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EXTINCTION COEFFICIENTS OF Fe^{3+} SPECTRAL BANDS IN OXIDES AND SILICATES AS INDICATORS OF LOCAL CRYSTAL COMPOSITION

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Abstract

Extinction coefficients (ε) for the transitions ${}^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ in octahedral'y-coordinated Fe^{3+} ions in a number of oxides and s:licates have been collated and shown to range from ~ 1 to 600. At the lower end of the ε-range minerals are lightly coloured and at the upper end almost black, the colour being due mainly to $O^{2-} \rightarrow Fe^{3+}$ *UV*-centred charge-transfer absorption. The crystal-field transitions borrow intensity from charge-transfer absorption, the intensity of which is dependent on the cation composition of the second nearest neighbour sites. Charge-transfer is particularly intense in materials containing Fe^{3+}_{VI}-O-M_{IV} units, where $M = Al^{3+}$ and Fe^{3+}. It is suggested that ε-values of octahedral-Fe^{3+} crystal-field bands can be used as indicators of metal ions present in the second-nearest neighbour sites. Muscovite and orthoclase are used as examples.

Introduction

Because crystal-field transitions in Mn^{2+} and Fe^{3+} ions are spin-forbidden, extinction coefficients (ε) are expected to be in the range 0.1-1. While this is generally the case for Mn^{2+} bands (Manning 1968a), ε-values of Fe^{3+} bands vary considerably from one mineral to another. For example, ε-values for the ${}^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transitions in octahedral-Fe^{3+} ions in andradite and schorlomite are 1.5 and 15 respectively (Manning & Townsend 1970). The large ε-value for schorlomite was attributed to intensity-stealing from intense $O^{2-} \rightarrow Fe^{3+}$ charge-transfer absorption, charge-transfer being facilitated by replacement of second-nearest neighbour Si^{4+} ions by less-covalent Al^{3+} and Fe^{3+}. A similar mechanism was invoked to explain enhanced Mn^{3+} crystal-field and charge-transfer absorption in black tourmalines (Manning 1972a).

In the current work, ε-values have been collated for Fe^{3+} transitions in a number of silicates and oxides. The principal aim is to establish whether ε-values can be used as probes of local crystal composition, in particular the cation composition of the second-nearest neighbour sites. Recent crystal-field interpretations of diffuse interstellar bands have highlighted the need for an understanding of factors controlling intensities of Fe^{3+} bands (Manning 1972b).

Discussion

A plot of log ε against *N*, the number of Fe^{3+}-centred-octahedron oxygens not bonded to Si, for Fe^{3+} bands in a variety of oxides and silicates, is shown in Figure 1. A point for Fe^{3+} in a phosphate glass is also included. Extinction coefficients are calculated from

$$\varepsilon = A/C.l \qquad \text{(in litres/mole-cm)}$$

where A = net absorbance, C = cation concentration in moles/litre, and l = sample thickness in cm. Where ε-values are accurate to ± 25%, as, in points a-c, no error bars are included. For most minerals, however, ε-values are difficult to calculate either because Fe^{3+} ions are distributed between two different sites or, as in the case of hematite, charge-transfer absorption is so intense that bands marking the ${}^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transitions, expected at ~22700 cm^{-1} (Vernon 1962; Huffman 1970), have not been resolved. Nevertheless, the general shape of the curve in Figure 1 is readily evident. The ε-values range over three orders of magnitude. Since the octahedral sites in garnets are regular (Abrahams & Geller 1958; Weidenborner 1961), it would seem that site distortions from octahedral symmetry can be ignored. Note that points a-c in Figure 1 pertain to lightly-coloured materials for which *d-d* bands can be resolved for specimens ~0.1 cm thick (Manning 1967b, 1969). In contrast, intense charge-transfer in schorlomite and gadolinium iron garnets requires specimens be thinned to 0.0015 cm (Manning & Harris 1970) and 0.5 μm (Levenson & Sawatsky 1969) respectively, to permit resolution of *d-d* bands. The earlier suggestion that crystal-field bands of Fe^{3+} borrow intensity from $O^{2-} \rightarrow Fe^{3+}$ charge-transfer absorption is confirmed.

Calculation of ε-values

Andradite. The molecular formula of the Stanley Peak andradite studied earlier (Manning 1967a) based on electron-probe analysis is

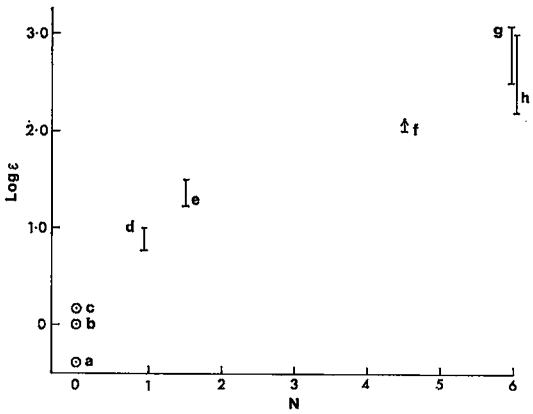

FIG. 1. A plot of log. ε, for the $^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transition in octahedral Fe^{3+}, against N, the number of Fe^{3+}-centred-octahedron oxygens not bonded to Si^{4+}. Also included is a point (a) for Fe^{3+} in a phosphate glass. b = grossular; c = andradite; d = titanaugite; e = schorlomite; f = kimzeyite (not less than 2.0); g = gadolinium iron garnet; h = hematite.

$Ca_{6.1}(Fe^{3+}_{3.95}Mn_{0.08})Si_{5.95}$ The ε-value (=1.5) was calculated from the total-Fe concentration (=21%).

Grossular. The spectrum of a grossular containing 3.4% Fe has been reported earlier (Manning 1969). The 8-coordinate Fe^{2+} concentration is 1%, based on the absorbance of the 8200 cm^{-1} Fe^{2+} band and assuming that the ε-value is the same as that (ε = 1) for the corresponding 7800 cm^{-1} Fe^{2+} band in almandines (Manning 1967b). The octahedral-Fe^{3+} concentration is therefore 2.4% and ε = 1. Fe^{2+}:Fe^{3+} ratio was confirmed to within ± 20% by complete chemical analysis.

Phosphate glass. The spectrum is typically that of octahedral-Fe^{3+} (Kurkjian & Sigety 1968). The ε-value was calculated from the total-Fe concentration.

Titanaugites. Titanaugites have the general formula $Ca(Mg, Fe^{2+}, Fe^{3+}, Al^{3+})_1(Si_{2-x}Al^{3+}_x)O_6$, where $x \sim 0.3$ (Deer, Howie & Zussman 1962). The $^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transition in octahedral-Fe^{3+} is seen at 22000 cm^{-1} and $\varepsilon.C = A/l = 12$ (Manning & Nickel 1969). Chemical analysis gave a formula close to that of a specimen from Poland (Deer, Howie & Zussman 1962, analysis 1, p. 123), giving $x = 0.31$ and $N = 0.93$. Each Fe^{3+}-centred-octahedron oxygen is bonded to a tetrahedral ion. Based on 4.5% Fe_2O_3 and assuming Fe^{3+} and Al^{3+} are uniformly distributed over 0.17 octahedral and 0.31 tetrahedral sites (out of 2.0), ε = 9. The minimum ε-value based on Fe^{3+} having a preference for the octahedral site is 6. An upper limit of ε cannot be calculated because there are sufficient tetrahedral positions to take up all Fe^{3+} ions.

Schorlomite. Schorlomite contains both octahedral- and tetrahedral-Fe^{3+} ions (Manning 1972c; Burns 1972). Several chemical analyses of the Magnet Cove crystals have been reported, all in reasonable agreement. Our Fe, Ti and Mn values agreed well with those of Howie & Woolley (1968). Assuming that Fe^{3+} and Al^{3+} distribute uniformly between octahedral and tetrahedral sites, the molecular formula is $Ca_6(Fe^{3+}_{1.52}Al^{3+}_{0.65}Ti^{4+}_{1.83})(Si^{4+}_{4.51}Fe^{3+}_{0.95}Al^{3+}_{0.39}Fe^{2+}_{\sim 0.1})$, whence $N = 1.5$ and, from the spectrum of Manning & Harris (1970), ε = 24. Each octahedral ion in garnet has six second-nearest neighbour Si^{4+} sites. The extreme values of ε based on Fe^{3+} and Al^{3+} having preference for the octahedral sites are 17 and 32 respectively.

Strictly, schorlomite should be represented in Figure 1 by two points corresponding to $N = 1$ and $N = 2$. The schorlomite spectra cannot be resolved into two sets of octahedral-Fe^{3+} bands, hence only average values of N and ε are considered.

Kimzeyite. The formula of the Magnet Cove kimzeyite (Milton *et al.* 1961) is

$$Ca_{3.11}(Zr^{4+}_{1.42}Ti^{3+}_{0.40}Mg^{2+}_{0.07}Nb^{5+}_{0.05}Fe^{2+}_{0.07})$$
$$(Al^{3+}_{1.26}Fe^{3+}_{0.98}Si^{4+}_{0.94})O_{12.00}.$$

Although the formula indicates the absence of octahedral-Fe^{3+}, the spectrum shows octahedral-Fe^{3+}bands at 16700 cm^{-1} and 22700 cm^{-1} of comparable intensity to tetrahedral-Fe^{3+} bands (Manning 1972c). The formula suggests that it would be unreasonable to expect > 10% of the total-Fe to be octahedral-Fe^{3+}, and because the ε-value for tetrahedral-Fe^{3+} bands is not likely to be < 10 (see below), a minimum ε-value for octahedral-Fe^{3+} is 100.

Gadolinium iron garnet. An ε-value of ~600 can be calculated from the measured absorbance of a 0.5 μm section (Levenson & Sawatsky 1969). The $^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transition is observed at 22600 cm^{-1}, in agreement with the energy of the same transition in andradite, kimzeyite and schorlomite. The ε-value is good within a factor of, say, 2.

Hematite. The $^6A_1 \rightarrow {}^4A_1\,{}^4E(G)$ transition in hematite has not been resolved. Huffman (1970) estimates the ε-value to be ~320, based on the assumption that the absorbance of the band is 10 times that of the band marking transitions to the Fe^{3+} $^4T_1(G)$ levels at 12000 cm^{-1}. A ratio of ~10 is valid for octahedral-Fe^{3+} bands in garnets. A lower limit of ε is likely to be 160 (corresponding to 5 times) and the upper limit possibly around 1000.

Corundum, kyanite and epidote. The calculated ε- and N- values for Fe^{3+} ions in corundum ($\varepsilon = 5$, $N = 6$; Lehman & Harder 1970), kyanite ($\varepsilon = 2$, $N = 1.75$; Faye & Nickel 1969) and epidote ($\varepsilon \sim 5$, $N = 1$; Burns & Strens 1967) do not fit the curve in Figure 1. The common factor here is that the second-nearest neighbour ions are Al^{3+}, also octahedrally-bonded. Oxygen-Fe^{3+} charge-transfer is not as prominent in corundum ($N = 6$) as it is in schorlomite ($N = 1.5$). It would seem, therefore, that intensity-stealing from oxygen $\rightarrow Fe^{3+}$ charge-transfer is suppressed where the second-nearest neighbour ions are octahedrally-bonded Al^{3+} and tetrahedrally-bonded Si^{4+}, hence the relatively low ε-values for Fe^{3+} crystal-field bands. Although the Fe^{3+} bands in andalusite spectra (Faye & Harris 1969) are weak, the approximate ε-values of 0.5-1 are consistent with all second-nearest neighbours being Si or octahedrally-bonded Al^{3+}.

Idocrase (vesuvianite). Fe^{3+} substitutes for Al^{3+}. Of the six Fe^{3+}-centred-octahedron oxygens, 5 are bonded to Si and one to an OH group (Warren & Modell 1931). Idocrase crystals containing ~2% Fe^{3+} are a light green, and the calculated ε-value is 1-2 (Manning 1968b). Hydroxyl-Fe^{3+} charge-transfer is clearly unimportant. This is consistent with the low ε-value of $Fe(OH_2)_6^{3+}$ ions (Burns & Strens 1967).

ε-values for tetrahedral-Fe^{3+}. Two bands at ~20000 cm^{-1} marking the transitions ${}^6A_1 \rightarrow {}^4T_1(G)$ and $\rightarrow {}^4T_2(G)$ in tetrahedral-Fe^{3+} have been observed in spectra of an unusual phlogopite (ε ~ 15 in unpolarized light, Faye & Hogarth 1969), black tourmaline (ε > 10; Manning 1972a) and schorlomite (Manning 1972c). From the schorlomite spectrum and assuming the molecular formula calculated above, ε ~ 10. Bands marking transitions to the ${}^4A_1{}^4E(G)$ levels are stronger, e.g., ~ 30 in the phlogopite referred to above.

General discussion

It would appear that in minerals where second-nearest neighbour ions are Si of SiO_4 tetrahedra, P of PO_4, Al of AlO_6 octahedra and H of OH, ε-values for the octahedral-Fe^{3+} ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition are not greater than 5. Substitution of these second-nearest neighbours, in particular Si by Al^{3+} or Fe^{3+}, leads to dramatic increases in ε, probably for the reasons that oxygen-Fe^{3+}_{VI} charge-transfer intensifies or shifts to lower energy. Energy overlap with *d-d* bands in increased. Si-O, Al_{VI}-O and O-H bonds are highly covalent, electronic charge is then withdrawn from the oxygens to the cation. Evidently, the bonding in SiO_4 tetrahedra is more covalent than in AlO_6 octahedra (ε-values for Fe^{3+} in corundum and epidote are greater than in grossular and andradite), whereas Al-O bonds are more covalent in AlO_6 octahedra than in AlO_4 tetrahedra (ε-values are greater for Fe^{3+} in schorlomite than in corundum). It is significant that SiO_4 tetrahedra and AlO_6 octahedra are the fundamental building units of aluminosilicates, and that aluminosilicates such as garnets are resistant to weathering. Schorlomite garnet, in which approximately 25% of Si sites are occupied by Al^{3+} or Fe^{3+}, and in which the Al^{3+}_{VI} content is low, is more friable than grossular and the pyralspites.

The interest in Fe^{+3} ε-values lies in their potential use as probes of local crystal composition, particularly where substitution into SiO_4 tetrahedra leads to $M^{3+}_{(VI)}$-O-Fe^{3+}/$Al^{3+}_{(IV)}$ units, where M^{3+} is an octahedrally-bonded transition-metal ion. Where the M^{3+} concentration is low, information could be gained on the ordering of metal ions. In the dioctahedral mica muscovite, Fe^{3+} substitutes for octahedrally-coordinated Al^{3+}. These Al^{3+} ions lie in a plane parallel to the 001 and are sandwiched between Al/SiO_4 layers. Four-sixth of the octahedral sites are filled and the composition of the tetrahedral sites is 0.25 Al, 0.75 Si. Each octahedral-Al^{3+} ion has four second-nearest neighbour tetrahedral sites, hence $N = 1$. The expected ε-value based on this average distribution of Al and Si ions is 8-10 (see titanaugite), whereas the calculated value is 1 (Faye 1968; Manning 1969). All Fe^{3+} ions have four Si and two protons as second-nearest neighbours. A muscovite studied earlier (Manning 1969) contained 6% Fe, mostly as Fe^{3+}, corresponding to a 1/7th occupancy of the octahedral positions. It is probable that, at these and higher concentrations, Fe^{3+} may be clustered in the octahedral sites, thus sharing Si ions and protons as second-nearest neighbours.

Orthoclase, (K, Na)($AlSi_3O_8$), is a framework silicate in which (Si, Al)O_4 tetrahedra are linked to one another by shared oxygens. Jones & Taylor (1961) have shown a partial ordering of (Si, Al) atoms, with (0.30 Al + 0.70 Si) at the S_1 site and (0.19 Al + 0.81 Si) at site S_2. The calculated ε-value for Fe^{3+} in orthoclase is ~2 (Faye 1969), showing that all second-nearest neighbours are Si. If Fe^{3+} substitutes into S_1 sites, further (Si, Al) ordering in the S_2 sites is indicated, because an average of 20% of second-nearest neighbour ions would be Al^{3+}_{IV}.

Conclusion

In summary, it would appear that ε-values of M^{3+} bands depend largely on intensity-stealing from $O^{2-} \rightarrow M^{3+}$ charge-transfer absorption.

Attributing high ε-values to distortions of local site symmetry alone is therefore suspect. This has been done, for example, by Burns & Strens (1967) in explaining site populations of Mn^{3+} and Fe^{3+} ions in epidote. Where second-nearest neighbour ions are Al of AlO_6, ε-values are still considerably larger than for materials in which all second-nearest neighbours are Si.

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