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

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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 15800 cm⁻¹ (633 nm) and 17500 cm⁻¹ (571 nm) 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⊥c spectra. The former band is attributed to Fe³⁺ → Fe⁸⁺ 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 Fe⁸⁺ in eight coordination.

A weakly polarized multi-component envelope in the 21000 cm⁻¹ to 25000 cm⁻¹ region of the spectrum is assigned to the crystal-field transitions A₁→A₁,E(G) in ferric ions in two or more coordination sites.

INTRODUCTION

Ferric ions in eight coordination (Fe⁸⁺,viii) have not been detected in minerals and well-authenticated X-ray-supported occurrences of Fe⁸⁺,viii in solids generally are rare (King et al. 1971). A collation of magnetic and Mössbauer and infrared spectroscopic studies suggests that Fe⁸⁺,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 Fe³⁺,viii ions are not likely to be greatly different from spectra of ferric ions in octahedral or tetrahedral coordination. However, the polarization properties of Fe³⁺,viii→Fe⁸⁺ 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 Fe³⁺ → Fe⁸⁺ charge-transfer between ions on adjacent antiprismatic sites. Previously published Mössbauer spectra of vesuvianites are re-examined and reliable isomer shifts and quadrupole splittings for Fe⁸⁺,viii are proposed.

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⊥c modes, where E is the vibration direction of the electric vector of incident light. The E⊥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⊥c mode. However, O²⁺2p→Fe 3d₁s 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 Fe³⁺. Neither is there evidence of a band at 23000cm⁻¹ polarized in E//c marking Fe³⁺→Ti⁴⁺ 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 ⁴A₁→⁴A₁,E(G) in Fe³⁺ 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 ⁴A₁→⁴T₂(G) transition in Fe³⁺ (e.g. Manning 1972; Moore & White 1972) or (ii) Fe³⁺→Fe⁵⁺ charge-transfer (e.g. Faye et al. 1974; Robbins &
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 $^4A_{1g}E(G)$ 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$^{3+} \rightarrow$ Fe$^{2+}$ 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 $3d$ 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 $e$-value of the process is 500, then the concentration of Fe$^{3+} \rightarrow$ Fe$^{2+}$ 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$^{3+} \rightarrow$ Fe$^{2+}$ 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 $\approx$18800cm$^{-1}$ (532nm) may mark the $^4A_{1g} \rightarrow$$^2T_{2g}(G)$ transition in one or more of Fe$^{3+}$ or Fe$^{2+}$.

It was proposed tentatively (Manning & Tricker 1975) that the 10% of total Fe in the Lowell vesuvianite with the Mössbauer parameters isomer shift $= 0.62$mm/s and quadrupole splittings $= 0.89$mm/s is Fe$^{3+}$ or Fe$^{2+}$. These parameters are in good agreement with those measured for Fe$^{3+}$ in the dialkali salts of dihydrogendiethylenetriaminepentaacetatoferate (III), in which there is additional spectroscopic and mag-
Fig. 3. Spectrum of Lowell vesuvianite in $E//c$ mode in 13000 to 20000 cm$^{-1}$ range and, inset, $E\perp c$ spectrum in 13000 to 17000 cm$^{-1}$ range. Specimen thickness = 0.185 cm. The 15800 cm$^{-1}$ band is at least 15 times more intense in the $E//c$ orientation.

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

Magnetic evidence for Fe$^{3+}$ (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$^{3+}$ ions have isomer shifts and quadrupole splittings of, respectively, 0.6 to 0.7 mm/s and 0.8 to 1.0 mm/s$^{-1}$.

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REFERENCES


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