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Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: the series $Fe(OH)SO_4{\cdot}nH_2O$ and the jarosites[1]

GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences, California Institute of Technology
Pasadena, California 91125

Abstract

Optical and infrared absorption and magnetic susceptibility data are reported for the ferric iron hydroxy sulfate minerals and compounds: basic iron sulfate, $Fe(OH)SO_4$; butlerite, $Fe(OH)SO_4.2H_2O$; parabutlerite, $Fe(OH)SO_4.2H_2O$; fibroferrite, $Fe(OH)SO_4.5H_2O$; jarosite, $KFe_3(SO_4)_2(OH)_6$; and stewartite, $MnFe_2(H_2O)_6(OH)_2(PO_4)_2$. The relationships among intensity of color, indices of refraction, pleochroism, antiferromagnetic interaction among Fe^{3+} ions, and structure are discussed for 7Å corner-linked chain structures and the two-dimensional Fe^{3+} sheets of the jarosites. For all of these compounds the greatest intensity of the Fe^{3+} absorption bands and the highest refractive index occur when the vibration direction of the incident light is aligned with the cation chains or in the plane of the jarosite sheets. The ligand-field absorption band intensities of all of these compounds are enhanced up to two orders of magnitude above what they are in magnetically dilute compounds.

Introduction

Minerals which have structures containing clusters or chains of transition metal cations bridged by oxide and hydroxide ions can have physical properties which are substantially different from the properties of related substances which contain only transition metal ions well isolated from each other.

In the first paper in this series exploring the relationship among the intensity of the absorption of light, pleochroism, magnetic susceptibility and cation clusters (Rossman, 1975), it was shown that the intensities of spin-forbidden optical absorption bands of Fe^{3+} in the hydroxobridged dimeric unit in magnesiocopiapite, $MgFe_4(SO_4)_6(OH)_2.20H_2O$, were more than an order of magnitude more intense than those in ferric sulfates which contain magnetically isolated ferric ions. A direct result of the intensification of the absorption bands is the enhancement of color in this material. Even greater intensification was observed in botryogen, $MgFe(SO_4)_2(OH).7H_2O$, which contains infinite chains of antiferromagnetically coupled hydroxobridged ferric iron. The intense absorption occurs only when the vibration direction of the incident light is along the Fe–Fe axis of the dimers and chains. Consequently, magnesiocopiapite and botryogen are strongly pleochroic.

The principles presented regarding the intensification of color and pleochroism resulting from the clustering of metal ions can be applied to two series of ferric iron hydroxy sulfates. The basic iron sulfates have the general formula $Fe(OH)SO_4.nH_2O$. Three members of this series are known: $Fe(OH)SO_4$, basic iron sulfate, known only from synthetic laboratory preparations, and $Fe(OH)SO_4.2H_2O$, which occurs as the triclinic mineral butlerite and as the orthorhombic mineral parabutlerite. The mineral fibroferrite has a stoichiometry close to $Fe(OH)SO_4.5H_2O$, which suggests that it may also be a member of this series. The second series of iron hydroxy sulfates, the jarosites, is named after the mineral jarosite, $KFe_3(SO_4)_2(OH)_6$. Several members of this series are known with various cations substituting for potassium.

This paper reports the results of optical spectroscopic and magnetic susceptibility studies conducted on members of these series of minerals and examines how the results are controlled by the interconnection of the cations.

Basic iron sulfates—structural considerations

The structures of basic iron sulfate (Johanson, 1962), butlerite (Fanfani *et al.*, 1971), and para-

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butlerite (Borène, 1970) contain linear chains of Fe^{3+} oriented parallel to each other. Each Fe^{3+} in the chain is bridged by a single hydroxide ion and one sulfate group. In basic iron sulfate, the chains are interconnected through sulfate groups, whereas in butlerite and parabutlerite the coordination about iron is completed by water molecules, and the chains are not cross-linked by sulfate tetrahedra.

Fibroferrite remains structurally uncharacterized. Cesbron (1964) concluded from X-ray studies that the mineral is hexagonal. Earlier studies reviewed by Cesbron had concluded that the mineral was either monoclinic or orthorhombic. These differences may be due to the ease with which the mineral dehydrates at room temperature to other uncharacterized phases.

Refractive index, pleochroism, and structure correlations

In the hydroxobridged ferric iron cluster and chain compounds, the direction of the greatest color intensity is the vibration direction of the highest refractive index. This correlation is shown in Table 1. In all cases, the refractive index has its greatest value when the electric vector of the incident light is aligned with the Fe–OH–Fe chains.

Crystals of $Fe(OH)SO_4$ are elongated along γ, which agrees with the observations of Posnjak and Merwin (1922). Johanson (1962) reported that the crystals are elongated along [001], which is also the direction of the Fe(OH)Fe chains. The hydroxobridged Fe^{3+} chains in butlerite are parallel to [010] (Fanfani *et al.*, 1971) which is also the direction of γ. Lausen (1928) reported only weak pleochroism in butlerite from Arizona. However, the Arizona specimens used in this study were strongly pleochroic, varying from colorless to yellow. Bandy (1938) reported that for parabutlerite γ = [100], the direction along which the Fe(OH)Fe chains run (Borène, 1970).

TABLE 1. Refractive index—pleochroism correlation

Compound	n_D and Color			References
	α	β	γ	
$Fe(OH)SO_4$	1.78 colorless	1.81 colorless	1.92 yellow	1
butlerite	1.59 colorless	1.68 faint yellow	1.75 yellow	1
parabutlerite	1.59 colorless	1.66 faint yellow	1.75 yellow	2
magnesiocopiapite	1.51 light yellow	1.54 colorless	1.57 yellow	2,3
botryogen	1.52 colorless	1.53 pale brown	1.58 yellow	2,3
stewartite	1.63 colorless	1.658 pale yellow	1.66 yellow	2
	ω	ϵ		
jarosite	1.82 brownish yellow	1.72 colorless		2
fibroferrite	1.53 colorless	1.57 yellow		2

1. Posnjak and Merwin (1922)
2. Palache <u>et al.</u> (1951)
3. Rossman (1975)

This correlation also applies to the hydroxobridged minerals reported in the first part of this series (Rossman, 1975). The hydroxobridged dimeric units are oriented along γ in magnesiocopiapite, and the chains of hydroxobridged Fe^{3+} are aligned along γ in botryogen. The refractive index-pleochroism correlation is applicable to a wide variety of minerals containing cation clusters and chains.

Optical spectra

The optical spectra of the compounds which are known to contain only linear chains of hydroxobridged Fe^{3+} display similar spectra. They have three salient characteristics: (1) the single crystal spectra are highly anisotropic; (2) in the direction of the intense color, the ligand-field spectrum of Fe^{3+} appears as if only the first ($^6A_{1g}\rightarrow{}^4T_{1g}$) and the third ($^6A_{1g}\rightarrow{}^4A_{1g},{}^4E_g$) bands of octahedral Fe^{3+} are present; (3) the intensities of the absorption bands are greatly enhanced compared to the intensity observed in their magnetically dilute counterparts. These characteristics are observed in the spectra of the basic iron sulfates.

The spectrum of powdered $Fe(OH)SO_4$ in KBr pellets shows a broad absorption band at 945 nm, a shoulder at ~490 nm located on a rising absorption, and a sharp band at 428 nm. The 945 nm band can also be observed in a powdered sample mulled with refractive index oil (n_D = 1.700). Determinations of the ϵ value of the 945 nm band range from 2.8 to 3.6. Past experience with the determination of ϵ values from the spectra of fine powders embedded in a supporting matrix is that the values are generally higher than those obtained from single crystals because of the tortuous path the light follows in traversing the sample. The true value, estimated to be 2.5, is still much greater than that of magnetically isolated ferric iron in octahedral oxygen coordination. The $Fe(OH)SO_4$ spectrum (not illustrated) is similar to that of parabutlerite.

In γ-polarization the spectrum of parabutlerite (Fig. 1) consists of the lowest energy Fe^{3+} band at 912 nm ($^4T_{1g}$) and the ($^4A_{1g},{}^4E_g$) band at 426 nm. The ϵ values, 2.5 and 28, respectively, are more than an

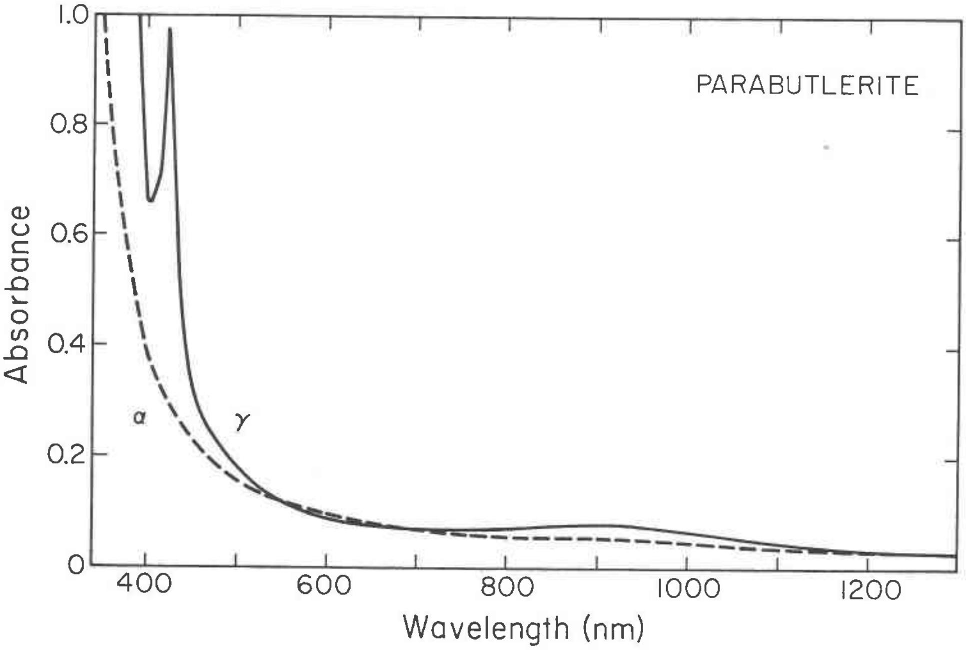

FIG. 1. Optical absorption spectrum of a parabutlerite crystal 20 μm thick from Yazd, Iran, showing the intense absorptions in γ-polarization.

order of magnitude greater than the corresponding values for magnetically dilute ferric sulfates (Rossman, 1975). In β-polarization (Fig. 2) a Fe^{3+} band occurs at 478 nm (ε ~ 2.4). Spectral data for other weaker Fe^{3+} bands are included in Table 2.

The spectrum of butlerite is similar to that of parabutlerite. In γ-polarization the intensified bands occur at 920 nm (ε = 2.4) and 424 nm (ε = 33). In β-polarization a band occurs at 488 nm (ε ~ 2.8) (Fig. 3).

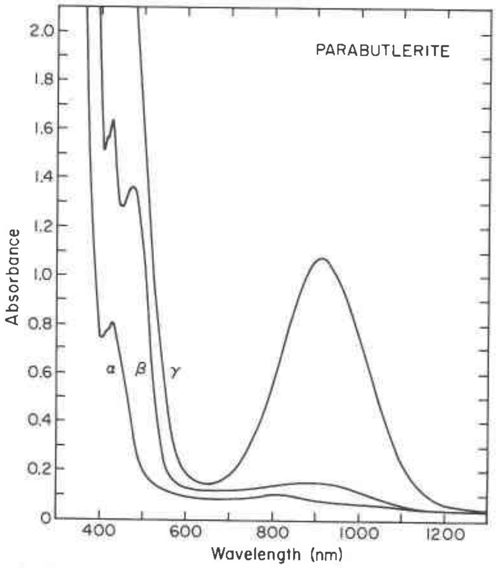

FIG. 2. Optical absorption spectrum of a parabutlerite crystal illustrating the enhancement of the first absorption band of Fe^{3+} at 912 nm in γ-polarization and the 478 nm β-feature; crystal 300 μm thick from Yazd, Iran.

It is possible that the 488 nm band in butlerite and the corresponding bands at ~490 nm in $Fe(OH)SO_4$ and 478 nm in parabutlerite correspond to the $^6A_{1g}$

TABLE 2. Optical spectroscopic data

Material	Polarization	Absorption Bands				
$Fe(OH)SO_4$	powder	945*		~490	428	
		(~2½)		–	–	
butlerite		920		488	424	
	β	–		(~2.8)	–	
	γ	(2.4)		–	(33)	
parabutlerite		912	816	478	426	416
	α	–	(~0.07)	–	(~0.8)	–
	β	( )	–	(~2.4)	–	–
	γ	(2.5)	–	–	(28)	–
stewartite		880			428	
	β	(~0.2)			(~1.1)	
	γ	(2.3)			(55)	
jarosite		933		~472	434	
	ω	(1.8)		–	(33)	
	ε	–		–	–	
fibroferrite		840		555	423	
	ω	(1.9)		(1.9)	(11)	
	ε	(0.5)		(0.5)	(6)	

* wavelengths in nm; ε values in parenthesis are expressed in liters per mole per cm. Where ε values are not tabulated, they either were too low to be accurately determined or the absorption band was not observed.

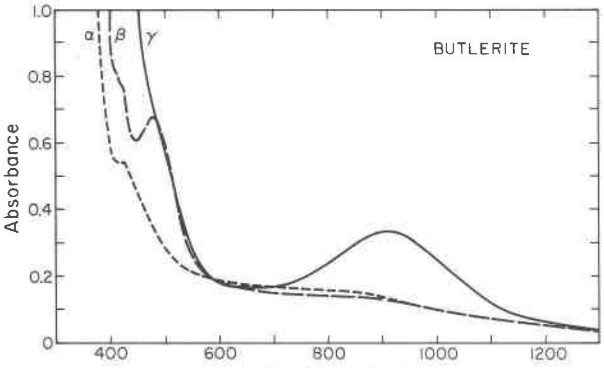

FIG. 3. Optical absorption spectrum of a butlerite crystal 106 μm thick from Jerome, Arizona.

$\rightarrow {}^4T_{2g}$ transition of Fe^{3+}; however, they occur at significantly lower wavelengths than the ${}^4T_{2g}$ transition in magnetically dilute Fe^{3+} sulfates. Alternatively, these features could arise from transitions to the components of the octahedral $({}^4A_{1g},{}^4E_g)$ state which has been split by the lower symmetry at each Fe^{3+} site. Resolution of this ambiguity will probably have to wait until detailed theoretical studies become available for magnetically coupled d^5 systems.

Magnetic susceptibility data

All the compounds display effective magnetic moments which are reduced below the value of 5.9–6.0 Bohr magnetons found in magnetically dilute ferric sulfates. The reduced magnetic moments which decrease at low temperatures indicate that the Fe^{3+} cations are antiferromagnetically coupled. The magnetics of $Fe(OH)SO_4$ have been previously reported by Cattrall *et al.*, (1971) and Powers *et al.*, (1975). The effective magnetic moment per iron decreases from μ = 3.84 B.M. at 298°K to 2.0 B.M. at 85° and 0.84 B.M. at 15°. The gram magnetic susceptibility, χ_g, of parabutlerite is 2.5×10^{-5} cgs (296 K, 10.0 *kθe*) corresponding to an effective magnetic moment per iron μ = 3.3 B.M. For butlerite $\chi_g \simeq 3.1 \times 10^{-5}$ cgs and $\mu \simeq 3.8$ B.M. Due to both the limited quantity of sample available for the magnetic study and to the presence of impurity phases, the values for butlerite must be considered approximate.

Discussion—7Å chains

Moore and Araki (1974b) noted the close physical similarity among compounds that possess 7Å octahedral corner-linked chain structures. In particular, they observed that minerals with 7Å structures involving chains of Fe^{3+} in six-fold oxygen coordination are yellow to orange in color. The common color of these structures can be understood in terms of the enhancement of color which occurs in antiferromagnetically coupled linear chains of OH-bridged Fe^{3+}. The structural prototype of the 7Å chain is $Fe(OH)SO_4$. Its yellow color is determined largely by the intensity enhanced ${}^6A_{1g}\rightarrow({}^4A_{1g},E_g)$ absorption band of Fe^{3+} which absorbs the violet and blue components of the visible spectrum. Butlerite and parabutlerite are further examples of this class of compounds.

Stewartite, $MnFe^{3+}_2(H_2O)_6(OH)_2(PO_4)_2$, is one of the minerals with the 7Å Fe^{3+} chain structure referred to by Moore and Araki (1974b). The mineral is strongly pleochroic from orangish-yellow (γ) to colorless (α). Cleavage platelets (010) of stewartite provide nearly centered Bx_a figures which allow γ and β spectra to be conveniently obtained. The optical spectrum (Fig. 4) is similar to that of the ferric hydroxy sulfates, consisting of the ${}^4T_{1g}$ band at 880 nm and the $({}^4A_{1g},{}^4E_g)$ band at 428 nm. Both bands show intensity enhancement indicating antiferromagnetic exchange coupling of the Fe^{3+} cations in the chain. It is interesting to note that the spectroscopic features of

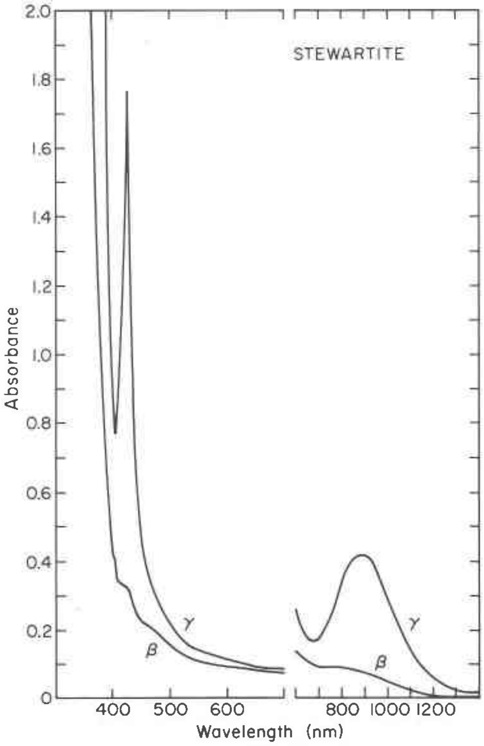

FIG. 4. Optical absorption spectrum of a stewartite crystal showing enhanced Fe^{3+} absorption bands and Mn^{2+} bands without enhancement. Crystal from the Fletcher Pegmatite, N. Groton, N. H.: for λ = 300–700 nm, 22 μm thick; for λ = 700–1400 nm, 150 μm thick.

Mn^{2+}, which is isoelectronic with Fe^{3+} and present in stewartite in the ratio of one Mn^{2+} to two Fe^{3+}, have very low intensities. The ${}^4T_{1g}$ and (${}^4A_{1g}$,${}^4E_g$) bands of Mn^{2+} would be expected to occur in the vicinity of 550 nm and 400 nm respectively. For comparison, they are found at 540 nm and 402 nm in $MnSO_4.4H_2O$ (Lohr and McClure, 1968). The weakness of these bands in the spectrum of a thin crystal of stewartite indicates that the Mn^{2+} ions are not situated structurally in clusters or extended chains. The determination of the stewartite structure by Moore and Araki (1974a) shows that the Mn^{2+} is arranged in octahedra isolated from adjacent Mn^{2+} by hydrogen bonds and from Fe^{3+} by intervening PO_4 tetrahedra.

The similarity of the stewartite spectrum to the spectra of the hydroxy-sulfates underscores the dominant role of the hydroxobridged chain in determining the color and spectroscopy of these substances and illustrates that the change from SO_4^{2-} to PO_4^{3-} ligation does not constitute a large perturbation upon the intrinsic properties of the chain. In the hydroxy sulfate series it was observed that the change from SO_4^{2-} coordination to coordination by H_2O did not significantly alter the dominant spectroscopic features of the hydroxobridged chain.

Fibroferrite

Optical and magnetic data suggest that the Fe^{3+} in fibroferrite share OH^-, but that the fibroferrite structure is fundamentally different from other members of the basic iron sulfate series. The optical spectrum shows three Fe^{3+} absorption bands at 840, 555, and 423 nm, all polarized parallel to the fiber axis (Fig. 5). The absorption bands have enhanced intensities (Table 2) indicative of cation interaction. The fibroferrite spectrum differs from the spectra of the other $Fe(OH)SO_4$ compounds in several respects. The 840 nm band is at higher energy than the ${}^4T_{1g}$ bands of the other compounds; the well-resolved 555 nm band is at an energy expected for the ${}^4T_{1g}$ band, but is at significantly lower energy than the ~490 nm band in β-polarization in the others; the ϵ-values, while greater than in magnetically dilute compounds, are not as great as in the other basic iron sulfates. The lower ϵ values can be anticipated when the intensity of color of parabutlerite and fibroferrite are compared.

Fibroferrite in the form of slightly greenish-yellow fibers has a magnetic moment of 3.72 B.M. at 297°K. When the mineral alters (dehydrates?) to a yellow crumbly material, the moment rises to 4.40 B.M. Because of the difficulty in obtaining fibroferrite completely free of the yellow alteration product, the value 3.72 B.M. may be somewhat higher than the true value. The antiferromagnetic interaction and the enhanced intensities of the absorption bands suggest that the Fe^{3+} are joined through OH bridges, although the exact details of this linkage cannot be ascertained from these data.

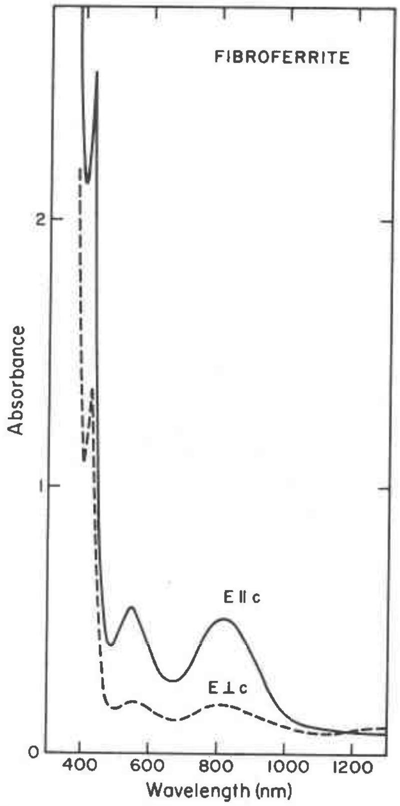

FIG. 5. Optical absorption spectrum of a bundle of fibroferite fibers 250 μm thick soaked in a liquid with n_D = 1.54 (specimen from Cyprus).

Jarosites—two-dimensional cation sheets

The second series of minerals is typified by the mineral jarosite, $KFe_3(SO_4)_2(OH)_6$. The optical spectroscopic study of jarosite constitutes a major extension of the work with enhanced absorption intensities in antiferromagnetically coupled systems from structures with one-dimensional interactions to structures with two-dimensional interactions. Jarosite is isostructural with alunite, $KAl_3(SO_4)_2(OH)_6$ (Hendricks, 1937). The alunite structure (Wang *et al.*, 1965) consists of two-dimensional sheets of hydroxo- and sulfate-bridged Al^{3+} wherein each Al^{3+} is coordinated to 3 OH^- groups and 3 SO_4^{2-} groups. Each OH^- group bridges two Al^{3+}. The hydroxobridged sheets are separated from each other by the potassium ions. Minerals and compounds which have various cations substituting for potassium are isostructural with jarosite (Hendricks, 1937) and are referred to as jarosites.

The refractive index–pleochroism–structure correlation can be easily extended from one-dimensional clusters and chains to the two-dimensional hydroxobridged Fe^{3+} sheets of jarosite, natrojarosite, argentojarosite, hydronium jarosite, and plumbojarosite. All of the jarosites are markedly pleochroic. The color is more intense when the vibration direction of the incident light is parallel to the cation sheets (ω). In this direction the refractive index is about 0.1 greater than in the ϵ direction (Larsen and Berman, 1934; Posnjak and Merwin, 1922). The spectroscopic features found for the minerals containing the linear hydroxobridged chains are also observed in the spectra of the two-dimensional jarosite sheet. The single-crystal spectrum of a Pershing County, Nevada, jarosite shows absorption bands in ω at 933 nm (ϵ = 1.8) and at 434 nm (ϵ ~33) (Fig. 6). These features are greatly enhanced in the ω spectrum compared to the ϵ spectrum. The spectrum of synthetic jarosite obtained as a paste in a liquid of high refractive index is similar to the spectrum of the natural crystal. The Fe^{3+} ions in jarosite are antiferromagnetically coupled. At 298 K, μ = 3.54 B.M. and falls to 0.85 B.M. at 15 K. (Powers *et al.*, 1975).

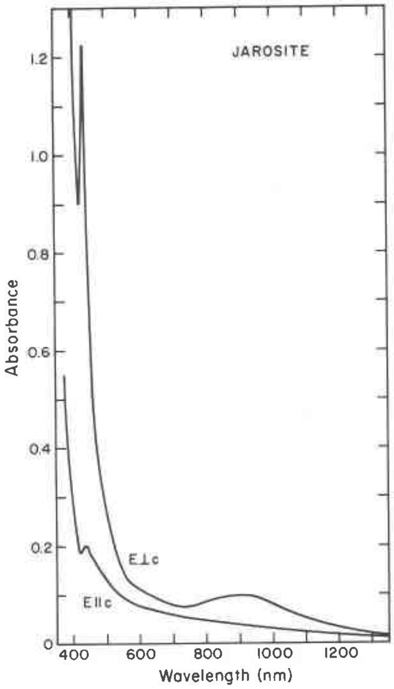

FIG. 6. Optical absorption spectrum of a jarosite crystal 22 μm thick from Pershing County, Nevada.

Conclusions

(1) Minerals with 7Å corner-linked Fe^{3+} chains show Fe^{3+} absorption bands of enhanced intensity when the vibration direction of the incident light is along the cation chain.
(2) Enhanced Fe^{3+} absorption bands are found in the spectra of minerals such as jarosite which contain extended two-dimensional hydroxybridged Fe^{3+} sheets when the vibration direction of the incident light is in the plane of the cation sheet.
(3) The enhanced intensities of the spin-forbidden bands and the resulting pleochroism are associated with antiferromagnetic coupling among the Fe^{3+} ions.
(4) Anistropy and enhanced absorption band intensity indicate sharing of Fe^{3+} polyhedra but do not uniquely define the structural arrangement.

Experimental details

Several batches of basic iron sulfate were prepared by the methods of Johanson (1962) and Posnjak and Merwin (1922). Their identity was confirmed by powder X-ray diffraction, infrared spectra, and wet chemical analysis (Powers *et al.*, 1975). Butlerite (NMNH # 95953) was from the United Verde Mine, Jerome, Arizona (Lausen, 1928). Its identity was verified by its distinctive color, locality, and crystal morphology. Parabutlerite was from Yazd, Iran. Its identity was confirmed by external morphology, optics, and wet-chemical analysis. Analysis: calculated for $Fe(OH)SO_4.2H_2O$: Fe, 27.2 found: Fe, 26.8, 26.8. The fibroferrite was from Cyprus. Its identity was confirmed by morphology and refractive indices. Analysis: calculated for $Fe(OH)SO_4.5H_2O$: Fe, 21.6; found: Fe, 21.6. The jarosite spectrum which is discussed was obtained from mm-sized brown crystals from Sulfur, Pershing County, Nevada, which were labeled carphosiderite [hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$] CIT #6583. The identity as jarosite was confirmed by infrared spectra which in the 1500–1700 cm^{-1} region were more nearly identical to the spectrum of synthetic jarosite than to the spectrum of synthetic hydronium jarosite. There was, however, some indication of the 1575 cm^{-1} feature discussed by Wilkins *et al.* (1974) indicating some substitution of H_3O^+ for K^+. Synthetic jarosite was prepared by the method of Fairchild (1933) and characterized by powder X-ray diffraction, infrared spectra, and wet chemical analysis (Powers *et al.*, 1975). Other samples of natural jarosite produced results similar to the synthetic material. Stewartite from the Fletcher pegmatite, N. Groton, New Hampshire, was provided by P. B. Moore of the University of Chicago. The general experimental methods and instrumentation used have been described (Rossman, 1975). All data were obtained at room temperature.

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References

Bandy, M. C. (1938) Mineralogy of three sulfate deposits of northern Chile. *Am. Mineral.* **23**, 669–760.

Borène, J. (1970) Structure cristalline de la parabutlerite. *Bull. Soc. fr. Mineral. Cristallogr.* **93**, 185–189.

Cattrall, R. W., K. S. Murray and K. I. Peverille (1971) Magnetic properties of some polynuclear hydroxy-bridged iron(III) sulfate complexes. *Inorg. Chem.* **10**, 1301–1304.

Cesbron, F. (1964) Contribution à la minéralogie des sulfates der fer hydratés. *Bull. Soc. fr. Minèral. Cristallogr.* **87**, 125–143.

Fairchild, J. G. (1933) Artificial jarosites—the separation of potassium from cesium. *Am. Mineral.* **18**, 543–547.

Fanfani, L., A. Nunzi and P. R. Zanazzi (1971) The crystal structure of butlerite. *Am. Mineral.* **56**, 751–757.

Hendricks, S. B. (1937) The crystal structure of alunite and the jarosites. *Am. Mineral.* **22**, 773–784.

Johanson, G. (1962) On the crystal structures of $FeOHSO_4$ and $InOHSO_4$. *Acta Chem. Scand.* **16**, 1234–1244.

Larsen, E. S. and H. Berman (1934) The microscopic determination of the nonopaque minerals. *U. S. Geol. Surv. Bull.* **848**, 266 p.

Lausen, C. (1928) Hydrous sulfates formed under fumerolic conditions at the United Verde Mine. *Am. Mineral.* **13**, 203–221.

Lohr, L. L. and D. S. McClure (1968) Optical spectra of divalent manganese salts. II. The effect of interionic coupling on absorption strength. *J. Chem. Phys.* **49**, 3516–3521.

Moore, P. B. and T. Araki (1974a) Stewartite, $Mn^{2+}Fe_2^{3+}(OH)_2[PO_4]_2.2H_2O$; Its atomic arrangement. *Am. Mineral.* **59**, 1272–1276.

——— and ——— (1974b) Jahnsite, $CaMn^{2+}Mg_2(H_2O)_8Fe_2^{3+}(OH)_2[PO_4]_4$; A novel stereoisomerism of ligands about octahedral corner-chains. *Am. Mineral.* **59**, 964–973.

Palache, C., H. Berman and C. Frondel (1951) *Dana's System of Mineralogy*, 7th Ed. Vol. II, Wiley and Sons, New York.

Posnjak, E. and H. E. Merwin (1922) The system, Fe_2O_3–SO_3–H_2O. *J. Am. Chem. Soc.* **44**, 1965–1994.

Powers, D. A., G. R. Rossman, H. J. Schugar and H. B. Gray (1975) Magnetic behavior and infrared spectra of jarosite, basic iron sulfate and their chromate analogs. *J. Solid State Chem.* **13**, 1–13.

Rossman, G. R. (1975) Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: Intensification of color in iron(III) clusters bridged by a single hydroxide ion. *Am. Mineral.* **60**, 698–704.

Wilkins, R. W. T., A. Mateen and G. W. West (1974) The spectroscopic study of oxonium in minerals. *Am. Mineral.* **59**, 81–819.

Wang, R., W. F. Bradley and H. Steinfink (1965) The crystal structure of alunite. *Acta Crystallogr.* **18**, 249–252.

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