

The optical spectroscopic comparison of the ferric iron tetrameric clusters in amarantite and leucophosphate¹

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Abstract

Optical absorption spectra and magnetic susceptibility data are presented for two minerals, amarantite, $\text{Fe}_2(\text{SO}_4)_2\text{O} \cdot 7\text{H}_2\text{O}$, and leucophosphate, $\text{K}_2[\text{Fe}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4] \cdot 2\text{H}_2\text{O}$, which contain nearly planar ferric iron tetrameric units. These data are compared to corresponding single crystal optical data for phosphosiderite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Pronounced enhancement of the intensities of the absorption bands and absorption anisotropy, which are associated with the strong antiferromagnetic coupling ($\mu_{\text{Fe}} = 2.53$ B.M. at 297°K) of the oxobridged amarantite tetramer, is noted for amarantite. Synthetic leucophosphate exhibits a much weaker antiferromagnetic interaction ($\mu_{\text{Fe}} = 5.13$ B.M.). Natural leucophosphate displays little optical absorption anisotropy and much lower absorption intensity than amarantite.

Introduction

Amarantite, $\text{Fe}_2(\text{SO}_4)_2\text{O} \cdot 7\text{H}_2\text{O}$, and leucophosphate, $\text{K}_2[\text{Fe}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4] \cdot 2\text{H}_2\text{O}$, are two minerals which contain nearly planar, ferric-iron tetrameric units as part of the crystal structure. The leucophosphate tetramer is joined through hydroxide bridges (Moore, 1972), and the amarantite tetramer is joined through oxide bridges (Süsse, 1968). The structure of these tetrameric units is illustrated in Figure 1. In spite of the similarities between the two tetrameric structures, there is a profound difference between the color of the two minerals. Leucophosphate is light amber-green, whereas amarantite is deep blood-red. Noting that amarantite has a smaller Fe-Fe distance through the shared edge (2.90 Å) than leucophosphate (3.11 Å), Moore (1972) proposed that amarantite may exhibit greater antiferromagnetic spin coupling between the Fe^{3+} ions and thereby have more intense color in a fashion similar to that observed for the dimer of the ferric iron complex with N-hydroxyethylenediaminetriacetate (HEDTA). Schugar *et al.* (1967, 1972) have shown that monomeric Fe^{3+} complexes of HEDTA which are light yellow become dark red when dimerized through an oxo-bridge. The dimerization and color enhancement are accompanied by strong antiferromagnetic coupling

of the two Fe^{3+} ions in the molecular dimer. The deep red color of the oxobridged amarantite is visibly similar to the oxobridged iron dimer with HEDTA, suggesting that similar mechanisms are operating in both systems.

Crystalline salts of the oxobridged HEDTA dimer show pronounced pleochroism. The crystals are deep red when the electric vector is parallel to the Fe-Fe axis but colorless when it is perpendicular. Rossman (1975, 1976) has studied the quantitative optical spectroscopy of the hydroxobridged minerals copiapite, $\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$, botryogen, $\text{MgFe}(\text{SO}_4)_2(\text{OH}) \cdot 7\text{H}_2\text{O}$, and a series of ferric hydroxy sulfates and jarosites and has found that in all cases the minerals are pleochroic such that when the electric vector is oriented along the Fe-Fe axis, the absorption intensities are as much as two to three orders of magnitude higher than when it is oriented perpendicular to the axis. It is of interest to determine if similar anisotropy of the ligand-field bands of Fe^{3+} occurs in the two tetrameric units and to determine if a greater antiferromagnetic interaction occurs in amarantite as Moore (1972) proposed. Consequently, a spectroscopic and magnetic study of amarantite and leucophosphate was undertaken.

Experimental details

Mineral samples: Amarantite, NMNH # R6254, from Sierra Gorda, Chile, was obtained in the form of deep orange-red radiating crystal aggregates of

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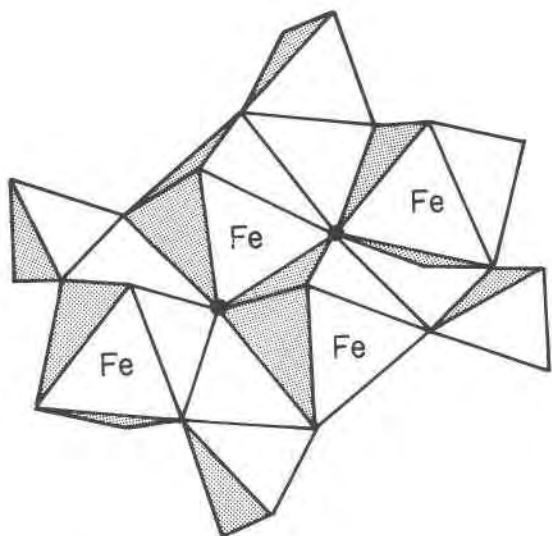


FIG. 1. The structure of the tetrameric cluster in amarantite (after Süsse, 1968). The ions bridging the iron are O^{2-} , and the tetrahedra are SO_4^{2-} . The structure of leucophosphite is similar, with phosphate tetrahedra and bridging OH^- .

5–10 mm size from which mm-sized cleavage flakes were readily obtained. These were oriented, epoxyed to glass discs, ground to the appropriate thickness, and polished with $0.3 \mu m$ Al_2O_3 powder. Analysis: calculated for $Fe_2(SO_4)_2 \cdot 7H_2O$; Fe, 25.0. Found: Fe, 24.6.

Leucophosphite from the Tip Top pegmatite, Custer, South Dakota, was supplied by P. B. Moore in the form of mm-sized crystals extending into a cavity in rockbridgeite. Two crystals were chosen which displayed good crystal morphology and were relatively free of dark inclusions. One was ground parallel to the (100) face (pseudo-orthorhombic orienta-

tion of Lindberg, 1957) to provide an α orientation. The other crystal was ground parallel to the (010) direction to provide the β and γ orientations.

Synthetic $K_2[Fe_4(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$ (leucophosphite) was prepared by the method of Haseman *et al.* (1950) using the procedure for product I but at 100° for 35 days. The product, obtained in high yield, was separated from a small amount of unreacted starting material by sluicing under water. Its identity was verified by X-ray powder diffraction.

Phosphosiderite from Kreuzberg, Pleystein, Bavaria, Germany, (Los Angeles County Museum of Natural History #4336) was obtained as 0.5–1.5 mm crystals in rockbridgeite. Their identity was confirmed by crystal optics, morphology, and mineral associations. They were first oriented with respect to crystal faces which were polished, epoxyed to a fused silica disc, and ground and polished.

Strengite, from Germany (California Institute of Technology Oke Collection #1512) was a mm-sized crystal in rockbridgeite. Its identity was verified by crystal optics.

Experimental methods are identical to those reported earlier (Rossman, 1975). Because of the extreme dispersion in the β - γ section of amarantite, it was necessary to reorient the crystal between the near-infrared and visible portions of the spectrum.

Phosphosiderite

To provide a basis of comparison against which the leucophosphite spectrum can be discussed, the spectra of two polymorphs of $FePO_4 \cdot 2H_2O$ were determined. $FePO_4 \cdot 2H_2O$ crystallizes in an orthorhombic and a monoclinic form, occurring in nature as the orthorhombic mineral strengite and as the mono-

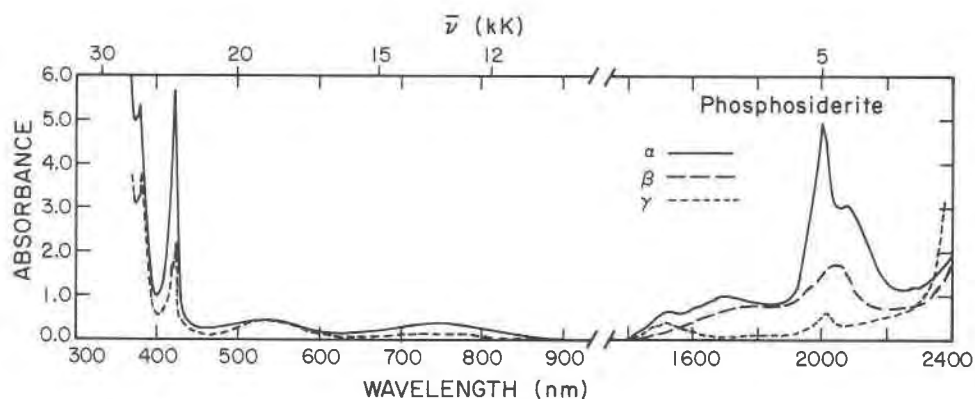


FIG. 2. Absorption spectrum of Kreuzberg phosphosiderite, $FePO_4 \cdot 2H_2O$. Data presented for a 1.00 mm thick crystal at $296^\circ K$. The β spectrum is not shown for wavelengths less than 1000 nm, where it nearly superimposes with the α spectrum.

TABLE 1. Optical absorption spectroscopic data*

	Band Assignments ${}^6A_{1g} \rightarrow$			
	${}^4T_{1g}$	${}^4T_{2g}$	$({}^4A_{1g}, {}^4E_g)$	${}^4T_{2g}$
Phosphosiderite				
α	746 nm (0.21)	529 (0.23)	423, 418 (3.75)	379 --
β	743 (0.22)	531 (0.24)	422 (4.28)	384 --
γ	722 (0.10)	532 (0.27)	423, 417 (1.51)	381 --
Leucophosphate				
α	800 (0.78)	538 (0.58)	441.5, 428, (0.4), (6.8)	421 **
β	(0.60)	(0.61)	(8.4), (7.6),	--
γ	(0.36)	(0.49)	(4.1), (6.9),	--
Amarantite				
α	866 nm	500 nm	442 434	424 **
β	--	--	--	--
γ	(~1.5) (12.7)	(~3) (~50)	(~5) --	(~3) (~45)

* ϵ values (in liters per mole per cm) are given in parentheses below the wavelength values (in nm). They are calculated assuming that all Fe^{3+} contribute equally to the absorption.

** Not observed.

clinic mineral phosphosiderite (also called metastrengite). The structure of phosphosiderite and a comparison to the strengite structure have been presented by Moore (1966). Both minerals contain isolated Fe^{3+} ions in an approximately octahedral oxygen coordination environment composed of four oxygens

from PO_4^{3-} units and two oxygens from two water molecules in *cis*-configuration. The individual octahedra are linked into a three-dimensional array through PO_4^{3-} tetrahedra. Differences in the twist of the PO_4^{3-} groups distinguish the structure of the orthorhombic dimorph from the monoclinic form.

The spectrum of phosphosiderite consists of molecular water absorptions at wavelengths greater than 1000 nm and the Fe^{3+} ligand-field spectra below 1000 nm (Fig. 2). The Fe^{3+} spectrum consists of bands at ~743 nm (polarized $\beta \approx \alpha > \gamma$; $\epsilon_\beta = 0.22$), 530 nm (polarized $\gamma \geq \alpha \approx \beta$; $\epsilon_\gamma = 0.27$), 423 nm (polarized $\beta > \alpha > \gamma$; $\epsilon_\beta = 4.28$), a shoulder at 417 nm on the high energy side of the 423 nm band, and 383 nm. The spectrum resembles the spectrum of isolated Fe^{3+} in andradite, $Ca_3Fe_2(SiO_4)_3$ (Manning, 1967, 1972) and coquimbite (Rossman, 1975) and is assigned accordingly (Table 1). The spectrum of the strengite recorded only with light incident upon the (111) face is similar to phosphosiderite. It consists of bands at 760, 552, 428, and 422 nm.

A few features of the spectra of the $FePO_4 \cdot 2H_2O$ dimorphs are worth noting: (1) The spectra are nearly idealized d^5 spectra. The absence of splitting of the ${}^4T_{1g}$ and ${}^4T_{2g}$ bands indicates that the differences in

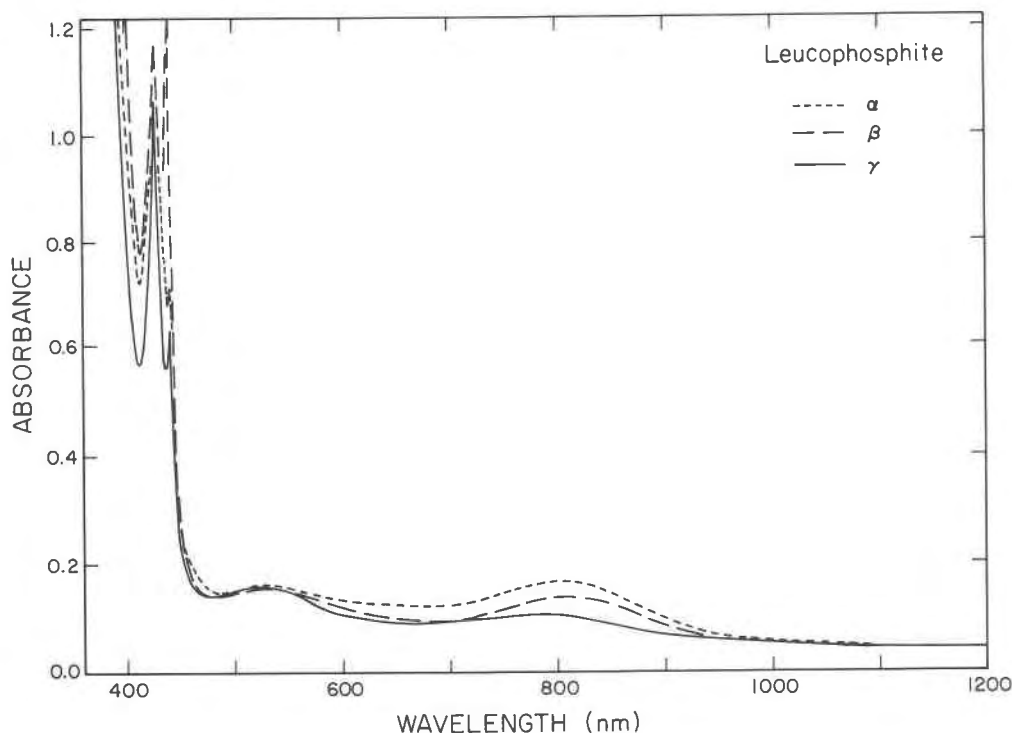


FIG. 3. Absorption spectrum of Tip Top pegmatite leucophosphate, $K_2[Fe_4(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$. Data presented for a 100 μm thick crystal at 296°K.

Fe-O bond lengths and the presence of the two water molecules are not a spectroscopically large perturbation of the octahedral geometry of the ligand field. (2) The ϵ values of the ligand field bands in the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ dimorphs are greater than the values for a comparable concentration of Fe^{3+} in 30 percent H_3PO_4 (ϵ values: ${}^4T_{1g}$ and ${}^4T_{2g}$, 0.04; ${}^4A_{1g}$, 4E_g , 0.36). This difference, which may be a result of the bond length differences and nonequivalent ligation, serves to emphasize the caution which must be exercised in using solution spectra as standards for solid state materials. (3) The anisotropy of absorption of the ligand field bands is low. The largest differences are on the order of a factor of three. This value is small compared to the anisotropy which can be associated with metal ion aggregation.

The absorption spectrum of leucophosphate (Fig. 3) consists of two broad bands at 800 and 538 nm, a pair of sharper bands at 441 and 428 nm, and a weaker shoulder at 421 nm, followed by rising absorption in the ultraviolet. The bands show weak pleochroism. The pattern is that of octahedral Fe^{3+} . Band assignments are analogous to $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and along with ϵ values are included in Table 1. Presumably, the pair of bands at 428 and 441 nm represent the two nonequivalent types of Fe^{3+} .

The intensities of the leucophosphate bands are greater than the corresponding bands in $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ by about a factor of four. There is no clear basis for distinguishing between attributing this enhancement to additional distortion of the Fe sites in the tetramer or to the effects of band enhancement

by antiferromagnetically interacting metal-ion clusters. Furthermore, there is no preferred direction along which the intensity of absorption is greatest. This contrasts greatly with the behavior of amaranthite.

The optical spectrum of amaranthite differs in several ways from the leucophosphate spectrum. The lowest energy Fe^{3+} band at 870 nm, which is most intense in the γ direction, is more than an order of magnitude more intense ($\epsilon = 12.7$) than the corresponding band in leucophosphate. This difference is illustrated by the spectra (Fig. 4) obtained on equal thicknesses of amaranthite and leucophosphate with light polarized in the direction of maximum absorption. The band is strongly pleochroic. Additional absorption bands can be seen in the spectrum of thin crystals in the γ direction at ~ 500 nm and at 434 and 424 nm (Fig. 5). The 434 and 424 nm pair are on order of magnitude more intense ($\epsilon_\gamma \sim 90$) in amaranthite than the corresponding bands at 441 and 428 nm in leucophosphate.

Magnetic data

Both leucophosphate and amaranthite display antiferromagnetic coupling but differ in the magnitude of the interaction. The room temperature effective magnetic moment per iron of synthetic leucophosphate is 5.13 B.M. This is well below the 5.9–6.0 B.M. found for magnetically isolated Fe^{3+} . The extent of the magnetic interaction is comparable to that in a dihydroxo-bridged ferric dimer for which the effective moment at 298° K is 5.17 B.M. (Schugar *et al.*, 1969).

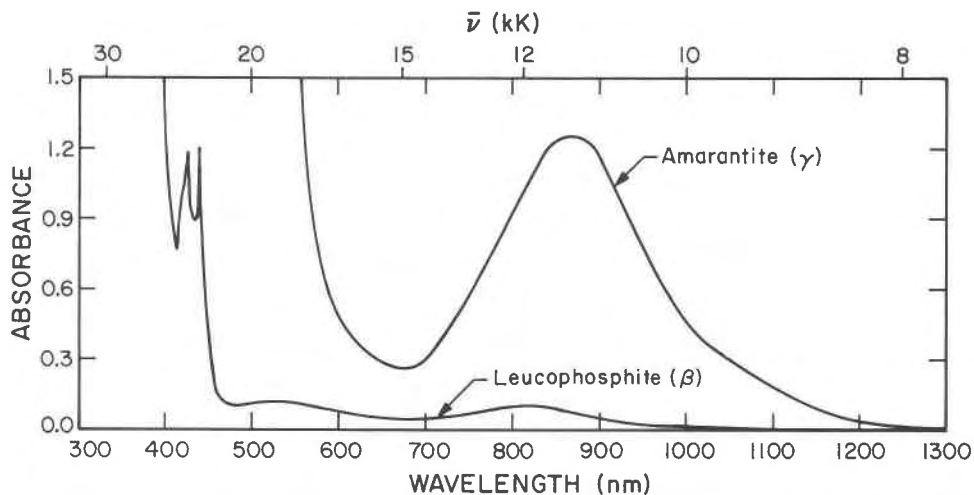


FIG. 4. Comparison of the leucophosphate β -spectrum and the amaranthite γ -spectrum in 100 μm thick crystals at 296° K.

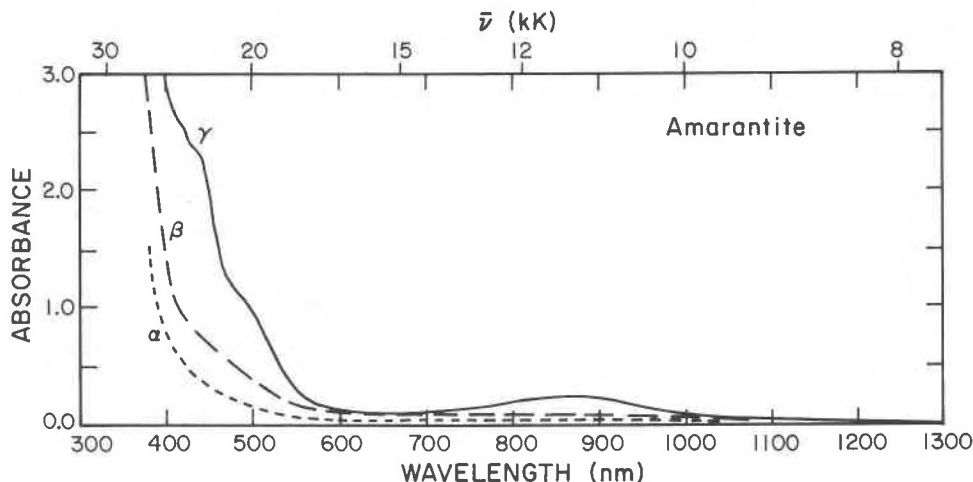


FIG. 5. Absorption spectrum of Sierra Gorda amarantite, $\text{Fe}_2(\text{SO}_4)_2\text{O}\cdot 7\text{H}_2\text{O}$. Data presented for a $14\ \mu\text{m}$ thick crystal at 296°K .

The effective magnetic moment of amarantite is greatly reduced by antiferromagnetic coupling. At 298°K it is 2.53 B.M. This value compares to a 298° value of 1.92 B.M. in a typical oxobridged ferric dimer (Schugar *et al.*, 1972) but is lower than the 4.45–5.11 B.M. at 298° found for μ_2 -dialkoxobridged ferric dimers (Bertrand and Eller, 1974; Wu *et al.*, 1972).

Discussion

The tetrameric clusters in leucophosphite are positioned in the crystal so that no principal polarization direction is entirely either within the plane of, or normal to the plane of, the (nearly) planar tetramers. In the (010) plane (monoclinic orientation of Moore, 1972), a fourfold screw axis related equivalent tetrameric units, thereby scrambling their orientation with respect to β and γ . Looking at the α vibration direction, {010}, the plane of the tetramers is inclined so as to give α both in- and out-of-plane components of the tetramer.

In the amarantite structure, the tetrameric clusters are all oriented in the same direction but are tilted with respect to the crystallographic axes so that the principal axes of the tetrameric unit do not correspond to the crystallographic axes. The axes of the optical indicatrix, unrestrained by symmetry in the triclinic crystal, correspond to neither the crystallographic nor the tetramer's axes. The orientation data of Bandy (1938) indicate that the γ direction has a large component in the plane of the tetramer, and the α direction has a small component. The γ direction is the direction of the unusually intense absorption. In the case of the dimeric and infinite linear

chain clusters, the direction of most intense absorption corresponded to the axis of the cluster. Expectedly, the direction of greatest absorption in the amarantite cluster is in the plane of the tetramer. Unfortunately, the internal orientation of the tetramer within the crystal does not allow a clear and unambiguous determination of the magnitude of the effect along two axes within the plane of the tetramer. Hopefully, other compounds containing oxobridged tetramers will be synthesized in crystal systems of higher symmetry on which it will be possible to make more detailed measurements.

The proposal by Moore (1972) of greater antiferromagnetic interaction in amarantite is confirmed, although the shorter Fe–Fe distance through the shared edge may not be as important as the difference in oxo- *vs.* hydroxobridging. Bridging oxide ions have more electron density available for participation in the magnetic superexchange process than do hydroxide ions, for which part of the electron density is tied up in bonding with the hydrogen ion. The correlation of color is Fe^{3+} minerals with the degree of antiferromagnetic exchange (Rossman, 1975) is well exemplified by the leucophosphite–amarantite pair. The hydroxobridged, weakly magnetically coupled leucophosphite is close to light yellow-green in color, whereas the strongly magnetically coupled oxobridged amarantite is deep red-orange.

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