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FERROUS-FERRIC INTERACTION ON ADJACENT FACE-SHARING ANTIPRISMATIC SITES IN VESUVIANITES: EVIDENCE FOR FERRIC ION IN EIGHT COORDINATION

P. G. MANNING
Inland Waters Directorate, Environment Canada, 562 Booth St., Ottawa, Ontario K1A 0E7

ABSTRACT

Polarized optical absorption spectra of green vesuvianites from two localities are reported. The most interesting features in the spectra are two strongly polarized bands at 15800cm^{-1} (633nm) and 17500cm^{-1} (571nm) having maximum intensity in *E*//*c* spectra, where *E* is the vibration direction of the electric vector of incident light. Both bands are almost completely extinguished in $E \perp c$ spectra. The former band is attributed to $Fe^{2+} \rightarrow Fe^{3+}$ interaction between ions located at the centres of adjacent face-sharing antiprisms. The antiprismatic sites lie on the 4-fold axis which is parallel to the *c*-crystallographic axis. The band is therefore evidence for Fe^{3+} in eight coordination.

A weakly polarized multi-component envelope in the 21000cm^{-1} to 25000cm^{-1} region of the spectrum is assigned to the crystal-field transitions $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in ferric ions in two or more coordination sites.

SOMMAIRE

Les spectres d'absorption optique, en lumière polarisée, de vésuvianite verte provenant de deux gîtes différents sont caractérisés par deux bandes fortement polarisées, l'une à 15800 cm^{-1} (633 nm) et l'autre à 17500 cm^{-1} (571 nm), d'intensité maximale dans les spectres *E*//*c*, où *E* est le vecteur électrique de la lumière incidente. Les deux bandes sont presque complètement éteintes dans les spectres $E \perp c$. La première bande est attribuée à l'interaction $Fe^{2+} \rightarrow Fe^{3+}$ entre ions situés au centre de deux antiprismes à face commune. Les sites antiprismatiques se trouvent sur un axe d'ordre 4. La bande milite donc en faveur du Fe^{3+} octocoordonné.

Une enveloppe à composantes multiples faiblement polarisées dans la région 21000 à 25000 cm^{-1} du spectre est attribuée aux transitions de champ cristallin $^6A_1 \rightarrow {}^4A_1$ $^4E(G)$ dans des ions ferriques dans deux ou plus de deux sites coordination.

(Traduit par le journal)

INTRODUCTION

Ferric ions in eight coordination ($Fe^{3+}{}_{VIII}$) have not been detected in minerals and well-authenticated X-ray-supported occurrences of $Fe^{3+}{}_{VIII}$ in solids generally are rare (King *et al.* 1971). A collation of magnetic and Mössbauer and infrared spectroscopic studies suggests that $Fe^{3+}{}_{VIII}$ occurs in some ferric salts (Hall *et al.* 1968). Cation:anion size ratios and anion-anion repulsions militate against such high coordination numbers, but calculations suggest that eight coordination is more likely to be achieved through bidentate ligandcy than monodentate (Blight & Kepert 1972). The optical absorption spectra of $Fe^{3+}{}_{VIII}$ ions are not likely to be greatly different from spectra of ferric ions in octahedral or tetrahedral coordination. However, the polarization properties of $Fe^{2+} \rightarrow Fe^{3+}$ intervalence charge-transfer processes can be useful indicators of ferric ion site distributions. In this article, a strongly polarized band in the red region of the spectra of green vesuvianites is attributed to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer between ions on adjacent antiprismatic sites. Previously published Mössbauer spectra of vesuvianites are re-examined and reliable isomer shifs and quadrupole splittings for $Fe^{3+}{}_{VIII}$ are proposed.

The colours of vesuvianites — greens, browns and yellows — arise from the presence of a few percent Fe and Ti. X-ray diffraction (Rucklidge *et al.* 1975, Coda *et al.* 1970), optical absorption and Mössbauer studies (Manning 1975; Manning & Tricker 1975) show that these ions are distributed mainly over octahedral Al/Fe positions (Al/Fe-O distance = 1.945Å) and square-pyramidal *B* positions (*B*-O = 2.11Å). Smaller amounts of Fe^{2+} and Ti^{4+} ions are located on 8-coordinate sites. An optical absorption study of the green vesuvianites from Lowell County, Vermont, has been described earlier (Manning 1968).

EXPERIMENTAL DETAILS

Polarized optical absorption spectra of green vesuvianites from Lowell County and from Pakistan were recorded by the method described previously (Manning 1975). The spectra of both specimens are similar, and the spectrum of the Lowell material only is discussed in detail. Spectra were run at room temperature on a Cary-14 spectrophotometer and using Glan polarizing prisms. Crystals were donated by Prof. R. A. Howie, King's College, London and by Mr. H. G. Ansell, Geological Survey of Canada, Ottawa. Mr. D. Owens, CANMET, Ottawa, performed the electron microprobe analyses and Dr. W. Petruk, also of CANMET, aided in orientation of the specimens. The Lowell crystals contained 4.9% Fe and 0.2% Ti.

Absorption envelopes were resolved using a Dupont Model 360 Curve-Resolver. The positions of individual bands were checked against obvious inflexions in the parent curves.

Extinction coefficients (ϵ) are calculated from the net band absorbance divided by the product of the cation concentration (in moles litre^{-1}) and the specimen thickness (in cm). Units of ϵ are litres moles^{-1} cm^{-1}.

Results and Discussion

Details of the polarized spectra of the Lowell vesuvianite are presented in Figures 1-3. Apart from the two strongly polarized bands at 15800 cm^{-1} (633nm) and 17500cm^{-1} (571nm), the spectra are very similar in both $E /\!/ c$ and $E \perp c$ modes, where E is the vibration direction of the electric vector of incident light. The $E \perp c$ spectrum is shown in Figure 1. The net absorption envelope in the 21000 to 25000cm^{-1} range, after subtraction of ultraviolet-centred charge-transfer absorption, is ~15% more intense in the $E \perp c$ mode. However, $O^{2-}2p \rightarrow Fe\ 3dt_2$ charge-transfer absorption is more intense in $E /\!/ c$ and overall the crystals are a darker green in the $E /\!/ c$ mode.

The 21000cm^{-1} to 25000cm^{-1} envelope and a suggested resolution scheme are presented in Figure 2. The curve-fitting procedure is highly subjective and the proposed solution is not unique. Mössbauer spectra of the Lowell (Manning & Tricker 1975) and Pakistan vesuvianites show no measureable amounts of ferrous ion (<2% of total Fe), hence all peaks are caused by Fe^{3+}. Neither is there evidence of a band at 23000cm^{-1} polarized in $E /\!/ c$ marking $Fe^{2+} \rightarrow Ti^{4+}$ processes (Manning 1975). None of the individual bands has a half-width exceeding 1000cm^{-1}, hence it would seem that they mark the field-independent transitions ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in Fe^{3+} ions in two or more sites of different symmetry. The dominant doublet in the Lowell Mössbauer spectrum is relatively broad, with a half-width of 0.43mm^{-1}, suggesting some form of next-nearest-neighbor interaction. The half-width of the 21600cm^{-1} band (~200cm^{-1}) confirms the field-independent nature of this transition, and marks ferric iron in one type of site only.

The area under the 15800cm^{-1} band greatly exceeds that under the 17500cm^{-1} (Fig. 3). The electronic processes responsible for the 15800cm^{-1} band occur therefore with greater probability than the processes causing the 17500cm^{-1} absorption. From its energy, the 15800cm^{-1} band marks either (i) the ${}^6A_1 \rightarrow {}^4T_2(G)$ transition in Fe^{3+} (e. g. Manning 1972; Moore & White 1972) or (ii) $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer (e. g. Faye *et al.* 1974; Robbins &

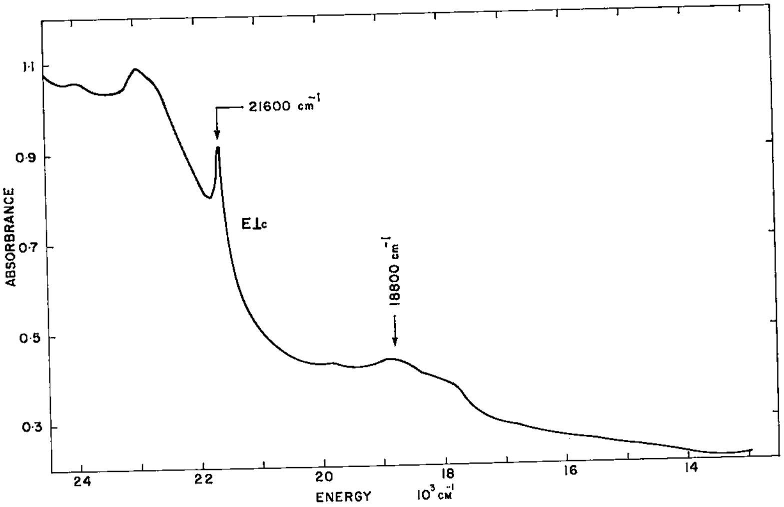

FIG. 1. Optical absorption spectrum of Lowell vesuvianite in $E \perp c$ mode. This spectrum is similar to that in $E /\!/ c$ above 18000cm^{-1}. Specimen thickness = 0.185cm.

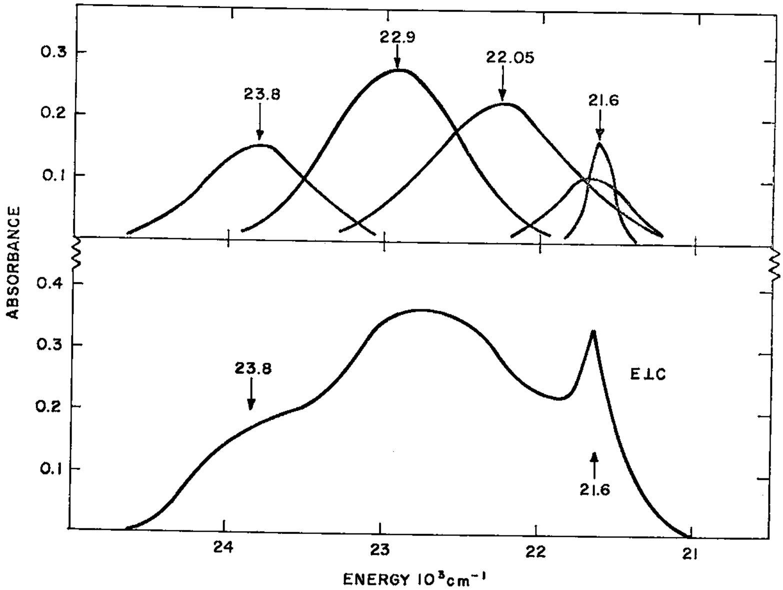

FIG. 2. Net absorption envelope in the 21000 to 25000cm^{-1} region of the Lowell vesuvianite in $E \perp c$ mode (lower spectrumfl and resolved components of the envelope (upper spectrum). Specimen thickness = 0.185cm. This is not a unique solution. However, the individual bands have sufficiently small half-widths to suggest that they are caused by the transitions $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in ferric ions.

Strens 1972) between ions on adjacent sites lying along the *c*-direction. The strong polarization of the band supports (ii). Polarization of ferric crystal-field bands can also occur through antiferromagnetic coupling of spins of neighboring ferric ions (Rossman 1975), but this mechanism also polarizes the more prominent $^4A_1{}^4E(G)$ bands. The crystal structure on the 4-fold axis, which is parallel to the *c*-crystallographic axis, is shown in Figure 4. The *B* and *C* positions are half-occupied (Rucklidge *et al.* 1975), and presumably if a *C* position is occupied the adjacent *B* position is empty. It seems reasonable to assign the 15800cm^{-1} band to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer between cations at the centres of adjacent face-sharing antiprisms. The internuclear axis (dashed line in Fig. 4) is parallel to the c-direction. The internuclear separation (2.61Å) is short enough for a metal-metal bond in which case the 15800 cm^{-1} band represents transitions between bonding and antibonding molecular orbitals. In antiprismatic coordination the lowest energy 3*d* orbital is the axially-symmetrically $3d_z{}^2$ (Randic 1960), which is oriented parallel to the *c*-crystallographic direction and overlaps with the $3d_z{}^2$ orbital of the adjacent *C*-cation. The absorbance of the 15800cm^{-1} band is 0.155 for a specimen 0.185cm thick, and assuming that the ε-value of the process is 500, then the concentration of Fe^{2+}–Fe^{3+} pairs is 0.0017 molar. If the 10% of the Fe (0.21 molar) with the unusual Mössbauer parameters (Manning & Tricker 1975) marks Fe^{3+} on the antiprismatic positions, then on a statistical basis one *C*-position out of 125 is occupied by Fe^{3+}. The ferrous requirement on the antiprismatic sites is <1% of total Fe, which is difficult to detect by Mössbauer methods.

The origin of the 17500cm^{-1} band is not known, but the polarization properties suggest $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer parallel to the *c*-direction. The band may reflect such interaction between ions on *B* and *C* positions, which are separated by 3.67Å. The weakly polarized two-component envelope at ~18800cm^{-1} (532nm) may mark the $^6A_1 \rightarrow {}^4T_2(G)$ transition in one or more of $Fe^{3+}{}_{viii}$ or $Fe^{3+}{}_{vi}$.

It was proposed tentatively (Manning & Tricker 1975) that the 10% of total Fe in the Lowell vesuvianite with the Mössbauer parameters isomer shift = 0.62mms^{-1} and quadrupole splittings = 0.89mms^{-1} is $Fe^{3+}{}_{viii}$. These parameters are in good agreement with those measured for Fe^{3+} in the dialkali salts of dihydrogendiethylenetriaminepentaacetatoferrate (III), in which there is additional spectroscopic and mag-

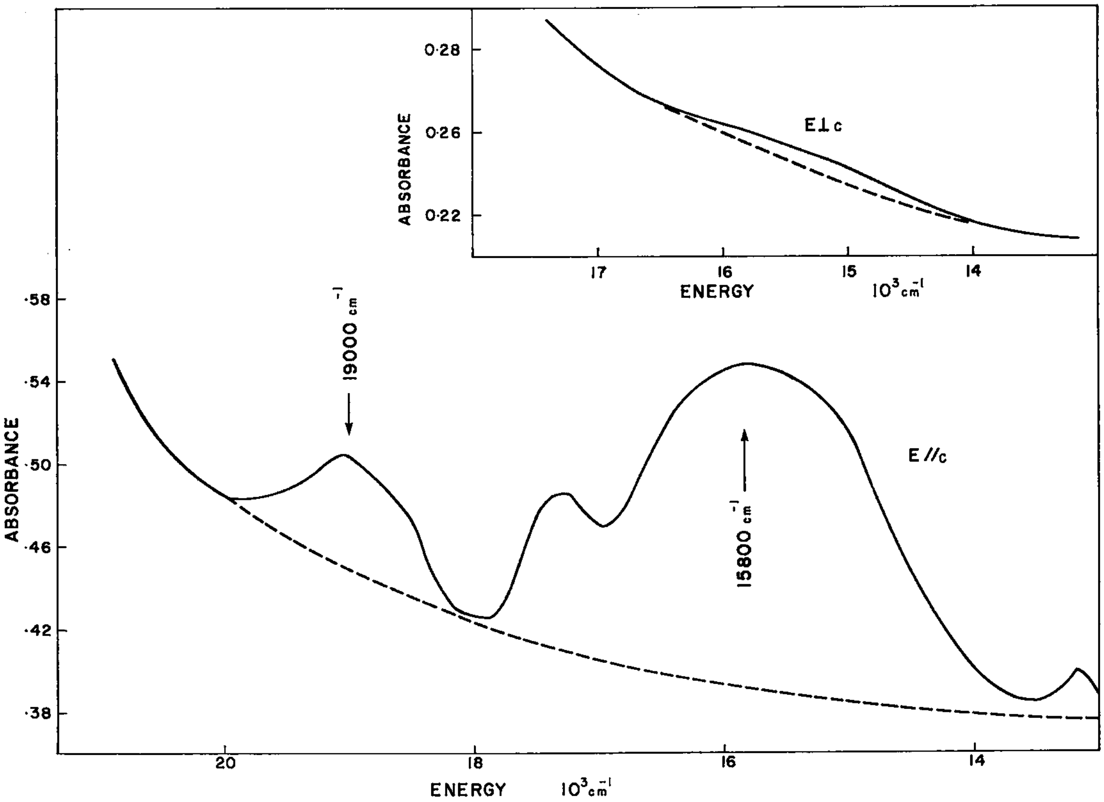

FIG. 3. Spectrum of Lowell vesuvianite in $E/\!/c$ mode in 13000 to 20000cm^{-1} range and, inset, $E \perp c$ spectrum in 13000 to 17000cm^{-1} range. Specimen thickness = 0.185cm. The 15800cm^{-1} band is at least 15 times more intense in the $E/\!/c$ orientation.

netic evidence for Fe^{3+}_{viii} (Hall *et al.* 1968). It seems reasonable to suggest therefore, in light of consistency of interpretation of optical and Mössbauer spectra of green vesuvianites, that Fe^{3+}_{viii} ions have isomer shifts and quadrupole splittings of, respectively, 0.6 to 0.7mms^{-1} and 0.8 to 1.0mms^{-1}.

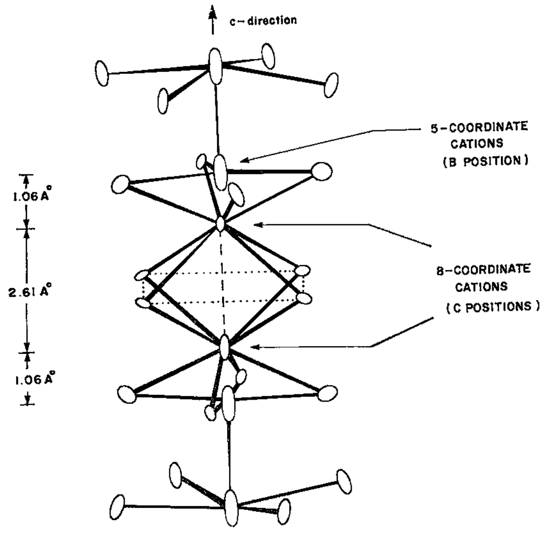

FIG. 4. Structure of the 4-fold axis projected onto a plane containing the c-crystallagraphic direction. Dashed line represents the Fe^{2+}–Fe^{3+} axis of ions on adjacent antiprismatic sites.

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