Chalcophanite, $ZnMn_3O_7 \cdot 3H_2O$: New crystal-structure determinations

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ABSTRACT

Single-crystal X-ray structure refinements of the layer zinc-manganese oxide mineral chalcophanite, using crystals from Bisbee, Arizona, and Sterling Hill, New Jersey, yielded unit-cell parameters $a = 7.533(3)$ Å, $c = 20.794(7)$ Å (Bisbee) and $a = 7.541(3)$ Å, $c = 20.824(8)$ Å (New Jersey) and converged to residuals of $R = 0.043$ and $R = 0.041$, respectively, in space group $R\bar{3}$. The structures are similar to one previously reported as triclinic but with significant differences in atom positions and bond lengths. Modeling of the orientation of the water molecule using structure-energy calculations has delineated the hydrogen-bonding scheme in chalcophanite. Probable hydrogen bonds occur between water molecules and between the water oxygen atom and two oxygen atoms in the octahedral sheets, contributing to the binding force between layers.

INTRODUCTION

Chalcophanite, a hydrated zinc-manganese oxide with a layer structure, was originally described by Moore (1875) from Sterling Hill, New Jersey. Subsequently, the mineral has been recognized as a common weathering product in many Mn-bearing base-metal deposits. The crystal structure was determined by Wadsley (1955) in space group $P\bar{1}$ using Weissenberg film data ($R = 0.15$), and he proposed the ideal chemical formula $ZnMn_3O_7 \cdot 3H_2O$.

Chalcophanite is one of a family of tetravalent manganese oxide minerals with layer structures (phyllomanganates) including lithiophorite, birnessite, ranceite, takanelite, and perhaps vernadite. Of these, besides chalcophanite, only the crystal structure of lithiophorite has been thoroughly investigated (Wadsley, 1952; Post and Appleman, unpub. data). It has been suggested that the other phyllomanganates listed above are structural analogues of chalcophanite (e.g., Giovanoli et al., 1970; Chukhrov et al., 1985). Unfortunately, the poorly crystalline nature of these phases has prevented any detailed studies of their structures or crystal chemistry.

As part of a continuing study of the tetravalent manganese oxide minerals, we have completed detailed structure refinements, using single-crystal X-ray diffraction data, for chalcophanite crystals from New Jersey and Arizona. We have determined that the chalcophanite structure has trigonal symmetry, not triclinic as determined by Wadsley (1955), and have obtained accurate atom positions and bond distances in space group $R\bar{3}$. We have also employed structure-energy minimization methods to determine the likely orientation of the water molecule.

EXPERIMENTAL DETAILS

Single crystals of chalcophanite were selected from samples from Sterling Hill, New Jersey (NMNH C1814), the same sample that supplied the crystal used by Wadsley (1955), and from Bisbee, Arizona (NMNH R12334). The crystals are platelets measuring approximately 0.60 mm × 0.30 mm × 0.16 mm (Bisbee) and 0.30 mm × 0.30 mm × 0.01 mm (Sterling Hill). Precession and Laue photographs show an R-centered lattice in Laue Class $\bar{3}$ for both crystals, indicating space group $R3$ or $R\bar{3}$. The threefold axis is normal to the platelets. This does not agree with the triclinic ($P\bar{1}$) symmetry found by Wadsley (1955), but is consistent with Moore's (1875) initial description of chalcophanite as rhombohedral, based on crystal morphology. It is puzzling that Wadsley reported not observing any symmetry in a Laue photograph taken normal to the platelets. Wadsley's triclinic cell ($a = 7.54$ Å, $b = 7.54$ Å, $c = 8.22$ Å, $\alpha = 90°$, $\beta = 117.2°$, $\gamma = 120°$) is related to our trigonal cell (Table 1) by $/-1$, 0, 0 $/0$, -1, 0 $/2$, 1, $3/$. A pronounced R-centered subcell ($a = 2.88$ Å, $c = 20.79$ Å) is apparent in the precession photographs. The weaker reflections defining the true cell result from the ordering of vacancies in the octahedral layer (see below).

Electron-microprobe analyses of chalcophanite from Sterling Hill, New Jersey, reported by Ostwald (1985), yield a chemical formula that is very close to $ZnMn_3O_7 \cdot 3H_2O$, which is also consistent with microprobe analyses of the specimen from Bisbee, Arizona. In both cases, water was determined by difference.

Intensity data were collected with a Krisel-automated Picker four-circle diffractometer by the step-scan mode, using Zr-filtered Mo$K\alpha$ radiation. The experimental parameters are summarized in Table 1. The reflections were examined graphically and background points adjusted as needed. Reflections with intensities greater than 4σ and 3σ, for the Bisbee and New Jersey data sets, respectively, were tagged as observed. Many of the reflections are broad or partially split, especially for the Bisbee crystal, indicating slight misalignment between platelets. The data were corrected for absorption using the Gaussian integration method in the XTAL crystallographic computing package (Stewart and Hall, 1985) for $\mu = 88$ cm^{-1} (*International Tables for X-ray Crystallography,* 1974). Refinement of setting angles by the method of Hamilton (*International Tables for X-ray Crystallography,* 1974) for 20 reflections ($45° < 2\theta < 60°$) yielded the unit-cell parameters listed in Table 1.

The structure refinements were performed using the XTAL computing package (Stewart and Hall, 1985). Statistical distributions of the normalized structure factors strongly indicate a centrosymmetric structure ($R\bar{3}$). Scattering factors (Mn^{4+}, Zn^{2+},

TABLE 1. Crystal and structure refinement data

	Bisbee	New Jersey
Space group	$R\bar{3}$	$R\bar{3}$
a (Å)	7.533(3)	7.541(3)
c (Å)	20.794(7)	20.824(8)
2θ range (°)	3–70	3–60
Data collected	$\pm h, k, \pm l$	$\pm h, k, \pm l$
Step-scan parameters		
Step size (°)	0.04	0.04
Time/step (s)	4.0	4.0
Standard reflections	2	2
Time between standards (min)	180	180
Merging R factor for equivalent reflections (%)*	8.3	7.8
Unique reflections		
observed	824	587
unobserved	108	92
Parameters refined	43	43
R factor	0.043	0.041

* Calculated for observed and unobserved reflections.

Fig. 1. Projection of the chalcophanite structure along a.

O$^-$) and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974). The positions of the Mn and Zn atoms were determined by using a sharpened Patterson map, and the oxygen atoms were located with subsequent Fourier-difference syntheses. Full-matrix least-squares refinements with isotropic temperature factors of the Arizona and New Jersey chalcophanite structures yielded residuals of 0.050 and 0.043, respectively, for reflections tagged as observed (see Table 1). Inclusion of anisotropic temperature factors in the refinement resulted in final residuals of 0.043 and 0.041, respectively. Refinement of the occupancies of Zn, Mn, and water sites indicated that each was fully occupied. Difference-Fourier maps calculated using the final parameters showed maximum electron-density peaks near the Zn and Mn atoms of 1.2 and 1.0 e/Å³ for the Arizona and New Jersey structures, respectively. Most likely these difference peaks are the result of the poor quality (broadening and splitting) of many reflections and of crystal-measurement errors for the absorption correction.

Observed and calculated structure factors are given in Tables 2 and 3,[1] and atom positions and bond lengths are listed in Tables 4 and 5, respectively.

DISCUSSION

The structures reported here are similar to that determined by Wadsley (1955) but with significant differences in atom positions and bond lengths. There are no significant differences between the refined atom positions and bond lengths for the New Jersey and Arizona chalcophanite structures, and in the discussion below, all references are to the Bisbee structure unless otherwise stated.

The chalcophanite structure consists of sheets of edge-sharing $Mn^{4+}O_6$ octahedra alternating with layers of Zn cations and water molecules in the stacking sequence $\cdots Mn\text{-}O\text{-}Zn\text{-}H_2O\text{-}Zn\text{-}O\text{-}Mn\cdots$ (Fig. 1). One out of every seven octahedral sites in the Mn-O sheet is vacant (Fig. 2), and the Zn cations are above and below the vacancies.
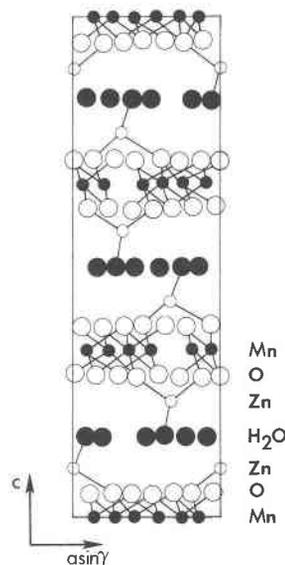
Our refinements confirm that the vacant octahedral sites in the Mn layers are completely ordered. The Mn coordination octahedron is distorted, with Mn–O bond lengths ranging from 1.857 Å to 1.967 Å (Table 5). The mean distance of 1.91 Å is typical for Mn^{4+} in octahedral coordination, e.g., the mean Mn^{4+}–O distance in pyrolusite is 1.887 Å (Baur, 1976). The Mn cations are displaced from the center of the octahedron toward the vacancy (and away from Mn cations in neighboring octahedra), resulting in distances to the O2 atoms (nearest the vacant site) of 1.857 Å and 1.869 Å, compared with 1.937 Å and 1.967 Å to O3 and O1, respectively (Fig. 2). The larger mean Mn–O distance (1.94 Å) found for lithiophorite (Post and Appleman, unpub. data) reflects the presence in that structure of both Mn^{3+} and Mn^{4+}. Previous studies have suggested that some lower-valence Mn might also occur in chalcophanite (Wadsley, 1955; Ostwald, 1985). The average Mn–O bond lengths observed in this study, however, indicate that our chalcophanites apparently have little if any lower-valence Mn in the Mn sites. If some lower-valence Mn is present in the octahedral layer, then the charge must be balanced by substituting hydroxyl for oxygen anions or by increasing the number of cations in the interlayer region. Fourier-difference maps show no evidence in either of our chalcophanite structures for extra interlayer cation sites, including the site observed by Wadsley (1955).

The Zn cations occupy sites directly above and below the vacancies in the Mn octahedral sheet and are coordinated to three O2 atoms (2.069 Å) and three water oxygen atoms (O4) (2.14 Å). The Zn cations are displaced

TABLE 4. Chalcophanite atom positions and temperature factors

		X	Y	Z	U_{iso}*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	B	0.71869(10)	0.57771(11)	0.99948(3)	68(2)	57(2)	58(3)	90(3)	29(2)	2(2)	1(2)
	NJ	0.71873(13)	0.57764(13)	0.99951(4)	58(2)	52(4)	55(4)	65(3)	28(3)	0(3)	−0.1(3)
Zn	B	0	0	0.09997(5)	105(2)	100(3)	100(3)	117(4)	50(1)	0	0
	NJ	0	0	0.09995(6)	101(3)	102(4)	102(4)	99(5)	51(2)	0	0
O1	B	0.52784(53)	0.62297(52)	0.04721(15)	83(6)	98(13)	83(13)	80(12)	50(12)	0(11)	−5(10)
	NJ	0.52817(65)	0.62287(63)	0.04701(19)	76(7)	94(19)	65(18)	76(17)	41(16)	7(14)	−3(14)
O2	B	0.26077(54)	0.20655(53)	0.05048(16)	101(6)	97(14)	95(14)	122(14)	55(12)	28(11)	26(11)
	NJ	0.26021(68)	0.20621(65)	0.05036(19)	87(8)	98(19)	87(19)	89(17)	54(16)	12(15)	−8(14)
O3	B	0	0	0.71250(27)	82(10)	93(15)	93(15)	63(22)	46(7)	0	0
	NJ	0	0	0.71224(33)	84(13)	95(21)	95(21)	63(30)	48(10)	0	0
O4	B	0.17900(63)	0.93107(63)	0.16435(19)	167(7)	152(17)	182(18)	160(15)	73(15)	−28(13)	4(14)
	NJ	0.17910(79)	0.92996(77)	0.16463(23)	160(9)	169(23)	166(23)	128(18)	69(17)	−19(18)	7(17)

Note: "B" indicates Bisbee crystal and "NJ" indicates New Jersey crystal.
* Temperature-factor coefficients are in $Å^2 \times 10^4$; anisotropic temperature factors have the form $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$.

along an octahedral triad axis toward the vacancy (Table 5). The mean Zn–O distance of 2.11 Å is the same as that predicted using the ionic radii of Shannon (1976).

The water molecules in chalcophanite, like the Mn atoms, form a hexagonal close-packed layer with one out of seven molecules absent. Infrared spectroscopic studies of chalcophanite by Potter and Rossman (1979) indicate a crystallographically ordered water molecule with about the same degree of hydrogen bonding as in water. Our structure refinement confirms the ordered nature of at least the water oxygen atom (as indicated by the reasonable thermal parameters refined for O4) and reveals one obvious hydrogen-bond distance of 2.765 Å between water oxygen atoms (O4-O4 in Table 5). Several distances in the range 2.87–3.06 Å from the water oxygen to O1 and O2 in the Mn octahedral layer suggest other possible hydrogen bonds. It was not possible to locate the H positions from difference-Fourier maps calculated for either chalcophanite structure. Consequently, we used structure-energy calculations to model the orientation of the water molecule.

The structure-energy calculations were performed using the computer program WMIN (Busing, 1981), modified to use short-range energy parameters derived from modified-electron-gas (MEG) calculations (Post and Burnham, 1986). Because the MEG theory does not permit calculation of parameters involving H⁺, we used short-range parameters for O–H interactions derived by fitting to observed layer silicate structures containing OH⁻ anions (Abbott et al., 1989). During the energy-minimization procedure, the chalcophanite framework was fixed to the structure refined for the Bisbee sample, and an idealized water molecule (O–H = 0.97 Å) was allowed to rotate and translate. Similar modeling of water molecules in other mineral structures (e.g., gypsum) has yielded excellent results, compared with experimental data (unpub. results). The fact that the minimized water oxygen–atom position for chalcophanite agrees to within 0.07 Å with the refined site also supports the validity of the model calculations. The minimum-energy orientation of the water molecule is shown in Figure 2, and the H positions are H1 (0.229, 0.025, 0.198); H2 (0.310, 0.940, 0.144).

The final Fourier-difference maps for each of the chalcophanite structures show 0.5 to 0.8 e/Å³ peaks close to the minimized H-atom positions, again giving us confidence that our model is correct. Pertinent distances and angles involving the H atoms, calculated using the minimum-energy H positions, are included in Table 5.

Table 5 lists three O–H distances less than 2.40 Å, the range typically indicative of significant hydrogen bonding (Baur, 1972): 1.98 Å (O4–H2), 2.11 Å (O2–H1), and 2.19 Å (O1–H2). The strongest hydrogen bond, assumed to correpond to the shortest O4···O and H···O distances, is between water molecules. The remaining two apparent hydrogen bonds are between the water molecule and O1 and O2 in the Mn octahedral layer, and they contribute to the binding force between the layers. The O3 atom does not significantly participate in the hydrogen-bonding scheme.

The results of our refinements are consistent with the composition $ZnMn_3O_7 \cdot 3H_2O$. Previous studies report a

TABLE 5. Selected Bisbee chalcophanite bond lengths (Å) and bond angles (°)

Mn–O1	1.967(4)	O2–O2 (× 2)	3.110(6)
–O1'	1.891(4)	–O2 (× 2)	2.762(7)
–O1''	1.913(7)	–O3	2.711(4)
–O2	1.857(5)	–O4	3.002(6)
–O2'	1.869(4)	–O4	2.871(7)
–O3	1.937(3)	–O4	2.941(5)
⟨Mn–O⟩	1.906		
		O3–O4 (× 3)	3.057(7)
Zn–O2 (× 3)	2.069(3)		
–O4 (× 3)	2.140(8)	O4–O4 (× 2)	2.765(6)
⟨Zn–O⟩	2.105	–O4 (× 2)	2.892(11)
		–O4	3.124(5)
O1–O1	2.586(5)		
–O1 (× 2)	2.866(8)	H1–O2	2.11
–O2	2.503(5)	–O3	2.41
–O2	2.815(9)		
–O2	2.754(5)	H2–O1	2.19
–O3	2.546(6)	–O4	1.98
–O3	2.853(5)		
–O4	2.914(6)	O2–H1–O4	144
–O4	2.961(6)	O3–H1–O4	125
		O1–H2–O4	130
		O4–H2–O4	135

Note: Bond lengths for the structure of New Jersey crystal are within errors of above values. H positions from structure-energy model were used in calculations of bond lengths and angles involving H atoms.
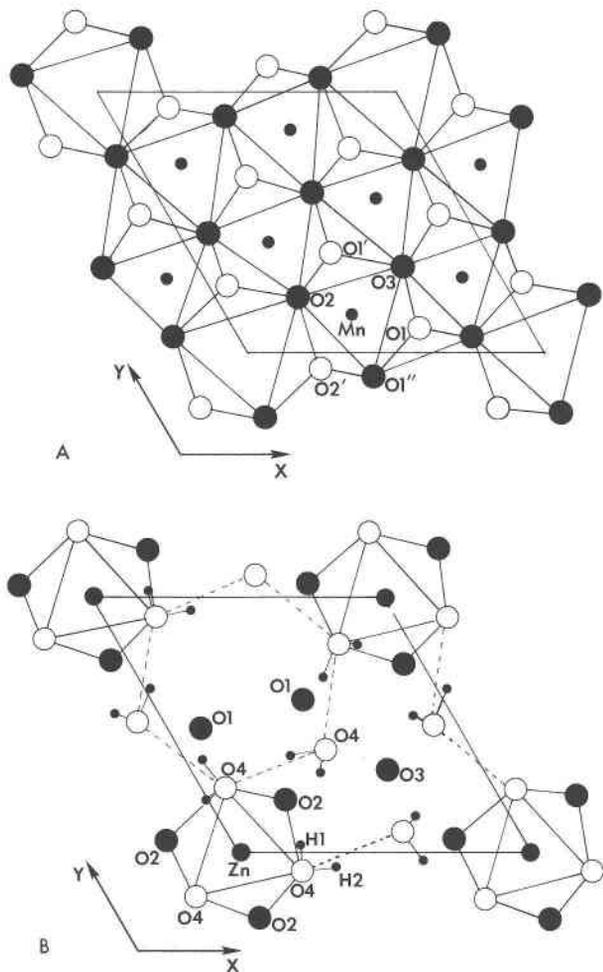
Fig. 2. (A) Mn,O octahedral layer in chalcophanite, projected down c. The small solid circles represent Mn atoms at about $z = 0$, and the large circles represent oxygen atoms at about $z = 0.05$ (solid) and $z = -0.05$ (open). (B). Zn and water (O4) layers in chalcophanite, projected down c. The large circles represent oxygen atoms at about $z = 0.05$ (solid) and $z = 0.165$ (open), and the medium-sized solid circles represent Zn atoms at $z = 0.100$. H-atom (small solid circles) positions are from structure-energy modeling. Probable hydrogen bonds between water molecules are indicated by dashed lines.

considerable range of chalcophanite compositions from several localities. For example, Mg- (Potter and Rossman, 1979), Ni- (Elias et al., 1981), and Ag-rich (Radtke et al., 1967) chalcophanites have been described. Ostwald (1985) also reported a possible Mn^{2+}-rich chalcophanite. In each of these cases, X-ray powder-diffraction and infrared studies suggest that the materials are isostructural with the Zn-bearing chalcophanite described here. Presumably the Mg, Ni, etc. substitute for the Zn. As mentioned above, it has been suggested that birnessite, ranceite, and takanelite are derivatives of chalcophanite, with Na^+, Ca^{2+}, K^+, and Mn^{2+} as the interlayer cations. Chukhrov et al. (1985) have proposed a birnessite structure based on that of chalcophanite but with a random arrangement of the vacancies in the Mn octahedral layers. X-ray powder-diffraction patterns of these layer Mn oxides show major differences as well as similarities to those of chalcophanite and cannot be indexed using the chalcophanite unit cell. In addition to having different interlayer cations, the phyllomanganate minerals listed above also typically contain less water than chalcophanite (Ostwald, 1985).

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