Spectroscopic and Magnetic Studies of Ferric Iron Hydroxy Sulfates: Intensification of Color in Ferric Iron Clusters Bridged by a Single Hydroxide Ion[1]

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Abstract

Optical and infrared spectroscopic data and magnetic susceptibility data are reported for the ferric hydroxy-sulfate minerals magnesiocopiapite and botryogen and the related mineral coquimbite. The physical properties of intensity of color, pleochroism, and magnetic susceptibility associated with the hydroxobridged Fe^{3+} dimer of magnesiocopiapite and with the hydroxobridged Fe^{3+} infinite chain of botryogen are compared to those of isolated Fe^{3+}. The hydroxobridged minerals show strong pleochroism with intensity enhancement of the spin-forbidden ligand field absorption bands occurring when the electric vector of the incident light is oriented in the direction of the Fe–OH–Fe axis. The intensity enhancement and pleochroism are associated with antiferromagnetic exchange coupling of the Fe^{3+} ions.

Introduction

A striking feature of materials which contain Fe^{3+} in six-fold oxygen coordination is the enormous range of intensity of color they display, which is often unrelated to the total iron concentration. Andradite garnet, $Ca_3Fe_2(SiO_4)_3$, with 21 percent Fe is pale lime-green; jarosite, $KFe_3(SO_4)_2(OH)_6$, with 33 percent Fe is light yellow; botryogen, $MgFe(SO_4)_2 \cdot 7H_2O$, with 14 percent Fe is dark orange-red. The quantitative study of the color, through the spectroscopic study of the ligand field absorption bands, as conveniently measured by the extinction coefficient (ϵ) values, varies by more than two orders of magnitude among various materials.

Manning (1973) has collated the ϵ values for the $^6A_{1g} \rightarrow (^4A_{1g}, \, ^4E_g)$ transition of Fe^{3+} which occurs in the 400–450 nm range in a number of oxides and silicates and found that they vary by a factor of 600. He proposed that an intensity-stealing mechanism is operating such that states involving spin-forbidden ligand-field transitions mix with nearby states that involve spin-allowed oxygen → metal charge-transfer transitions. Electronic transitions to the mixed state will have a spin-allowed component which will augment the intensity of the transition above that for a purely spin-forbidden process. The extent of mixing will depend in part upon the energy separation between the ligand-field and charge-transfer states. The location of the charge transfer band, in turn, was observed by Manning to be dependent upon the metal ions present in second nearest-neighbor sites. Manning felt that Al^{3+} and Fe^{3+} in tetrahedral coordination were especially effective next-nearest neighbors for causing intensification of the ligand field bands.

In those instances where an Fe^{3+} has as its next-nearest neighbor another Fe^{3+}, the possibility of another type of interaction occurs, namely, a magnetic interaction between the cations. This study will examine the relationship between the intensification of the absorption bands of Fe^{3+} in six-fold oxygen coordination and the aggregation of the Fe^{3+} cations into clusters, chains, and sheets in which an antiferromagnetic interaction can occur. In this and forthcoming papers, a series of minerals and chemical compounds containing ferric dimers, trimers, tetramers, chains, and sheets will be examined spectroscopically to examine the influence of the geometry of the cation cluster and the chemical nature of the bridging units upon the spectroscopic features. The correlation of intensification of absorption band with antiferromagnetic interactions will also be examined.

Magnetic-exchange-dependent intensification of

spin-forbidden spectral bands is a well-established phenomenon in extended lattice antiferromagnetic compounds. McClure (1963) observed abnormally high intensities in the spectra of Mn^{2+} doped into ZnS which were attributed to magnetic interactions between pairs of manganese ions. Cooperative intensification is established in the case of Mn^{2+} ions doped into $KZnF_3$ wherein at least part of the impurity ions order as next-nearest neighbor pairs (Ferguson, Guggenheim, and Tanabe, 1965). Ferguson *et al* (1966) proposed a theoretical mechanism by which the more-than-order of magnitude intensity enhancement of spin-forbidden absorption bands could occur in manganese fluorides. Lohr and McClure (1968) later demonstrated for a wide variety of Mn^{2+} compounds that interionic coupling could increase absorption band intensities. Both Mn^{2+} and Fe^{3+} are ions with five *d* electrons which have only spin-forbidden optical transitions. The experience with enhanced Mn^{2+} absorption intensities suggests that similar enhancements should be expected for Fe^{3+}. Reiff *et al* (1968) and Schugar *et al* (1972) have observed that the first ligand field band $^6A_{1g} \rightarrow {}^4T_{1g}$ in solutions of ferric oxobridged dimers is unusually intense ($\epsilon \sim 3$–6). In these molecular dimeric systems, antiferromagnetic interactions have been shown to be important. Krebs and Maisch (1971) have demonstrated that in Al_2O_3 doped with Fe^{3+} enhancement of Fe^{3+} absorption bands occurs and is associated with magnetic exchange-coupled pairs of Fe^{3+} ions. These absorption bands are also observed in natural sapphire. Mineral structures provide a great variety of interacting cation units which should show these same cooperative effects. It is, therefore, of interest to examine the role of these units in the study of mineral optical properties.

Also of interest is the correlation of the anisotropy of the absorption with the orientation of the cation cluster within the crystal. Large anisotropy in the absorption bands of Fe^{3+} has already been noted in oxobridged dimers (Schugar *et al*, 1972), which correlates with the Fe–O–Fe direction. Anomalously intense absorption bands and anisotropy in the direction of the cation chains have been observed in Cr^{3+} dimers and Ni^{2+} linear chains (Urushiyama, Nakahara, and Kondo, 1971; Urushiyama, 1972; Akerman, Holt, and Holt, 1974). A rule of thumb which has developed from these and other unpublished studies is that absorption will be greatest when the electric vector is in the direction of the cation-cation chains.

Materials

Magnesiocopiapite

From Queteña and Alcaparrosa, Chile; amber-yellow crystals in mixed sulfates. Identity confirmed by X-ray powder diffraction. Analysis for $MgFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$: calc: Fe, 18.3; found: Fe, 19.3.

Coquimbite

From the Dexter Mine, San Rafael Swell, Utah; CIT #6123; pale lavender 2–4 mm crystals in mixed iron sulfates. Identity verified by X-ray powder diffraction. Analysis for $Fe_2(SO_4)_3 \cdot 9H_2O$: calc: Fe, 19.9; found: Fe, 15.2, 15.3. The iron analysis is low presumably because of aluminum substitution for iron.

Botryogen

From Queteña, Chile, Los Angeles County Museum #7577, and CIT #1671; veins of orange-red crystals in mixed ferric sulfates. Identity confirmed by X-ray powder diffraction. Analysis for $MgFe(SO_4)_2(OH) \cdot 7H_2O$: calc: Fe, 13.5; found: Fe, 14.1.

Fe(NH₄)SO₄ · 12H₂O

Laboratory-analyzed reagent (Baker); recrystallized slowly from water 0.001 N in H_2SO_4 yielding cm-sized pale lavender crystals. Ferric ammonium sulfate was also used to calibrate the colorimetric Fe determinations using the 1,10-phenanthroline method (Sandell, 1959).

Experimental Methods

Experimental details used in this laboratory which have not previously been described are outlined below. Optical spectra were obtained with a Cary 17I spectrophotometer which has been modified to allow operation at constant slit-width by modulating the intensity of the tungsten source by means of a feedback signal from the reference amplifier circuit. This modification significantly improves the quality of data and baseline reproducibility when small crystals are being used. Polarized spectra were obtained with dual Glan-Thompson calcite polarizers in the sample and reference beams. Samples (and polarizers) were oriented so that an extinction direction is 45° from the polarization axis of the spectrophotometer. This provides the smoothest baseline, thereby minimizing the baseline corrections, and also minimizes the effect of the Woods' grating anomaly, which in the

spectrophotometer being used is particularly bad at 1257 nm.

Specimens were oriented where possible by reference to external crystal morphology. Samples were then mounted in molten sealing wax and hand ground and polished on the appropriate crystal face. The mounting wax was removed by dissolution in tetrachloroethylene, the crystal was turned over onto the polished face, remounted in wax, and ground and polished to the necessary thickness. Samples were then run in the spectroscopic experiment as self-supporting slabs placed over apertures of appropriate size and shape.

For specimens which cannot withstand the heat of the molten wax, or which are too friable to withstand grinding to the necessary thinness, the initial mounting was made in a nonrigid epoxy upon a glass microscope slide. After grinding and polishing the first surface, the epoxy and crystal were lifted from the glass, turned over, and remounted with a rigid epoxy upon a microscope slide. Grinding and polishing then proceeded with the specimen permanently mounted to the glass. This second method has the disadvantage that it is considerably more difficult to obtain an accurate measure of the thickness of the specimen because of the variable thickness of the epoxy layer between the crystal and the glass.

Sample thicknesses, which must be accurately known for accurate absorptivity and ϵ values, were determined by a mechanical micrometer or by a microscope micrometer in the case of self-supporting slabs. In the case of thin slabs epoxyed to glass, use is often made of a Beer's law calculation which has been calibrated against a thicker self-supporting crystal of known thickness.

Magnetic susceptibilities were determined with a PAR-FM-1 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$ (Figgis and Nyholm, 1958). Effective magnetic moments were computed for $\mu = 2.828 \sqrt{\chi'_{mole} \cdot T}$. Samples were run as coarse powders at ambient temperature.

Optical Spectra

To provide a point of reference against which the spectra of the hydroxobridged dimers and polymers could be compared, it was first necessary to examine the spectra of compounds which contain isolated, non-hydroxobridged Fe^{3+} in environments similar to that found in the basic sulfates. Two substances were chosen for this purpose: ferric ammonium sulfate,

$NF_4Fe(SO_4)_2 \cdot 12H_2O$, and coquimbite, $Fe_2(SO_4)_3 \cdot 9H_2O$. Ferric ammonium sulfate is an alum. X-ray structural studies have shown that the cubic α-alums contain the trivalent cations in nearly perfect octahedral coordination as isolated $[M(H_2O)_6]$ groups (Lipson and Beevers, 1935; Larson and Cromer, 1967). Coquimbite contains iron in three types of coordination environments, $[Fe(OSO_3)_6]$, $[Fe(H_2O)_6]$, and $[Fe(H_2O)_3(OSO_3)_3]$ (Fang and Robinson, 1970). Because the compound crystallizes in the hexagonal system, it provides a measure of the magnitude of optical absorption anisotropy that is associated with slightly distorted octahedra and an anisotropic local crystal-chemical environment. Both ferric ammonium sulfate and coquimbite behave as magnetically dilute systems in the temperature range in which they were examined spectroscopically: $Fe_2(SO_4)_3 \cdot 9H_2O$, $\mu_{Fe} = 5.87$ B.M. (= Bohr magnetons) at 283K (Amiel, Gourdonneau, and Vauthier, 1945); $NH_4Fe(SO_4)_2 \cdot 12H_2O$, $\mu_{Fe} = 5.89$ B.M. at 293K (König, 1966).

The optical spectrum of a single crystal of ferric ammonium sulfate (Fig. 1) consists of four band systems: a single band at 796 nm, $\epsilon = 0.055$, assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition; a band system near 520 nm which upon close inspection of the original data appears to be made up of two poorly resolved bands at 491 and 550 nm, assigned to components of the $^6A_{1g} \rightarrow {}^4T_{2g}$ transition; a band system with poorly resolved components at 412, 406, and 394 nm, $\epsilon \sim 0.13$, assigned to components of the $^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ transition; and a band at 361 nm assigned to the $^6A_{1g} \rightarrow {}^4E_g$ transition, but largely obscured by the charge transfer tail. In the near infrared, absorption from water sets in at about 1200 nm and begins to rise rapidly by 1350 nm. Because the crystals are isotropic, no polarizations were recorded. The general assignment scheme follows that of Bertrand and Eller (1974) for similar spectra from aqueous solutions of the compound.

The optical spectrum of coquimbite (Fig. 2) is similar to the ferric ammonium sulfate. The $^4T_{1g}$ band at 778 nm and the $^4T_{2g}$ band at 561 nm are both weakly polarized $E \perp c$, and components of the $({}^4A_{1g}, {}^4E_g)$ band at 433 and 427 nm are both strongly polarized $\parallel c$. A possible assignment scheme for these components is to assign the higher energy, more intense component at 427 nm to the more abundant $[Fe(H_2O)_3(SO_4)_3]$ groups, the 433 nm component to the $[Fe(SO_4)_6]$ units, and the weak 415 nm component to the $[Fe(H_2O)_6]$ units. Complete spectroscopic data are presented in Table 1.

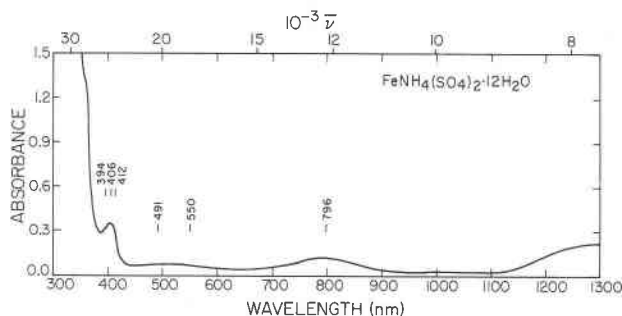FIG. 1. Optical absorption spectrum of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ crystal 4.2 mm thick at 296 K.

FIG. 2. Optical absorption spectrum of coquimbite, $Fe_2(SO_4)_3 \cdot 9H_2O$ from the Dexter Mine, Utah. Crystal 1.04 mm thick at 296 K. Polarized radiation $\parallel c$ (solid line) and $\perp c$ (dashed line).

Coquimbite is a member of the interesting class of minerals which change their apparent color depending upon whether they are illuminated by tungsten lamps, daylight, or fluorescent bulbs. This effect, similar to the "alexandrite effect" in chromium chrysoberyl discussed by White, Roy, and Crichton (1967), depends upon the physiological response of the human eye, the presence of transmission maxima in particular spectral regions, and the emission spectra of the source illumination. Under tungsten illumination coquimbite is lavender, but under sunlight it is pale grey-green.

The absorption spectra of ferric iron in several silicate minerals are similar to the spectra of coquimbite and ferric ammonium sulfate. For example, andradite garnet, $Ca_3Fe_2(SiO_4)_3$, is an isotropic Fe^{3+} mineral with an absorption spectrum which displays the basic Fe^{3+} pattern. The ϵ values for the $^4T_{1g}$ band, 0.08, and the $^4T_{2g}$ band set, $\sim$0.06, are similar to ferric ammonium sulfate, although the ($^4A_{1g}$, ^4E_g) set is sharper and has a correspondingly greater ϵ value of 1.5. The values reported here for a light yellow-green Val Malenco, Italy (demantoid variety) andradite, agree with Manning's (1973) value for the ($^4A_{1g}$, ^4E_g) band but are lower for both the $^4T_{1g}$ and $^4T_{2g}$ bands than the values reported by Moore and White (1972).

The spectroscopic features of these standards which are important to the discussion which follows are: (1) The basic pattern of two broad bands at lower energy ($^4T_{1g}$ and $^4T_{2g}$) followed by a sharp band ($^4A_{1g}$, ^4E_g) corresponding to the pattern predicted by ligand field theory for a d^5 octahedral system is observed. The splitting of the $^4T_{2g}$ and ($^4A_{1g}$, ^4E_g) bands into resolvable components indicating the lowering of the microsymmetry from rigorously octahedral is not of concern to the discussion which follows. (2) The ϵ values are of the order of magnitude normally encountered for spin-forbidden bands. The $^4T_{1g}$ and $^4T_{2g}$ bands have values of 0.05 to 0.15, and the sharp
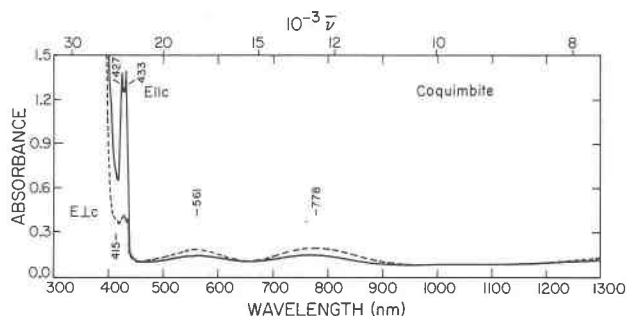
($^4A_{1g}$, ^4E_g) set ranges from 0.1 to 1.5. (3) The anisotropy of absorption in the non-isotropic crystal standard was such that the greatest difference in absorption in any single band was a factor of 5.

Hydroxobridged Fe^{3+}—Copiapite

The simplest case of aggregation of cations is the dimer. Molecular Fe^{3+} dimers have been prepared in a variety of solution chemical studies. Such Fe^{3+} dimers include several with a single oxobridge joining the iron ions, as well as examples with two oxobridges and two hydroxobridges. Many of these systems are reviewed by Murray (1974). No example of a dimer bridged by a single hydroxobridge has been reported. This is surprising in view of the extensive variety of minerals with hydroxybridged iron.

Copiapite provides the opportunity to examine the effect of a hydroxobridged Fe^{3+} pair. The copiapites constitute a family of minerals of general formula $AB_4(SO_4)_6(OH)_2 \cdot 20H_2O$ where $A = Fe^{2+}$, Mg, Cu,

TABLE 1. Spectral Parameters of Ferric Sulfates*

		$^6A_{1g} \rightarrow$		
	Polarization	$^4T_{1g}$	$^4T_{2g}$	($^4A_{1g}$, ^4E_g)
Ferric ammonium sulfate Fe(NH$_4$)(SO$_4$)$_2$·12H$_2$O	Isotropic	λ=796 ϵ=0.055	550, 491 0.028	412, 406, 394 0.13
Coquimbite Fe$_2$(SO$_4$)$_3$·9H$_2$O	ω	778 0.18	561 0.14	433, 427, 415 0.16 0.43 (0.05)
	ϵ	0.09	0.10	0.75 2.04 (0.05)
Magnesiocopiapite MgFe$_4$(SO$_4$)$_6$(OH)$_2$·20H$_2$O	α	864,$\sim$818 – 0.3	$\sim$598,$\sim$555 0.5 –	430 0.4
	β	0.2 –	– 0.4	–
	γ	1.7 –	– 0.9	36
Botryogen MgFe(SO$_4$)(OH)·7H$_2$O	α	939 –	$\sim$498 –	432, 412 – $\sim$1.1
	β	–	$\sim$1.8	0.4, –
	γ	3.4	–	96 $\sim$7.8

* All wavelengths in nm; ϵ in liter·mole^{-1}; values in parenthesis are difficult to determine exactly; ϵ values are computed from Fe concentrations determined by wet chemical analyses.
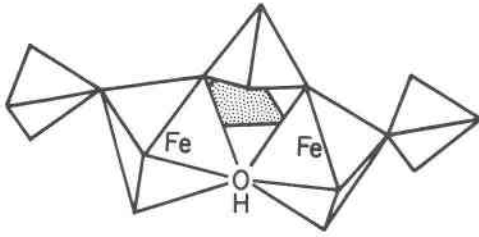
FIG. 3. The hydroxobridged dimeric unit in magnesiocopiapite. Positions in the ferric iron octahedron not bound to sulfate oxygen or hydroxide are coordinated to molecular water (after Süsse, 1972).

Zn and B = Fe^{3+}, Al. Copiapites possess a bright yellow color which contrasts strongly with the pale lavender coquimbite with which they are often associated in spite of the fact that both minerals contain about 19 percent Fe. Magnesiocopiapite (A = Mg, B = Fe^{3+}) occurs with nearly ideal end-member composition in the sulfate deposits of Chile. The structure of magnesiocopiapite has been described by Süsse (1972) and a ferrian copiapite by Fanfani et al (1973). The triclinic crystals contain chains of octahedral ferric iron along [101] which are bound to H_2O, OH, and sulfate tetrahedra. The chains can be visualized as being comprised of ferric dimers bridged by a single hydroxide and two sulfate tetrahedra, which in turn are linked through additional sulfate tetrahedra (Fig. 3). It is presumed that the magnetic exchange interactions are transmitted dominantly through the hydroxide bridge rather than through the SO_4^{2-} groups. Therefore, it is appropriate to view this material as containing isolated hydroxobridged dimers. The Fe(OH)Fe angle is approximately 131°.

The (010) cleavage flake of magnesiocopiapite allows optical spectra to be taken perpendicular to the Fe–Fe axis (β) and parallel to it (γ). Two prominent absorption bands are observed in γ at 855 nm and 430 nm (Fig. 4). Their shape and positions correspond to the $^6A_{1g} \rightarrow {}^4T_{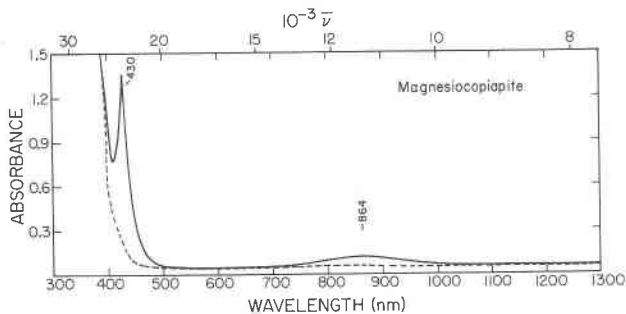1g}$ and $^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ transitions, respectively, but their intensities are anomalously high. The $^4T_{1g}$ band has an ϵ of 1.7, more than an order of magnitude higher than in the magnetically dilute reference compounds. The ϵ of the ($^4A_{1g}$, ^4E_g) band equals 36, up more than two orders of magnitude from the $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and more than an order of magnitude from coquimbite. In the spectra of samples thin enough to observe the full 430 nm band, the $^4T_{2g}$ band could not be observed. In these samples the ligand field bands were virtually unobservable in the β direction. In much thicker crystals, the $^4T_{1g}$ and $^4T_{2g}$ transitions could be observed in α and β (Fig. 5). Their intensities are somewhat higher than those of coquimbite, but much lower than the γ direction.

Hydroxobridged Chains—Botryogen

An extension of the case of the hydroxobridged dimer in magnesiocopiapite is the infinite linear chain of hydroxobridged Fe^{3+} ions. The mineral botryogen, $MgFe(SO_4)_2(OH) \cdot 7H_2O$, is a hydrated ferric hydroxy sulfate which contains chains of hydroxobridged Fe^{3+} ions. The mineral is a bright orange-red color which contrasts with the paler magnesiocopiapite with which it can be associated. Süsse (1968) has determined the crystal structure and found that the chains are parallel to the c axis. Each Fe^{3+} in the chain is joined to neighboring Fe^{3+} in the chain through a single hydroxide bridge and a single sulfate tetrahedron. In the (101) cleavage plane, the γ and β vibration directions are oriented nearly parallel and perpendicular to the chain direction, allowing spectroscopic measurements to be conveniently made to examine the role of the chains.
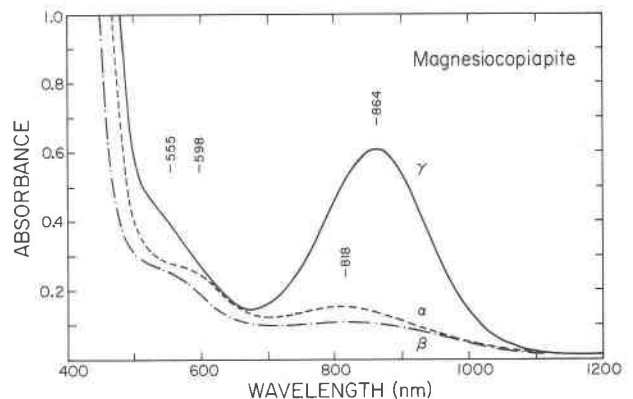
The optical absorption spectrum of botryogen dis-

FIG. 4. Optical absorption spectrum of magnesiocopiapite from Alcaparrosa, Chile; 45 μm thick; γ = solid line; β = dashed line; 296 K.

FIG. 5. Optical absorption spectrum of magnesiocopiapite from Alcaparrosa, Chile. Plotted for a 500 μm thick crystal. α = short dashed line; β = long dashed line; γ = solid line; 296 K.

plays large differences between the directions parallel and perpendicular to the chains. Figure 6 shows the $^4T_{1g}$ band at 939 nm strongly enhanced in the direction parallel to the chains (γ). The ϵ value, 3.4, in the parallel direction is at least fifty times greater than the values in the perpendicular directions. The $^4T_{2g}$ band which can be seen at ~498 nm in α and β is not apparent in the γ spectrum. The most spectacular enhancement is shown by the 432 nm ($^4A_{1g}$, ^4E_g) band (Fig. 7) for which ϵ in γ is ~96.

Magnetics

The gram magnetic susceptibility, χ_g, of magnesiocopiapite is 3.24×10^{-5} cgs (297 K, 7.8 $k\theta e$) corresponding to an effective magnetic moment per iron, $\mu = 4.70$ B.M. using the Fe content determined by chemical analysis. For botryogen $\chi_g = 1.68 \times 10^{-5}$ cgs (297 K, 9.0 $k\theta e$) and $\mu = 3.97$ B.M. Both of these magnetic moments fall well below the values of 5.9–6.0 B.M. found for magnetically dilute Fe^{3+}. Detailed studies of the temperature dependence of the susceptibility have not been conducted because they would be less meaningful than if conducted on synthetic materials free of impurity phases, once such materials become available. Assuming the Heisenberg interaction $\hat{H} = -2J\ \mathbf{S}_1 \cdot \mathbf{S}_2$, and using the Bleaney-Bowers equation (Bleaney and Bowers, 1952) with $g = 2.00$ and $N\alpha = 0.0$ for a $S = (5/2, 5/2)$ system to fit the 297 K point of magnesiocopiapite, the value of $J = -13.9$ cm^{-1} thus obtained provides an indication of the extent of the antiferromagnetic interaction. The extent of the magnetic coupling of the dimeric unit in magnesiocopiapite is much less than that for typical oxobridged ferric dimers for which $J = \sim -100$ and somewhat greater than that found in a dihydroxobridged ferric dimer where J = -8 cm^{-1} (Schugar *et al*, 1969, 1972).

Discussion

Several points of interest arise from the examination of the crystals with oriented hydroxobridged aggregates. (1) These materials are strongly pleochroic with the greatest absorption occurring when the electric vector is in the direction of the Fe–Fe axis. (2) The spectra taken in the direction of greatest absorption commonly appear as if only the $^4T_{1g}$ and ($^4A_{1g}$, ^4E_g) bands have undergone intensification. (3) The intensified bands are more than an order of magnitude stronger than those in the nonaggregated standards. (4) The extent of anisotropy associated with hydroxobridged aggregates is far greater than that as-
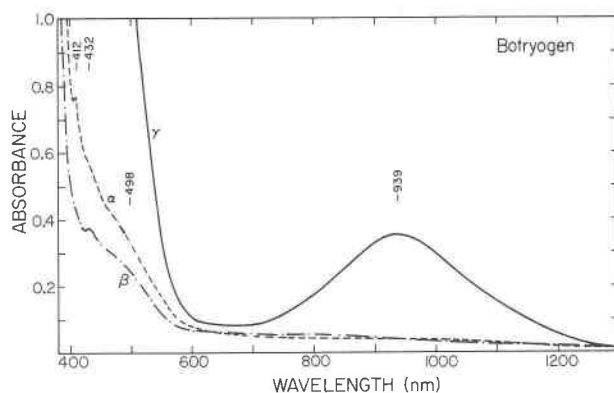

FIG. 6. Optical absorption spectrum of botryogen from Queténa, Chile. Plotted for a 200 μm thick crystal. α = short dashed line; β = long dashed line; γ = solid line; 296 K.

sociated with distorted octahedral coordination polyhedra.

Theoretical studies have been directed toward the understanding of the cooperative intensity mechanism. These studies and pertinent data have been reviewed by Lohr (1972). In essence, the proposed mechanisms consider the interacting system as a unit which has its own manifold of spin states among which components of spin-allowed transitions (for the unit) can occur, thereby obviating the spin-selection rules for the isolated ions. The electronic transition occurs when one member of the exchange-coupled pair is excited to a higher energy electronic state while the other member of the pair remains in the ground electronic state ($^6A_{1g}$).

A detailed theoretical treatment of the optical anisotropy of ferric clusters has not appeared. Experimental studies to date have shown that strong anisotropy, involving preferred absorption in the direction of the cation chains or in the plane of cation sheets, is a characteristic feature of the absorption spectroscopy of antiferromagnetic ferric iron materials. Hopefully, forthcoming reports of
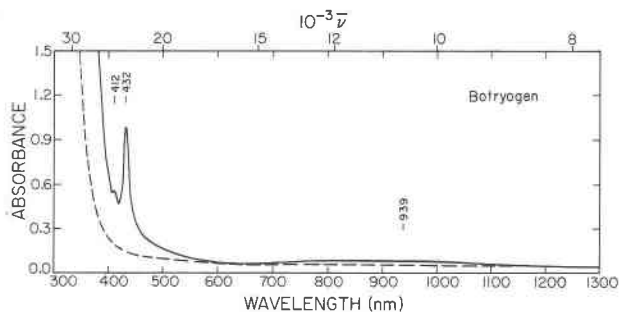

FIG. 7. Optical absorption spectrum of botryogen from Queténa, Chile; 15 μm thick; β = dashed line; γ = solid line; 296 K.

spectroscopic and magnetic studies of a variety of ferric iron clusters will not only serve to define the extent of the phenomena but also to stimulate the development of a deeper theoretical understanding.

It is now clear that the optical spectra of Fe^{3+} minerals can be strongly controlled by local cation aggregation. Although the intensity stealing mechanism proposed by Manning (1973) is undoubtedly operating in many mineral systems, cooperative intensification via magnetic coupling is more likely to be the dominant factor in the majority of systems. The materials which had the highest ϵ for the $^6A_{1g} \rightarrow (^4A_{1g}, {}^4E_g)$ transition on Manning's graph, namely hematite and gadolinium iron garnet, both exhibit strong magnetic interactions, whereas the systems with the lowest ϵ, phosphate glass:Fe and silicate garnets, are magnetically dilute systems.

An understanding of the role of cooperative intensification in natural systems should prove especially useful for the study of cation-ordering phenomena, although optical studies may necessarily have to be coupled with magnetic studies. A potentially useful aspect is the cooperative enhancement of the spin-forbidden bands of Fe^{2+}. The spin-allowed transitions of Fe^{2+} should not be subject to extensive enhancement of this sort, but the spin-forbidden bands may respond in a fashion similar to Fe^{3+}.

A useful rule-of-thumb correlation of color with magnetic interaction is developing from these studies. In the absence of other interferences, minerals which contain magnetically dilute Fe^{3+} in octahedral oxygen coordination are light lavender (sulfates and phosphates) or light green to yellow-green (silicates). However, they will be bright yellow to orange, if moderate antiferromagnetic interaction is present, and deep red if strong magnetic coupling occurs.

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