

Schoonerite: its atomic arrangement

ANTHONY R. KAMPF¹

Department of the Geophysical Sciences
The University of Chicago
Chicago, Illinois 60637

Abstract

Schoonerite, $\text{ZnMn}^{2+}\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{OH})_2(\text{H}_2\text{O})_7(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$, orthorhombic, a 11.119(4), b 25.546(11), c 6.437(3) Å, $Pmab$, $Z = 4$, is one of several structurally-related phosphate minerals having axial repeats approximating 6.4 Å. The structure was solved by Patterson and Fourier syntheses, and least-squares refinement converged to $R(hkl) = 0.085$ for 897 nonequivalent reflections.

Edge-sharing Fe^{2+} -O octahedral chains join by sharing corners with Fe^{3+} -O octahedra and $[\text{PO}_4]$ tetrahedra forming a sheet parallel to $\{010\}$. To this sheet are linked additional $[\text{PO}_4]$ tetrahedra, $[\text{MnO}_6]$ octahedra and $[\text{ZnO}_6]$ polyhedra. The resultant slabs are joined in the b direction by a network of hydrogen bonds only. Interlayer water molecules contribute to this hydrogen bond network.

Average interatomic distances are $^{56}\text{Fe}^{2+}(1)\text{-O}$ 2.12 Å, $^{56}\text{Fe}^{2+}(2)\text{-O}$ 2.15, $^{56}\text{Fe}^{3+}(3)\text{-O}$ 2.00, $^{55}\text{Mn}^{2+}\text{-O}$ 2.16, $^{65}\text{Zn}\text{-O}$ 2.09, $^{31}\text{P}(1)\text{-O}$ 1.54, and $^{31}\text{P}(2)\text{-O}$ 1.54.

Introduction

In the preceding paper, Moore and Kampf (1977) described the new species, schoonerite, $\text{ZnMn}^{2+}\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{OH})_2(\text{H}_2\text{O})_7(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$, $Z = 4$, from the Palermo No. 1 pegmatite in North Groton, New Hampshire. Although this species is rather widely distributed at Palermo, it occurs only sparingly as sprays of small, thin, feathery crystals in pockets and on fracture surfaces. A water determination was deemed unfeasible due to the difficulty in obtaining a sufficient quantity of pure material. The determination of the crystal structure of schoonerite was considered the best method for obtaining an accurate measure of its water content and for characterizing its rather complex crystal chemistry.

Besides accomplishing these ends, the crystal structure determination revealed a close similarity between the structures of schoonerite and montgomeryite, and in addition showed that schoonerite possesses octahedral and tetrahedral clusters locally similar to those in olmsteadite and melonjosephite.

Experimental

Good single crystals of schoonerite are exceedingly rare, and such crystals large enough for structure

analysis seemed for quite some time nonexistent. The crystal chosen, a thin rectangular tablet measuring $0.32 \times 0.01 \times 0.08$ mm along the three crystallographic axes, was mounted with the a axis parallel to the ϕ axis on a Picker automated diffractometer. The intensities of 2383 reflections (maximum $2\theta = 45^\circ$) were gathered, utilizing graphite-monochromatized $\text{MoK}\alpha$ radiation. A rather large mosaic spread necessitated wide half-angle scans of 1.0° with a scan rate of $2.0^\circ/\text{minute}$. Twenty-second background counting times were used on either side of each reflection. The least-squares refinement of 30 reference reflections ($2\theta = 20\text{--}30^\circ$) yielded cell constants, a 11.119(4), b 25.546(11), and c 6.437(3) Å. Systematic extinctions were consistent with either of the space groups $P2ab$ or $Pmab$.

The measured intensities were corrected for absorption using the Gaussian integral method described by Burnham (1966). The data were processed by conventional computational procedures. After averaging symmetry-equivalent reflections and rejecting all $I(hkl) < 3\sigma [I(hkl)]$, 897 independent data were available for the ensuing analysis.

Solution and refinement of the structure

The Patterson map, $P(uvw)$, revealed strong vector concentrations at the levels $u = 0, \frac{1}{4},$ and $\frac{1}{2}$, indicating that the twenty heavy atoms (Fe, Mn, Zn) in

¹ Present address: Geology-Mineralogy Section, Los Angeles County Museum of Natural History, 900 Exposition Blvd., Los Angeles, California 90007.

the unit cell (suggested by the probe analysis) were located on special positions of equipoint rank number four at $x = 0$ and $1/4$ for the space group $Pmab$. The five nonequivalent heavy atom positions with similar scattering powers resulted in a complicated Patterson map.

The 6.4 Å c -axis repeat suggested the existence of edge-sharing chains of octahedra and/or corner-sharing chains of alternating octahedra and tetrahedra, as noted in the structures of olmsteadite, melon-josephite, montgomeryite, and vauxite, all of which possess similar axial repeats in one direction. A large Patterson peak at $0, 0, 1/2$ confirmed the existence of edge-sharing chains of octahedra parallel to the c axis. Peaks at $1/2, 0, 0$ and $1/2, 0, 1/2$ indicated that the chains are separated by one-half of the a -axial repeat, and strong vector concentrations along the Harker lines $0, 1/2, w$ and $1/2, 1/2, w$ suggested that the cations in the chains occur on two nonequivalent special positions of the type $0, 1/4, z$. The placement of an octahedral cation on a special position on the mirror plane ($x = 1/4$) as suggested by a Patterson peak at $1/4, 0.06, 0.25$ and the proper orientation of the hypothetical octahedra about the cationic positions provided a clustering reminiscent of those in the aforementioned structures. By analogy, the linking PO_4 tetrahedra could be placed.

The Patterson peaks along the Harker lines $0, 1/2, w$ and $1/2, 1/2, w$ provided evidence for the location of the polyhedral sheet along the c axis; however, this evidence was clouded by homometricity. Fourier syntheses based on a first attempt at placing the polyhedral framework permitted resolution of most of the oxygens in the sheet as well as additional cations; however, R remained about 0.40. A good fit between observed and calculated $F(hkl)$'s indicated that the x and y atomic coordinates were essentially correct. Reexamination of the Patterson map provided a second possible positioning along z . Subsequent Fourier syntheses based on this positioning resolved all non-hydrogen atoms. Full-matrix least-squares refinement, using the NUCLS program, a modified version of ORFLS by Busing *et al.* (1962), and including all atomic coordinates and isotropic thermal vibration parameters converged to $R(hkl) = 0.085$ and $R_w(hkl) = 0.064$, where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2}$$

The scattering curves for Zn^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} ,

TABLE 1. Schoonerite. Cell multiplicities, atomic coordinates, and isotropic thermal parameters*

Atom	Mult.	x	y	z	B(Å ²)
Zn	4	0.2500	0.1034(1)	0.8538(6)	1.80(8)
Mn	4	.2500	.4149(2)	.2255(6)	1.41(10)
Fe(1)	4	.0000	.2500	.0879(6)	1.08(8)
Fe(2)	4	.0000	.2500	.5770(6)	1.57(9)
Fe(3)	4	.2500	.1871(1)	.3272(6)	0.67(8)
P(1)	8	.0303(5)	.1199(2)	.1427(7)	0.69(9)
O(1)	8	.024(1)	.3282(5)	.060(2)	1.4(3)
O(2)	8	.067(1)	.4153(5)	.228(2)	1.1(3)
O(3)	8	.091(1)	.0917(5)	.957(2)	1.6(3)
O(4)	8	.122(1)	.1320(4)	.320(2)	1.2(2)
P(2)	4	.2500	.2169(3)	.8248(12)	0.53(13)
O(5)	4	.250	.1820(7)	.022(3)	0.6(4)
O(6)	4	.250	.1788	.636(5)	0.7(3)
O(7)	8	.136(1)	.2505(5)	.825(2)	1.2(2)
OH	8	.124(1)	.2430(5)	.329(2)	1.5(3)
OW(1)	8	.260(1)	.3329(4)	.618(2)	1.1(3)
OW(2)	4	.250	.3451(7)	.437(3)	1.1(4)
OW(3)	4	.250	.3623(8)	.952(3)	2.0(5)
OW(4)	4	.250	.4614(7)	.517(3)	1.4(4)
OW(5)	4	.250	.4882(8)	.038(3)	2.0(4)
OW(6)	4	.250	.0659(8)	.584(3)	2.9(5)
OW(7)	8	.054(1)	.4815(5)	.763(2)	2.0(3)

* Estimated standard errors refer to the last digit.

P^0 and O^{1-} were obtained from Cromer and Mann (1968), and included the anomalous dispersion terms for Zn, Mn, and Fe. Atomic coordinates and isotropic thermal vibration parameters are given in Table 1, and the observed and calculated structure factors are listed in Table 2.²

Discussion

Description of the structure

Schoonerite possesses a rather complex sheet structure (Fig. 1) based on a clustering of Fe-O octahedra. Chains of edge-sharing Fe^{2+} -O octahedra parallel to the c axis are linked in the a direction to equivalent chains by Fe^{3+} -O octahedra. Some $[PO_4]$ tetrahedra further link the chains in the a direction, as well as the Fe^{3+} -O octahedra in the c direction, while others share each of their vertices with different cations, including Fe^{2+} , Fe^{3+} , Mn^{2+} , and Zn^{2+} . $[ZnO_5]$ polyhedra are linked to the sheet by sharing four of their vertices with $[Fe^{3+}O_6]$ and/or $[PO_4]$ polyhedra, the other vertex remaining unshared. $[MnO_6]$ octahedra link only by sharing two *trans*-vertices with $[PO_4]$ tetrahedra.

² To obtain a copy of this table, order Document AM-76-038 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for the microfiche.

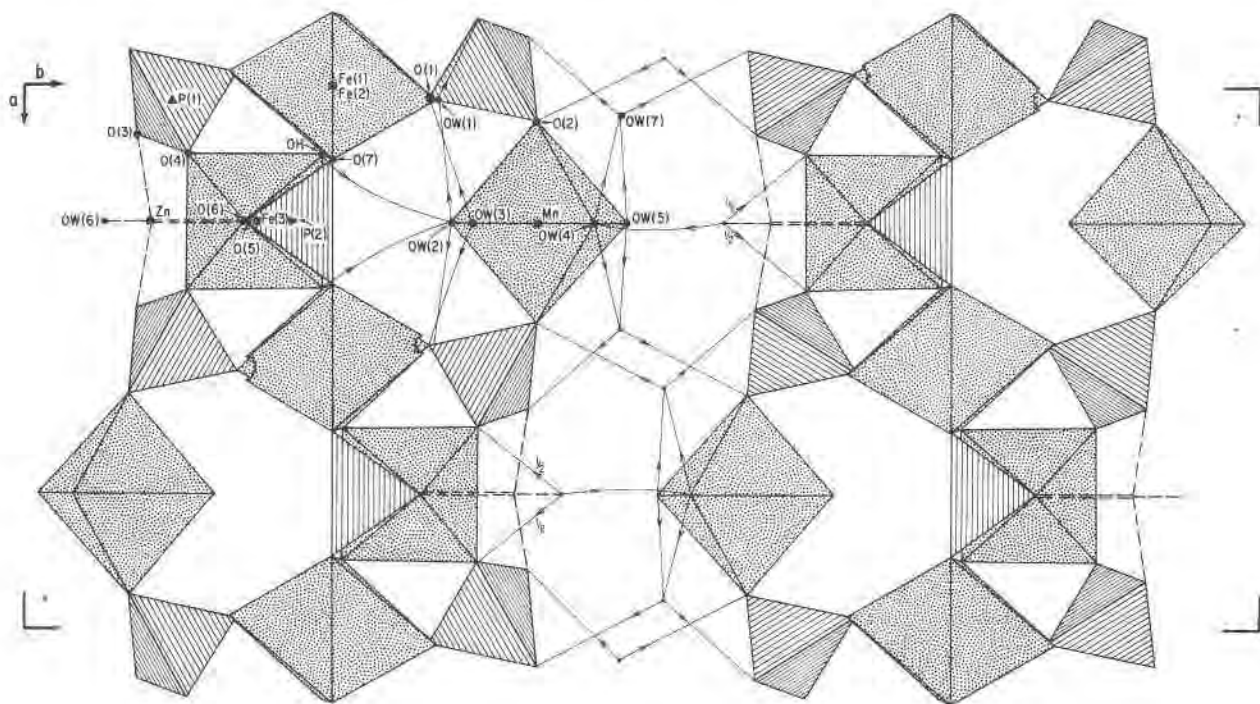


FIG. 1. The schoonerite crystal structure viewed down [001]. The Fe-O and Mn-O octahedra are stippled and the P-O tetrahedra are ruled. Zn-O bonds are shown as dashed lines and hydrogen bonds as thin lines with arrows pointing toward the acceptors of the hydrogen bonds.

Free water molecules are located between the sheets parallel to the {010} plane. These contribute to an extensive system of hydrogen bonding which serves as the only linkage between the sheets. This is consistent with the perfect {010} cleavage of schoonerite and the tendency of this mineral to form exceedingly thin crystals parallel to {010}.

Interatomic distances and angles

Interatomic distances and angles are listed in Table 3. Electrostatic bond strengths and their sums about the anions are tabulated in Table 4 for comparison with bond distances according to the extended electrostatic valence rule of Baur (1970).

The average Me-O distances compare favorably with the distances calculated using the ionic radii from the tables of Shannon and Prewitt (1969). The averages, followed by the calculated values in parentheses, are $^{16}\text{Fe}^{2+}(1)\text{-O}$ 2.12(2.13); $^{16}\text{Fe}^{2+}(2)\text{-O}$ 2.15(2.14); $^{16}\text{Fe}^{3+}(3)\text{-O}$ 2.00(2.01); $^{16}\text{Mn}^{2+}\text{-O}$ 2.16(2.18); $^{16}\text{Zn}^{2+}\text{-O}$ 2.09(2.04); P(1)-O 1.54(1.52), and P(2)-O 1.54(1.53 Å).

Deviations from average bond lengths can be roughly correlated with degree of bond strength undersaturation or oversaturation of the anions. The

most highly undersaturated oxygens, O(2) and O(3), participate in the short bonds Mn-O(2), P(1)-O(2), and Zn-O(3). Both O(5) and O(6), which form very long bonds with Zn, are appreciably oversaturated. Fe(1)-O and Fe(2)-O bond length variations are somewhat anomalous, however. In particular, the long bond lengths associated with the slightly undersaturated O(7) atom are inconsistent with the electrostatic model. These may result from structural restrictions coupled with an apparent attraction between Fe^{2+} cations across the OH-OH shared edge.

Moderate distortions in the Fe(1) and Fe(2) octahedra are further indicated by wide ranges of O-Fe-O angles. These are seen to be related in part to normal angular distortion associated with edge-sharing chains, *i.e.*, small OH-Fe-OH and O(7)-Fe-O(7) angles and large OH-Fe-O(7) angles.

An irregular 5-coordination occurs around the Zn site, which can be best described as a tetrahedron with one split vertex. The split vertex corresponds to O(5) and O(6), and the O(5)-Zn-O(6) angle is 64.4° . If these are merged into a single vertex along the edge of the P(2)O₄ tetrahedron, the distance between Zn and this vertex is 1.99 Å. This is comparable to the remaining Zn-O distances and yields an average

TABLE 3. Schoonerite. Interatomic distances and angles*

Zn		Fe(1)		Fe(2)		Fe(3)	
2 Zn	- O(3) 1.91(1) Å	2 Fe(1)-O(1)	2.02(1)	2 Fe(2)- OH	2.11(1)	Fe(3)- O(5)	1.97(2)
	-OW(6) 1.99(2)	- OH	2.08(1)	-OW(1)	2.15(1)	- O(6)	2.00(2)
	- O(5) 2.28(2)	-O(7)	2.27(1)	- O(7)	2.20(1)	2 - O(4)	2.00(1)
	- O(6) 2.38(2)	average	2.12	average	2.15	2 - OH	2.00(1)
average	2.09					average	2.00
Mn		P(1)		P(2)		Hydrogen Bonds	
2 Mn	- O(2) 2.03(1)	P(1)-O(2)	1.51(1)	2 P(2)-O(7)	1.53(1)	OH - OW(2)	3.04(2)
	-OW(3) 2.22(2)	-O(3)	1.55(1)	-O(5)	1.55(2)	OW(1)- O(1)	2.85(2)
	-OW(4) 2.22(2)	-O(1)	1.55(1)	-O(6)	1.56(2)	OW(1)- O(4)	2.69(2)
	-OW(5) 2.23(2)	-O(4)	1.56(1)	average	1.54	2 OW(2)- OW(1)	2.76(1)
	-OW(2) 2.24(2)	average	1.54			2 OW(3)- O(1)	2.75(2)
average	2.16					2 OW(4)- OW(7)	2.74(2)
		0(2)-O(3)	2.48(2)	0(5)-O(6)	2.49(2)	2 OW(5)- OW(7)	2.81(2)
		0(2)-O(4)	2.50(2)	2 0(5)-O(7)	2.50(2)	OW(6)-2 O(4)	2.78(2)
		0(1)-O(3)	2.51(2)	0(7)-O(7)	2.54(3)	OW(6)- OW(4)	2.75(3)
		0(1)-O(2)	2.52(2)	2 0(6)-O(7)	2.54(2)	OW(7)- O(2)	2.96(2)
		0(1)-O(4)	2.55(2)	average	2.52	OW(7)- O(3)	2.77(2)
		0(3)-O(4)	2.58(2)				
		average	2.52				

* Estimated standard errors refer to the last digit.

Zn-O distance of 1.95 Å, which is compatible with the calculated ⁴¹Zn-O distance of 1.96 Å.

Hydrogen bonding

A final difference synthesis failed to reveal the locations of hydrogen atoms; however, the interpretation of the hydrogen bonding scheme was straightforward on geometrical grounds. The OH, OW(1), OW(2), OW(3), OW(4), OW(5), OW(6), and OW(7) mole-

cules are potential hydrogen-bond donors. The proposed hydrogen bonds are summarized in Table 3, and are shown in Figure 1, as light arrowed lines. The angles between hydrogen bonds originating from water molecules range from 101.6° to 136.3°. One hydrogen bond from OW(6) appears to be bifurcated between two O(4) atoms (indicated by ½ bonds in Fig. 1). The electrostatic bond-strength sums about the oxygens support the assignment of OH and H₂O

TABLE 4. Schoonerite. Electrostatic bond strengths and their sums about the anions*

Anion	Fe ²⁺	Fe ³⁺	Mn ²⁺	Zn ²⁺	P ⁵⁺	H(d)	H(a)	Σ
O(1)	2/6	---	---	---	5/4	---	2x1/6	1.92
O(2)	---	---	2/6	---	5/4	---	1/6	1.75
O(3)	---	---	---	2/5	5/4	---	1/6	1.82
O(4)	---	3/6	---	---	5/4	---	3/2x1/6	2.00
O(5)	---	3/6	---	2/5	5/4	---	---	2.15
O(6)	---	3/6	---	2/5	5/4	---	---	2.15
O(7)	2x2/6	---	---	---	5/4	---	---	1.92
OH	2x2/6	3/6	---	---	---	5/6	---	2.00
OW(1)	2/6	---	---	---	---	2x5/6	1/6	2.17
OW(2)	---	---	2/6	---	---	2x5/6	2x1/6	2.33
OW(3)	---	---	2/6	---	---	2x5/6	---	2.00
OW(4)	---	---	2/6	---	---	2x5/6	1/6	2.17
OW(5)	---	---	2/6	---	---	2x5/6	---	2.00
OW(6)	---	---	---	2/5	---	2x5/6	---	2.07
OW(7)	---	---	---	---	---	2x5/6	2x1/6	2.00

* H(d) = hydrogen donor; H(a) = hydrogen bond acceptor.

TABLE 5. Schoonerite. Cations based on P = 3

	1	2	3	4	5	Average
Fe	3.35	3.13	3.07	2.82	2.65	2.98
Mn	0.60	0.68	0.76	0.82	0.88	0.75
Zn	0.48	0.54	0.75	0.73	1.04	0.71
Al	0.11	0.09	0.09	0.13	0.11	0.11
Mg	0.32	0.29	0.33	0.35	0.29	0.32
Ca	0.28	0.23	0.19	0.14	0.05	0.18
K	0.11	0.06	0.06	0.10	0.03	0.07
Total	5.25	5.02	5.24	5.05	5.05	5.12

to particular sites and the proposed hydrogen bonding scheme.

The OW(7) water molecule located between the polyhedral sheets does not participate as a ligand. It donates and receives two hydrogen bonds defining a distorted tetrahedron. Hydrogen bonds to and from OW(7), as well as from OW(6) to OW(4), provide the only bonding between the sheets. Hydrogen bonds to and from the water molecules ligated to Mn serve to inhibit the rotation of this octahedron about an axis defined by its apical O(2) ligands.

Crystal chemistry

Table 5 lists the results of five electron microprobe analyses of two schoonerite crystals from the same sample in terms of cation proportions normalized to P = 3.00. The pronounced inhomogeneity and compositional variations, particularly with respect to Fe, Mn, Zn, and Ca, suggest the likelihood of extensive substitutions over the cation sites.

The essential cations Fe²⁺, Fe³⁺, Mn²⁺, and Zn²⁺ were assigned to structural sites on the basis of interatomic distances and by analogy to similar compounds (in addition, the Zn site was indicated by its greater scattering power). Al³⁺ and Mg²⁺ are also distributed over these sites, Al³⁺ probably residing primarily at the Fe(3) site and Mg²⁺ in varying amounts at each of the sites.

The large sizes of Ca²⁺ and K⁺ preclude their entry into the aforementioned cation sites. These cations are probably accommodated between the sheets, perhaps at the origin of the unit cell surrounded by six sheet oxygens at distances between 2.5 and 2.8 Å, or in the vicinity of OW(6) with seven sheet oxygens at distances between 2.7 and 3.0 Å. The final difference synthesis failed to provide any conclusive evidence for locating possible Ca²⁺ and K⁺ sites.

The variations in Fe, Mn, Zn, and Ca seen in Table 5 show definite correlations. Notable are the reciprocal relationship between Fe and Mn, which suggests

the substitution of Fe²⁺ for Mn²⁺ in the Mn site, and the reciprocal relationship between Zn and Ca, which suggests that Ca²⁺ may be accommodated in the vicinity of the OW(6) site necessitating a local vacancy in the Zn site. In addition, the entry of Fe into the Zn site is indicated in analysis 1, and the entry of Zn into an Fe site is indicated in analysis 5.

Relationship to montgomeryite, olmsteadite, and melonjosephite

A striking relationship exists between the structures of schoonerite and montgomeryite. This can be seen by comparing Figure 1 of Moore and Araki (1974) with Figure 1 of this paper. The relationship is better expressed by writing schoonerite's formula as Mn₂²⁺Fe₂²⁺Zn₂²⁺(H₂O)₁₄[Fe₂²⁺Fe₂³⁺(OH)₄(PO₄)₆]4H₂O. If alternate Fe²⁺-O octahedra along the edge-sharing chain in schoonerite are voided, a *cis-cis* corner-sharing octahedral chain very similar to the *cis-trans* chain of montgomeryite results. The placement of the enveloping tetrahedra is virtually identical in the two structures, and the Zn²⁺ and Mn²⁺ sites in schoonerite are located in positions similar to those of Ca²⁺ and Mg²⁺ in montgomeryite. Slabs of octahedra and tetrahedra in both structures are oriented parallel to {010}.

The linkage of Fe(1)-O, Fe(2)-O, Fe(3)-O, and P(2)-O polyhedra in schoonerite is topologically identical to the linkage of Fe-O, Nb-O, and P(1)-O polyhedra in olmsteadite (Moore *et al.*, 1976). A similar arrangement is also found in melonjosephite (Kampf and Moore, 1977); however, in this case, edge-sharing chains of Fe²⁺-O octahedra are corner-linked by edge-sharing dimers of Fe³⁺-O octahedra rather than by single octahedra.

The edge-sharing chains of Fe²⁺-O octahedra in schoonerite, olmsteadite, and melonjosephite have an interesting property in common. The Fe²⁺-Fe²⁺ separations are appreciably shorter across the shared edges whose vertices link to phosphate tetrahedra. The Fe²⁺-Fe²⁺ separations are: schoonerite, 3.15 Å and 3.29 Å; olmsteadite, 3.14 Å and 3.35 Å; and melonjosephite, 2.97 Å and 3.40 Å. Metal-metal interactions perhaps involving spin-coupling may be reflected by these short separations.

Acknowledgments

Thanks are due Forrest F. Fogg and Robert W. Whitmore for supplying the specimen from which the crystal was obtained. This study was supported by NSF Grant GA-40543 (awarded to Professor Paul B. Moore) and an NSF Materials Research Grant awarded to The University of Chicago.

References

- Baur, W. H. (1970) Bond-length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Am. Crystallogr. Assoc.*, 6, 129-155.
- Burnham, C. W. (1966) Computation of absorption corrections and the significance of the end effect. *Am. Mineral.*, 51, 159-167.
- Busing, W. R., K. O. Martin and H. A. Levy (1962) ORFELS, a Fortran crystallographic least-squares program. *U.S. Natl. Tech. Inf. Serv.* ORNL-305.
- Cromer, D. T. and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.*, A24, 321-324.
- Kampf, A. R. and P. B. Moore (1977) Melonjosephite, calcium-iron hydroxy phosphate: its atomic arrangement. *Am. Mineral.*, 62, 60-66.
- Moore, P. B. and T. Araki (1974). Montgomeryite, $\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]$: its crystal structure and relation to vauxite, $\text{Fe}_2^{2+}(\text{H}_2\text{O})_4[\text{Al}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{PO}_4)_4] \cdot 4\text{H}_2\text{O}$. *Am. Mineral.*, 59, 843-850.
- , T. Araki, A. R. Kampf and I. M. Steele (1976) Olmsteadite, $\text{K}_2\text{Fe}_2^{2+}[\text{Fe}_2^{2+}(\text{Nb,Ta})_2\text{O}_4(\text{H}_2\text{O})_4(\text{PO}_4)_4]$, a new species: its crystal structure and relation to vauxite and montgomeryite. *Am. Mineral.*, 61, 5-11.
- and A. R. Kampf (1977) Schoonerite, a new zinc-manganese-iron phosphate mineral. *Am. Mineral.*, 62, 246-249.
- Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, B25, 925-946.

*Manuscript received, April 20, 1976; accepted
for publication, October 27, 1976.*