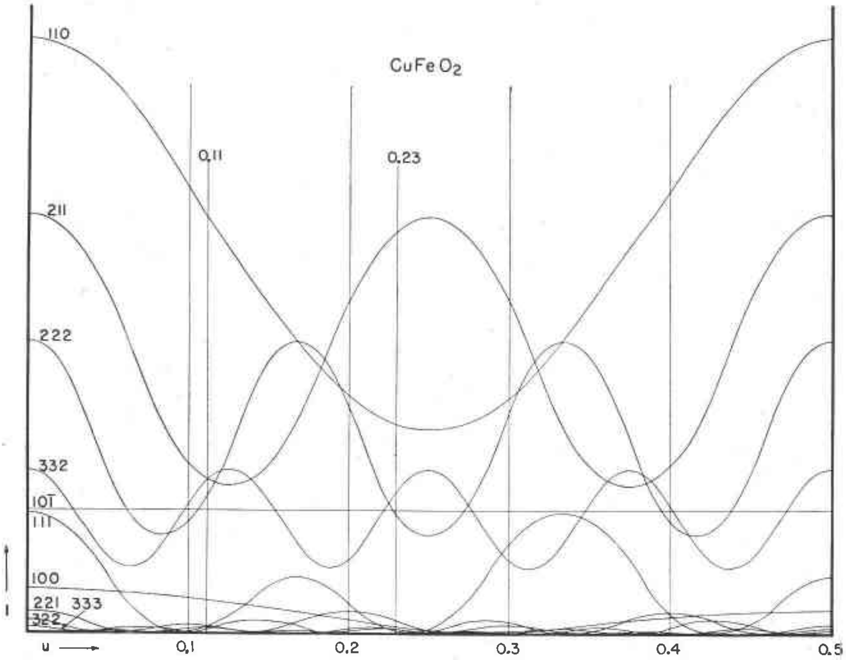

FIG. 1. Variation of intensities of the first ten possible powder lines of delafossite with variation of the oxygen parameter from 0 to $\frac{1}{2}$.

In Fig. 2*a* the radii of the circles representing the ions are made proportional to the ionic radii of Cu (0.96), Fe (0.67), and O (1.32) given by Evans.[5] It is seen that there is overlap of O on adjoining O and on Cu in this case.

If O is given the parameter 7/18, which is in equally good agreement with observed intensities, the configuration shown in the section in Fig. 2*b* results. In this case the overlaps are similar. The coordination, however, is quite different in the two cases. With the parameter 1/9 Cu has a twofold coordination of O about it and Fe a sixfold coordination of O about it. If the oxygen is at 7/18 these coordinations are interchanged.

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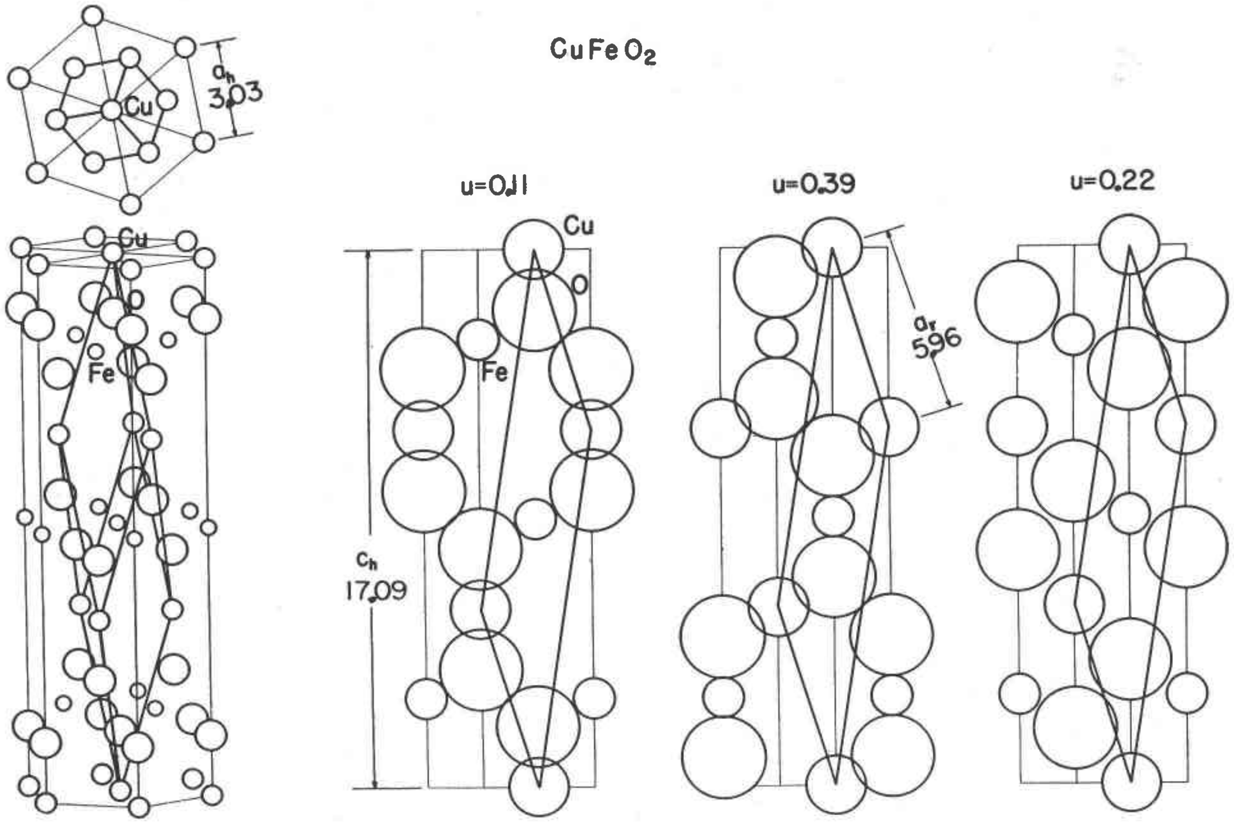
[5] Evans, R. C., *Crystal Chemistry*, Cambridge (**1939**), p. 171.



2 2a 2b 2c

FIG. 2. Clinographic projection of delafossite structure with oxygen parameter 1/9 or 0.11.
FIGS. 2*a*, 2*b* and 2*c*. $1\bar{2}10$ sections through delafossite structures with various oxygen parameters.

It is possible to find an oxygen position in which the distance from oxygen to both Fe and Cu is fully that required by ionic radii. If O is given the parameter 0.23, as in Fig. 2*c*, both Cu and Fe have sixfold coordination and there are no overlaps. If this parameter is decreased the O-O distance and the Fe-O distance are decreased, whereas the Cu-O distance is increased. Since parameters in this range are, however, excluded by intensity observations they will not be further considered no matter how reasonable the corresponding structures.

Table 3. Compounds Having the Crystal Structure Type F 5_1

Formula	$<\alpha$	a_r	u	Strukturbericht
$NaHF_2$	40° 2′	5.05	0.41	Vol. I
$CaCN_2$	43 50	5.11	0.37	Vol. I
NaN_3	38 43	5.48	0.42	Vol. I
$CsICl_2$#	70 42	5.46	0.31	Vol. I
$CuFeO_2$	29 26	5.96	0.11	Vol. III
$NaFeO_2$	31 20	5.59	0.22	Vol. III

In Strukturbericht I, $CsICl_2$ is referred to "Idealfall II" under type *F* 5_1. Wyckoff, on the other hand, makes this the type, his *d* of the RX_3 compounds, and refers the first three of this list to it.

In Volume III of the Strukturbericht $CuFeO_2$ is referred to type *F* 5_1 for which $NaHF_2$ was taken as the example in volume I. Table 3 lists the structures which have been referred to this type. It is seen that $NaFeO_2$ is the only one whose lattice dimensions approach closely those of $CuFeO_2$. The structure of $NaFeO_2$ was determined by Goldsztaub.[6] He assigned Na to 0, 0, 0; Fe to 1/2, 1/2, 1/2 and selected 2/9 for the value of the oxygen parameter. This is close to the value just considered for $CuFeO_2$ and discarded because of intensities, and gives both the Na and the Fe a sixfold coordination.

Table 4a. Interionic Distances and Coordination in Delafossite

	O in 1/9, 1/9, 1/9 and 8/9, 8/9, 8/9		O in 7/18, 7/18, 7/18 and 11/18, 11/18, 11/18	
	Distance	Coordination	Distance	Coordination
O-O	2.583	3	2.583	3
Fe-O	1.991	6	1.899	2
Cu-O	1.899	2	1.991	6

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[6] Goldsztaub, M. S., Etude de quelques derives de l'oxyde ferrique (FeO · OH, FeO_2Na, FeOCl); determination de leurs structures: *Bull. soc. fran. min.*, **58**, 6–76 (1935).

Referring to the structure of delafossite, interionic distances and coordinations for $u=1/9$ and $u=7/18$ are tabulated in Table 4A. A choice between these two parameters cannot be made from the x-ray data available to me and I am unable to say just how Soller and Thompson made their choice, or indeed, whether they considered 7/18 as a possibility. A comparison with known metal-oxygen distances and coordination numbers in the simple oxides of iron and copper is some help in this connection. The pertinent data with references are given in Table 4B. From this it may be seen that with the parameter 1/9 we may interpret delafossite as being cuprous metaferrite, $Cu'Fe'''O_2$, as surmised by Rogers, and that both copper and iron will then have the coordination and nearly the same metal-oxygen distances which have been found in the corresponding simple oxides. If we choose the parameter 7/18 and/or consider delafossite to be $Cu''Fe''O_2$ there is no way of obtaining such an agreement. Pending the availability of better x-ray data we may accept Soller and Thompson's choice of oxygen parameter and conclude that delafossite is indeed cuprous metaferrite as supposed by Rogers.

TABLE 4B. INTERIONIC DISTANCES IN SIMPLE OXIDES OF Cu AND Fe

Material	Interionic Distance	Coordination	Reference
Cuprite Cu_2O	1.843 Cu'-O	2	Niggli, *Zeits. Krist.*, **57,** 253 (1922).
Tenorite CuO	1.95 Cu''-O	4	Tunnell, Posnjak and Ksanda, *Zeits. Krist.*, **90,** 120 (1935).
Wustite FeO	2.14 Fe''-O	6	Wyckoff and Crittenden, *Zeits. Krist.*, **63,** 144 (1926).
Hematite Fe_2O_3	2.06 1.91 Fe'''-O	$\left.\begin{matrix}3\\3\end{matrix}\right\}6$	Pauling and Hendricks, *J.A.C.S.*, **47,** 781 (1925)