# THE CRYSTAL STRUCTURE AND COMPOSITION OF CREDNERITE, $CuMnO_2$

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The parameters of the monoclinic cell of synthetic crednerite have been refined. The formula $CuMnO_2$ assumed on the basis of crystal chemistry has been confirmed by the determination of the density and an analysis of the intensities of the lines. The structure of $CuMnO_2$ has been found to consist of alternating layers of oxygen octahedra and trigonal prisms. The $Mn^{+3}$ ions lie in the centers of the octahedra; the $Cu^{+1}$ ions, on the midpoints of the vertical edges of the prisms.

Heating of mixtures of copper and manganese oxides at temperatures above 1000°C results in the formation of a new phase different from the isometric spinel $CuMn_2O_4$ which forms at lower temperatures.

This phase has been observed by Kurlina, Prokhvatilov, and Sheftel' [1]. They called it the β-phase and pointed out that besides the high temperature, its formation is favored also by a higher copper content than that required by the spinel formula. McAndrew has established [2] the identity of the phase obtained under conditions close to those given above with the copper-manganese mineral crednerite. An investigation of the latter enabled him to determine both the dimensions of its monoclinic cell, a = 5.58 A; b = 2.88 A; c = 5.87 A; β = 104°, and the space groups C2/m, C2, and Cm (from the absence of reflections with odd sum h + k) to which it may possibly belong. From the chemical analyses of synthetic preparations obtained with a Cu : Mn ratio of 1 : 2, McAndrew derived the formula of crednerite in the form $Cu_2Mn_2O_5$. However, the number of molecules in the cell determined on the basis of this formula and the density 5.02 g/cm$^3$ used in his paper is far from being a whole number.

The present work is an attempt to determine the crystal structure and composition of crednerite.

The investigation was made on synthetic preparations obtained by heating pressed mixtures of powdered CuO and $MnO_2$ at 1000-1100°C for several hours and then rapidly cooling them (in air). The result is a dense grayish-black microcrystalline mass. The density of the preparations was determined in a pycnometer filled with water after the air in the pores had been pumped out. The x-ray diffraction photographs were taken with Fe-radiation in common powder cameras (phase analysis) and in the URS-50-I apparatus (to refine the parameters and measure intensities). Angular values corrected for the errors of the counter by the well-known formula [3] were plotted on a diagram. In computing structure amplitudes the values of the atomic amplitudes were corrected for ionization and, in the case of Mn, for dispersion, the latter correction being equal to 4.

It was found that the purest and best formed samples of synthetic crednerite are obtained when the Cu : Mn ratio is unity. The density of these preparations is 5.38 g/cm$^3$; i. e., it differs considerably from the value 5.03 [2] determined on samples of the mineral containing impurities. The powder photograph data are very near to the data given by McAndrew [2] for his synthetic samples. The cell dimensions calculated from our data differ somewhat from the dimensions of the natural crednerite. They are: a = 5.530 ± 0.005; b = 2.884 ± 0.002; c = 5.898 ± ± 0.005 A, β = 104.6 ± 0.1°.

The experimental and computed interplanar distances are given in the table.

| hkl | Interplanar distances and intensities of the lines of $CuMnO_2$ | | | | | hkl | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_{exp}$ | $d_{comp}$ | $F_{comp}$ | $F^2_{comp} P^*$ | $F^2_{exp} P^*$ | | $d_{exp}$ | $d_{comp}$ | $F_{comp}$ | $F^2_{comp} P^*$ | $F^2_{exp} P^*$ |
| 001 | | 5.696 | — 3.5 | 0 | — | $\bar{2}21$ | | 1.269 | —11.4 | 8 | |
| 002 | 2.849 | 2.848 | +30.3 | 29 | 24 | 220 | 1.267 | 1.267 | +26.8 | 45 | 53 48 |
| $\bar{2}01$ | | 2.693 | —16.4 | 9 | 64 | $\bar{4}03$ | — | 1.251 | — 3.9 | 0 | — |
| 200 | 2.672 | 2.672 | +42.0 | 55 | 81 | 401 | — | 1.233 | — 4.9 | 1 | — |
| 110 | 2.534 | 2.534 | —18.6 | 23 | 21 | 312 | (1.231) | 1.232 | —11.7 | 9 | 9 |
| $\bar{1}11$ | 2.428 | 2.425 | +37.1 | 86 | 95 | $\bar{2}22$ | 1.213 | 1.212 | +17.7 | 20 | 18 |
| $\bar{2}02$ | 2.252 | 2.252 | +25.1 | 20 | 21 | 221 | — | 1.206 | — 2.5 | 0 | — |
| 201 | — | 2.213 | + 0.8 | 0 | — | $\bar{1}14$ | — | 1.182 | — 4.6 | 1 | — |
| 111 | 2.220 | 2.219 | +26.4 | 44 | 40 | $\bar{3}14$ | — | 1.170 | —12.4 | 10 | — |
| $\bar{1}12$ | — | 2.017 | — 0.5 | 0 | — | $\bar{2}05$ | — | 1.158 | — 3.6 | 0 | — |
| 003 | 1.897 | 1.899 | —17.3 | 9 | 6 | 023 | — | 1.147 | —12.8 | 10 | — |
| 112 | — | 1.789 | — 7.8 | 4 | — | 204 | — | 1.142 | +17.1 | 9 | — |
| $\bar{2}03$ | — | 1.773 | —10.6 | 3 | — | 005 | — | 1.139 | — 3.0 | 0 | — |
| 202 | 1.741 | 1.741 | +32.6 | 33 | 27 | $\bar{4}04$ | 1.127 | $1.125_8$ | +25.2 | 20 | 9 |
| $\bar{1}13$ | 1.615 | 1.615 | +33.9 | 72 | 60 | $\bar{2}23$ | — | $1.117_3$ | — 8.9 | 2 | — |
| $\bar{3}11$ | 1.548 | 1.548 | +35.0 | 77 | 88 | 402 | — | $1.113_0$ | +26.6 | 22 | 54 38 |
| 310 | — | 1.514 | — 8.4 | 4 | — | 222 | 1.109 | $1.109_5$ | +22.6 | 32 | |
| $\bar{3}12$ | — | 1,475 | — 3.9 | 1 | — | $\bar{1}15$ | 1.088 | $1.088_5$ | +16.7 | 18 | 13 |
| 113 | 1.439 | 1.439 | +32.6 | 66 | 100 | 313 | 1.075 | $1.076_6$ | +22.9 | 33 | 20 |
| 020 | | 1.439 | +32.9 | 34 | 100 | $\bar{5}11$ | 1.028 | $1.028_1$ | +22.7 | 32 | 18 |
| 004 | 1.424 | 1.424 | +25.3 | 20 | 20 | $\bar{3}15$ | — | $1.021_4$ | +17.5 | 19 | — |
| $\bar{2}04$ | 1.412 | 1.413 | +31.1 | 30 | 27 | 024 | — | $1.012_2$ | +19.2 | 23 | — |
| 311 | 1.391 | 1.391 | +20.3 | 26 | 31 | $\bar{2}24$ | 1.009 | $1.008_2$ | +22.6 | 32 | 24 |
| 203 | — | 1.391 | —12.7 | 5 | — | 510 | — | $1.001_5$ | — 3.6 | 1 | — |
| 021 | — | 1.382 | — 5.9 | 1 | — | $\bar{4}05$ | — | $1.000_0$ | — 7.0 | 2 | — |
| $\bar{4}01$ | — | 1.382 | —14.3 | 6 | — | 223 | — | $1.000_0$ | — 9.8 | 6 | — |
| $\bar{4}02$ | — | 1.346 | +23.5 | 17 | 18 | | | | | | |
| 400 | | 1.338 | +22.3 | 15 | 48 | | | | | | |
| $\bar{3}13$ | 1.332 | 1.331 | +23.1 | 33 | 39 | | | | | | |
| $\bar{1}14$ | — | 1.310 | —10.3 | 6 | — | | | | | | |
| 022 | 1.284 | 1.284 | +20.7 | 27 | 22 | | | | | | |

* Arbitrary scale; P is the multiplicity factor.

The small dimensions of the unit cell make it possible to determine its content. Thus, the length of axis b = 2.88 A is characteristic of octahedral coordination and represents the length of the octahedral edge. The values of the other two dimensions suggest that the total number of oxygen octahedra in the cell is four. If all of these octahedra are filled, the content of the cell must be $Me^{I}_{2}Me^{II}_{2}O_4$, or, in our case, $Cu_2Mn_2O_4$. This conclusion is confirmed by determining the number of molecules in the cell which for the formula $CuMnO_2$ gives 1.98, i. e., $2(\rho_{x\text{-ray}} = 5.44, \bar{\rho}_{exp} = 5.39\ g/cm^3)$.

The structures of compounds with such a formula containing the oxides of a univalent and a trivalent metal are of two types. In one of these (including, among others, the low temperature form of $NaNiO_2$ [4], which also has a small monoclinic cell) the layers of octahedra, each filled with ions of one kind, alternate according to the cubic law. The other type, which includes compounds of univalent copper, $CuFeO_2$, $CuCoO_2$, $CuCrO_2$ [5], $CuAlO_2$ and $CuGaO_2$ [6], is characterized by the change of one layer of octahedra into a layer of trigonal prisms (structural type $NaHF_2$).* This change is probably caused by the tendency of the univalent copper toward a two-fold coordination with oxygen.

It was natural to assume that the structure of $CuMnO_2$ is similar to the second type. Indeed, the smallest monoclinic unit cell in this structure has parameters very near those of crednerite. The distribution of the ions

* The statement in paper [6] concerning the octahedral coordination of both ions in the structures of the $CuMeO_2$ type is incorrect. The two-fold coordination of the copper ions follows directly from the parameter of oxygen, which is 0.11-0.12.

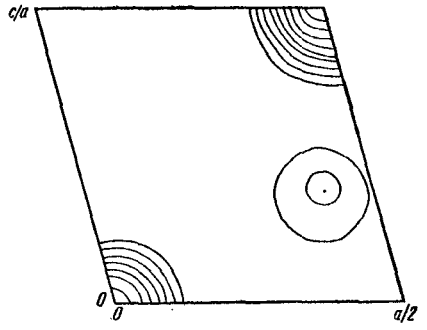


Fig. 1. Section of the electron density of $CuMnO_2$ in the (x0z) plane. The electron density is given in arbitrary units.

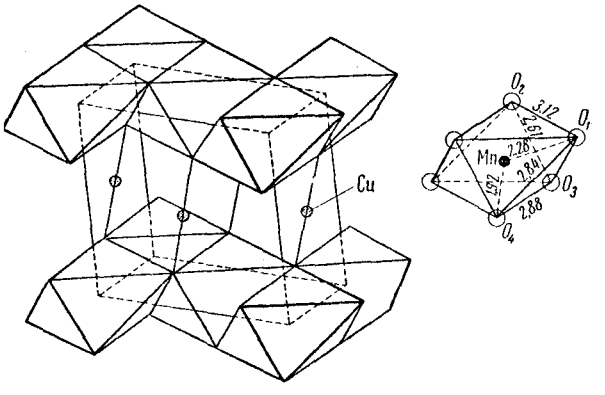


Fig. 2. Structure of $CuMnO_2$

in such a cell which does not contradict the intensities of the lines was assumed as a starting point. It corresponds to the space group C2/m. The Cu and Mn ions occupy positions without any degree of freedom; the ions of oxygen have two degrees of freedom (x and z). To determine the coordinates x and z, a section of the electron density in the (x0z) plane was constructed. The signs of all amplitudes were determined by the positions of the heavy atoms. A sharp oxygen maximum appeared on the section (Fig. 1). However, since only 37 reflections were used in constructing the section, the results cannot be claimed to be very exact.

The positions of the atoms for $CuMnO_2$ in the space group C2/m are as follows:

2Mn in 2(*a*) 000

2Cu in 2(*d*) 0 1/2 1/2

4O in 4(*i*) *x*0*z*,

where $x = 0.41_6$ and $z = 0.14_3$.

The structure factors computed from these coordinates are given in the table. The structure of $CuMnO_2$ is shown in Fig. 2. Within the alternating layers of octahedra and trigonal prisms, the manganese ions occupy the centers of the octahedra and the copper ions, the midedges of the prisms.

The interatomic distances are

| | | | |
|---|---|---|---|
| $Mn-O_1$ | 2.28Å | $O_1-O_2$ | 3.12Å |
| $Mn-O_4$ | 1.92Å | $O_1-O_4$ | 2.84Å |
| $Cu-O$ | 1.80Å | $O_2-O_3$ | 2.61Å |
| | | $O_3-O_4$ | 2.88Å. |

Of the six oxygens in the neighborhood of a manganese ion, four are at the distance of 1.92 A from it and two at the distance of 2.28 A. The shared edges of octahedra are contracted. The Cu–O distance in the chain O–Cu–O is a little shorter than in other compounds of this type [5].

The formula $CuMnO_2$ corresponds to the ideal composition. Some x-ray diffraction data, among them the above-mentioned differences in the unit cell parameters of the synthetic and natural crednerite, and the observed variations in the intensities of the lines on powder photographs of different samples, indicate that the composition of this phase may vary. This is due, evidently, to the change of a part of the metallic ions to a different valence state and a resulting change in the number of metallic ions.

Because of the close similarity of the monoclinic structure of $CuMnO_2$ to that of the rhombohedral copper compounds of the $CuMeO_2$ type, it was supposed by analogy with $NaNiO_2$ [4] that there exists a high-temperature rhombohedral phase. However, photographs taken at 500°C (in air) revealed only the appearance of the phase $CuMn_2O_4$. It is possible that the transition requires a higher temperature and isolation of the sample from atmospheric oxygen.

The structure of crednerite, $CuMnO_2$, is another example of the structural class with trigonal prisms containing atoms with a tendency toward two-fold coordination. Besides the already mentioned compounds of univalent copper, this class contains also the analogous silver compounds [7, 8], the halides ($NaHF_2$ with the $HF_2^-$ group) and the hydroxides $Al(OH)_3$ [9], $CoHO_2$ [10], $CrHO_2$ [11] and $(AlLi)MnO_2(OH)_2$ [12]. In the latter the formation of linear groups is connected with the manifestation of hydrogen bonding.

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