Evidence for Absorption by Exchange-Coupled $Fe^{2+} - Fe^{3+}$ Pairs in the Near Infra-red Spectra of Minerals

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Abstract. Reduction of Fe^{3+} to Fe^{2+} by heating in hydrogen reduces the absorbance of the bands at 9,000 and 13,800 cm^{-1} in the $E \perp c$ spectrum of tourmaline, and the 9,000 and 11,000 cm^{-1} bands in the $E \parallel (001)$ spectrum of biotite. This behaviour is consistent with the presumed d-d origin of these bands (which seems well established) only if they gain much of their intensity from exchange-coupling with neighbouring Fe^{3+} ions. Intensification of spin-forbidden bands in sapphire by $Fe^{3+} - Fe^{3+}$ exchange-coupling was recognized by Ferguson and Fielding (1971, 1972), but exchange-coupling has not previously been thought to intensify spin-allowed d-d bands.

Spin-allowed exchange-coupled bands resulting from $Fe^{2+} - Fe^{3+}$ pairs have features in common with both normal single ion d-d bands, which they resemble in energy, width and pressure dependence, and $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge transfer bands, which they resemble in temperature-, heat treatment-, composition-, and polarization-dependence. Distinction between normal d-d, charge transfer, and pair d-d absorptions is thus complicated, and criteria for assigning these bands are discussed.

Spin-allowed exchange-coupled pair bands should be sought in the spectra of transition metal clusters (trimers and polymers as well as pairs may be involved) whenever geometry favours their origin. It is possible that the bands near 10,000 and 11,500 cm^{-1} in blue sapphire, and at about 5,000 cm^{-1} in titanian garnets are of this type, but many other examples are likely to occur. Exchange-coupling may involve ions other than Fe^{3+} (e.g., Mn^{2+}, also d^5), although $Fe^{2+} - Fe^{2+}$ coupling is unlikely to be important at laboratory temperatures.

1. Introduction

Absorption features in the 4,000 to 50,000 cm^{-1} region of the optical spectra of minerals have usually been attributed to one of two types of electronic process, crystal field (Burns, 1970) or charge transfer (Faye et al., 1968; Smith

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Table 1. Representation of single ion, charge transfer and exchange-coupled pair transitions

Transition	Description	Reference
(1) $Fe^{2+}({}^5T_2) \rightarrow Fe^{2+}({}^5E)$	normal $d\text{-}d$ or single ion spin-allowed	Burns (1970)
(2) $Fe^{2+}({}^5T_2) + Fe^{3+}({}^6A_1) \rightarrow Fe^{3+}({}^6A_1) + Fe^{2+}({}^5T_2)$	metal-metal charge transfer	Faye et al. (1968) Smith and Strens (1976)
(3) $Fe^{2+}({}^5T_2) + Fe^{3+}({}^6A_1) \rightarrow Fe^{2+}({}^5E) + Fe^{3+}({}^6A_1)$	spin-allowed exchange-coupled pair	This work
(4) $Fe^{3+}({}^6A_1) + Fe^{3+}({}^6A_1) \rightarrow Fe^{3+}({}^4A_1, {}^4E) + Fe^{3+}({}^6A_1)$	spin-forbidden exchange-coupled pair	Ferguson and Fielding (1971, 1972)

and Strens, 1976; Langer and Abu-Eid, 1977). However, Ferguson and Fielding (1971, 1972) assigned absorption bands in the polarized spectra of yellow sapphires to $Fe^{3+} - Fe^{3+}$ exchange-coupled pair transitions.

Many mineral structures contain edge-sharing octahedra occupied by transition metal ions. Here, it is suggested that since cations in edge-sharing octahedra can give rise to metal-metal charge transfer bands in mineral spectra, then the same ionic configuration should favour absorption by exchange-coupled ion pairs. The problem is then the recognition of the pair bands, and their distinction from single ion and charge transfer bands.

The transitions to be considered are listed in Table 1. (1) is the single ion $Fe^{2+}\ {}^5T_2 \rightarrow {}^5E$ spin-allowed transition. (2) represents the metal-metal charge transfer transition between di- and trivalent iron. Both transitions are well known in mineralogical literature (refs. given above) and need no further comment at present. (4) represents an exchange-coupled pair transition, whereby an Fe^{3+} ion is excited from the ${}^6A_1$ to the ${}^4A_1$, ${}^4E$ states. The transition corresponding to (3) resembles (4) except, in this instance, an Fe^{2+} ion undergoes a transition from the ${}^5T_2$ to the ${}^5E$ state. Since absorptions arising from transitions of type (4) have not been generally recognized in mineral spectra, and since transitions of type (3) are a *new concept* proposed here, additional remarks are required.

In a series of papers on exchange-coupled ion pairs in cubic perovskite fluorides (Ferguson et al., 1966, 1967, 1975 and references therein) and also two papers on sapphire (Ferguson and Fielding, 1971, 1972), Ferguson and his coworkers have been concerned with pair bands which occur either close to the energy of a spin-forbidden transition ((4) and similar transitions), or close to the sum of the energies of two spin-forbidden transitions (i.e., a double excitation process). These bands do not obey Beer's law and have temperature variations dependent on the pair interaction involved. Also, again depending on the pair involved, a pair band occurring close to the energy of a spin-forbidden transition has an intensity one to two orders of magnitude greater than that

of a band due to isolated single ions, since the spin-selection rule $(\Delta S = O)$ has been partially overcome (see refs. above). It is worth noting that, as a result of antiferromagnetic coupling of Fe^{3+} ions, spin-forbidden bands in the spectra of ferric hydroxyl sulphates are up to 10 to 100 times more intense than absorptions due to single Fe^{3+} ions (Rossman, 1976).

Here, attention is focussed on the *concept of intensification of spin-allowed bands by exchange-coupling (3)*. A band of this type (3) should occur close to the energy of the single ion Fe^{2+} $^5T_2 \to {}^5E$ spin-allowed transition. Further, since a pair is involved, this band would not be expected to display the same compositional, heat treatment, temperature, and pressure dependences as single ion Fe^{2+} spin-allowed absorptions. However, the magnitude of intensity of a band arising from (3) relative to that of the single ion Fe^{2+} spin-allowed absorption is uncertain, since the Fe^{2+} $^5T_2 \to {}^5E$ transition is in accord with the spin-selection rule.

The purpose of this paper is to list and evaluate properties of pair bands which are proposed to arise from transitions of type (3). Possible pair effects in tourmaline, biotite, and blue sapphire are discussed. The near infra-red spectrum of titaniferous garnet is also considered.

2. Experimental Details

A "book" of Australian biotite (locality unknown) was kindly provided by Mr. D. McColl, museum curator at the Bureau of Mineral Resources, Canberra. Basal sections were cleaved from the biotite "book" and samples of uniform colour and thickness selected. Analyses of the biotite samples (by the method of Reed and Ware, 1973) showed (in wt%) 35.61 SiO$_2$, 1.34 TiO$_2$, 19.14 Al$_2$O$_3$, 17.77 FeO, 0.61 MnO, 10.27 MgO, 0.15 Na$_2$O, 9.70 K$_2$O, ≤ 0.1 Cs$_2$O, ≤ 0.07 V$_2$O$_3$, ≤ 0.08 Cr$_2$O$_3$ (total 94.59) No analyses were made of the Fe$_2$O$_3$ or water content in the biotite.

Optical absorption spectra were measured with a Cary 17 spectrophotometer. A tube furnace was used for heating the biotite in a continuous flow of hydrogen at 550° C.

3. Results and Discussion

Tourmaline

Absorption bands near 9,000 and 13,800 cm^{-1} in the E∥c and E⊥c polarized spectra of tourmalines have been assigned to components of the spin-allowed transition of Fe^{2+}($^5T_2 \to {}^5E$) by Smith and Strens (1976). The polarized optical spectra of blue, green, brown, and black tourmalines have recently been reported by Smith (1978). It was concluded that the bands near 9,000 and 13,800 cm^{-1} in the E∥c polarized spectra of tourmalines were indeed due to components of the single ion Fe^{2+} $^5T_2 \to {}^5E$ spin-allowed transition (1), but that absorption bands at similar energies in E⊥c polarized spectra owed much of their intensity to Fe^{2+} — Fe^{3+} pair interactions (3).

Table 2. A comparison of the properties of tourmaline $Fe^{2+} - Fe^{3+}$ charge transfer absorptions with the properties of single ion $Fe^{2+}\,{}^5T_2 \rightarrow {}^5E$ spin-allowed and $Fe^{3+} + Fe^{2+}$ $\rightarrow Fe^{3+} + Fe^{2+}$ charge transfer absorptions

| Absorption band	Energy (cm^{-1})	$w_{1/2}$ (cm^{-1})	Oscillator strength (f)	Polarization	Effect of $Fe^{2+} \rightarrow Fe^{3+}$ oxidation	Temperature dependence	Pressure dependence
$Fe^{2+}\,{}^5T_2 \rightarrow {}^5E$ (single ion)	10,000	2,000	5×10^{-6} to 5×10^{-5}	dependent on site symmetry	continual decrease in intensity (3)	loss of intensity or band maintains equal areas on cooling (1, 5)	intensification, narrowing, and movement of band to higher energy with increasing pressure (2, 4)
$Fe^{2+} - Fe^{3+}$ pair (tourmaline)	single ion Fe^{2+} ${}^5T_2 \rightarrow {}^5E$ (3)	2,500–3,000	5×10^{-3} to 10^{-2} (8)	along $Fe^{2+} - Fe^{3+}$ vector (3)	parabolic behaviour in intensity (3)	increase in intensity on cooling (3)	intensification, narrowing, and movement of bands to higher energy with increasing pressure (4)
$Fe^{2+} + Fe^{3+} \rightarrow$ $Fe^{3+} + Fe^{2+}$ (charge transfer)	12,000–18,000 (5 and 6)	3,000–7,000	10^{-3} to 10^{-2}	along $Fe^{2+} - Fe^{3+}$ vector	parabolic behaviour in intensity	increase in intensity on cooling (5)	narrowing and movement of band to lower energy with increasing pressure (4, 7)

References: (1) Lever (1968), (2) Shankland et al. (1974), (3) Smith (1978), (4) R.G.I. Strens (private communication), (5) Smith and Strens (1976), (6) Loeffler et al. (1975), (7) Abu-Eid (1976), (8) f-values calculated for $E \perp c$ polarized $13,800\ cm^{-1}$ bands in room temperature spectra of blue/green tourmalines using equation (3) of Smith and Strens (1976). It was assumed that the majority of iron was in the b-sites and that $\approx 4\%$ of total iron was Fe^{3+}.

A final property of importance is that of *compositional dependence.* Single ion $Fe^{2+}\ {}^5T_2 \rightarrow {}^5E$ spin-allowed transitions give rise to Beer's law plots. For the $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge transfer absorption at $14,000\ cm^{-1}$ in micas, a graph of α_0 (linear extinction coefficient at band maximum to the base e) versus the product ($\%FeO \times \%Fe_2O_3$) was essentially linear (Robbins and Strens, 1972). For the 9,000 and $13,800\ cm^{-1}$ $Fe^{2+} - Fe^{3+}$ pair bands in tourmaline, plots of $\alpha_0/10 \log_e 10$ versus total FeO content were non linear (Smith, 1978). (N.B. α_0 is expressed in units of cm^{-1}.)

For the properties of $Fe^{3+} - Fe^{3+}$ exchange-coupled pair bands, reference is made to Ferguson and Fielding (1971, 1972).

Fig. 1. The room temperature unpolarized spectrum of a basal section of biotite measured before (——) and after (– – –) heat treatment in hydrogen at 550° C for 6 h. Sample thickness is 0.031 m.m
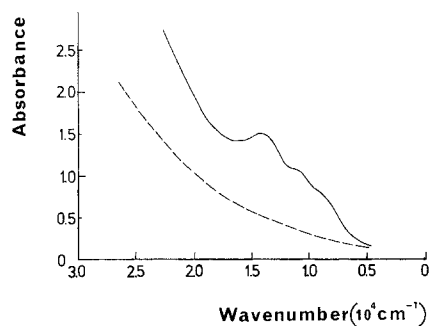
A comparison of the known properties of the near infra-red $E \perp c$ polarized absorption bands in blue and green tourmalines with corresponding properties of single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ crystal field (1) and Fe^{2+} + Fe^{3+} → Fe^{3+} + Fe^{2+} metal-metal charge transfer (2) bands is given in Table 2. It is noted (Table 2) that although the Fe^{2+} — Fe^{3+} pair bands in tourmaline spectra ($E \perp c$ polarization) occur close to the energies of the single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ crystal field absorptions in the $E \| c$ spectra of the mineral, the pair bands have similar properties (oscillator strength, polarization, temperature dependence, reaction to heat treatment) to those of Fe^{2+} + Fe^{3+} → Fe^{3+} + Fe^{2+} charge transfer absorptions. However, the pressure dependence of the Fe^{2+} — Fe^{3+} pair bands is similar to that displayed by single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ spin-allowed absorptions (Table 2).

Biotite

The structure of biotite partly comprises of a network of edge-sharing octahedra running parallel to the 001 plane. In this plane, both Fe^{2+} and Fe^{3+} occupy six-fold $M1$ and $M2$ positions (Annersten, 1974). The unpolarized spectrum of a basal (001) section of biotite shows three prominent bands near 9,000, 11,000, and 14,000 cm^{-1} (Faye, 1968; Robbins and Strens, 1972). Measurements of the polarized $E \perp (001)$ spectrum of biotite also reveals bands near 9,000 and 11,000 cm^{-1}, but the 14,000 cm^{-1} absorption is largely absent. Considering the structure of biotite, and the strong pleochroism of the 14,000 cm^{-1} absorption band, these authors assigned this band to the Fe^{2+} + Fe^{3+} → Fe^{3+} + Fe^{2+} charge transfer transition (2). The bands near 9,000 and 11,000 cm^{-1} ($E \| (001)$ and $E \perp (001)$ spectra) were attributed to components of the single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ spin-allowed transition (1).

Figure 1 shows the effect of heat treatment in hydrogen on the unpolarized spectrum of a basal section of biotite. It is seen that the three bands at 9,000, 11,000, and 14,000 cm^{-1} have all lost intensity. Room temperature Mössbauer spectra of the unannealed biotite showed the presence of both Fe^{2+} and Fe^{3+}. After annealing the biotite in hydrogen, Mössbauer spectra revealed that a considerable reduction of Fe^{3+} had occurred. Therefore, a feasible explanation

for the optical results obtained on heat treatment (Fig. 1) is that, as before, the 14,000 cm^{-1} absorption is due to the $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge transfer transition, and that much of the intensity of the 9,000 and 11,000 cm^{-1} absorption bands in the spectrum of the basal section of biotite arises from $Fe^{2+} - Fe^{3+}$ pair interactions (3).

Additional evidence for a $Fe^{2+} - Fe^{3+}$ pair assignment in biotite comes from temperature dependence studies of the unpolarized E∥ (001) and polarized E ⊥ (001) spectra of the mineral. On measuring the unpolarized spectrum of a 001 section of a Plenty River biotite at 293 and 5.5 K, Smith (1977) pointed out that not only did the 14,000 cm^{-1} band increase in intensity on reducing sample temperature, a behaviour consistent with a $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge transfer assignment to the band (Smith and Strens, 1976), but also the absorptions near 9,000 and 11,000 cm^{-1}. Hence, the temperature dependence of the 9,000 and 11,000 cm^{-1} bands in biotite (E∥ (001) polarization) resembles that of the E ⊥ c polarized near infra-red bands in tourmaline (Table 2). Measurements made at room temperature and helium temperatures of the E ⊥ (001) polarized spectrum of biotite (sample used in heat treatment study discussed above) revealed that the absorptions at 9,000 and 11,000 cm^{-1} have a single ion temperature dependence[1]. This is again consistent with the single ion assignments made to the near infra-red bands in the E∥c spectra of tourmalines (Smith, 1978). Hence, these temperature dependence measurements of biotite spectra indicate that, as in tourmaline, the near-infra-red bands in biotite which arise from $Fe^{2+} - Fe^{3+}$ pairs are polarized along the $Fe^{2+} - Fe^{3+}$ metal-metal vector. In fact, the 9,000 and 11,000 cm^{-1} $Fe^{2+} - Fe^{3+}$ pair absorptions in biotite appear to have the same polarization properties as the higher energy 14,000 cm^{-1} $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge transfer absorption. Finally, high pressure optical spectra of basal sections of biotite and tourmaline have shown that the near infra-red absorptions have similar pressure dependences (R.G.J. Strens; private communication).

Blue Sapphire

The E∥c and E⊥c polarized spectra of blue sapphire show absorption bands near 10,000 and 11,500 cm^{-1} respectively. Faye (1971) assigned the bands to components of the single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ spin-allowed transition (1). On cooling a blue sapphire from 293 to 10 K, Ferguson and Fielding (1971) observed increases in intensity of the 10,000–12,000 cm^{-1} bands and assigned the absorptions to $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ metal-metal charge transfer transitions (2). Confirming the temperature dependence measurements of Ferguson and Fielding (1971); Smith and Strens (1976) agreed with a charge transfer interpretation, and showed that the low energies of the 10,000 and 11,500 cm^{-1} bands, in comparison with $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ absorptions in other minerals, were consistent with the short metal-metal distances of 2.65 and 2.79 Å in

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[1]   The temperature variation of the 9,000 and 11,000 cm^{-1} bands in the E∥ (001) spectrum of the biotite used in heat treatment studies was similar to that of bands at the same energy in the Plenty River biotite

blue sapphire (in biotite, the metal-metal distance is 3.1 Å and the $Fe^{2+} + Fe^{3+}$ $\rightarrow Fe^{3+} + Fe^{2+}$ band is located near 14,000 cm^{-1}).

However, since Ferguson and Fielding (1971, 1972) have shown that $Fe^{3+} - Fe^{3+}$ pair transitions ((4) and similar transitions) are responsible for many of the features in the spectra of yellow sapphires, it may well be that $Fe^{2+} - Fe^{3+}$ exchange-coupled pairs (3) could account for the 10,000–12,000 cm^{-1} absorptions in blue sapphire. The bands have energies typical of the single ion Fe^{2+} $^5T_2 \rightarrow {}^5E$ spin-allowed transition, and also a temperature dependence similar to the $Fe^{2+} - Fe^{3+}$ pair bands assigned in the tourmaline and biotite spectra. It is considered that the interpretation of the near infra-red bands in blue sapphire should be left open until another perturbation technique, possibly high pressure, can confirm the origin of these absorptions.

Titaniferous Garnet

A broad band near 5,000 cm^{-1} in melanites and schorlomites has been assigned to tetrahedral Fe^{2+} (Manning and Harris, 1970; Huggins et al., 1977), tetrahedral Ti^{3+} (Burns, 1972), and to $Ti^{3+} + Ti^{4+} \rightarrow Ti^{4+} + Ti^{3+}$ charge transfer (Moore and White, 1971). The various features of the band are that it has structure, occurs in the energy range of the single ion $^5E \rightarrow {}^5T_2$ spin-allowed transition (Fe^{2+} or Ti^{3+} in four-fold coordination), and increases in intensity with decreasing temperature (Fig. 3 of Moore and White). As Moore and White observed, the band has a half-width and intensity in keeping with a single ion assignment, but a temperature dependence characteristic of a charge transfer transition. Due to the structural and chemical complexity of titaniferous garnets (Moore and White, 1971; Burns, 1972; Huggins et al., 1977) no definite assignment will be made here. However, it is possible that the 5,000 cm^{-1} band is due to a spin-allowed exchange-coupled pair interaction ($Fe^{2+} - Fe^{3+}$, $Fe^{2+} - Ti^{3+}$, $Ti^{3+} - Fe^{3+}$, etc.) involving Fe^{2+} or Ti^{3+} in the tetrahedral site of garnet rather than a single ion or charge transfer transition.

Mechanism of $Fe^{2+} - Fe^{3+}$ Pair Transition and Properties of $Fe^{2+} - Fe^{3+}$ Pair Bands

A physical understanding of the mechanism which operates for the proposed $Fe^{2+}(^5T_2) + Fe^{3+}(^6A_1) \rightarrow Fe^{2+}(^5E) + Fe^{3+}(^6A_1)$ transition has yet to be reached. It is presumed that pair intensity results from the electromagnetic vector of incident light interacting with magnetically coupled $Fe^{2+} - Fe^{3+}$ ions. This would be consistent with the studies of Tsang et al. (1971) who have shown the existence of magnetic exchange effects in tourmaline. However, magnetic susceptibility measurements reported for biotite (Anagnostopoulos et al., 1973) have indicated that Fe^{2+}, Fe^{3+}, and Mn^{2+} ions in this mineral tend to be "magnetically free", with a lack of strong exchange interactions.

Comments have previously been made concerning the temperature dependence and polarization of $Fe^{2+} - Fe^{3+}$ pair bands in tourmaline spectra (Smith,

1978). No explanation of the pressure dependence of $Fe^{2+} - Fe^{3+}$ pair bands is offered at the present time. It is noted, however, that the intensities of the bands assigned to $Fe^{2+} - Fe^{3+}$ pairs in tourmaline and biotite should have a component arising from the single-ion Fe^{2+} spin-allowed transition. Both here and in Smith (1978), reduction studies of tourmaline and biotite have failed to conclusively detect this single ion Fe^{2+} absorption.

4. Final Remarks

Ferguson and Fielding (1971, 1972) have shown that $Fe^{3+} - Fe^{3+}$ pair absorptions occur in the spectra of yellow sapphires. Here, and in Smith (1978), it has been proposed that much of the intensity of the near infra-red bands in the $E \parallel (001)$ and $E \perp c$ spectra of biotite and tourmaline respectively results from $Fe^{2+} - Fe^{3+}$ pair interactions which occur close to the energy of the single ion Fe^{2+} ${}^5T_2 \to {}^5E$ spin-allowed transition. A summary of the properties of the proposed $Fe^{2+} - Fe^{3+}$ pair bands in tourmaline has been presented. Blue sapphire and titaniferous garnet have been cited as further possible examples of pair centres.

It is considered that pair absorptions may play an important role in mineral spectra, and that bands originally attributed to single ion or charge transfer transitions may originate in pair effects. We note that Bakhtin and Vinokurov (1978) have recently suggested that bands in the 13,000 to 18,000 cm^{-1} region of the spectra of pyroxenes, amphiboles, and micas do not, as previously proposed[2], originate from $Fe^{2+} + Fe^{3+} \to Fe^{3+} + Fe^{2+}$ charge transfer interactions, but arise from the $Fe^{2+}({}^5T_2) + Fe^{3+}({}^6A_1) \to Fe^{2+}({}^5T_2) + Fe^{3+}({}^4T_2)$ exchange-coupled pair transition. It can only be added that experimental data presented here and in Smith (1978) to substantiate $Fe^{2+} + Fe^{3+} \to Fe^{3+} + Fe^{2+}$ metal-metal charge transfer assignments also favour the pair proposal of Bakhtin and Vinokurov. The intriguing question of how to distinguish between a band arising from this particular pair transition and a $Fe^{2+} + Fe^{3+} \to Fe^{3+} + Fe^{2+}$ charge transfer band remains to be answered. Suitable electric or magnetic field experiments may be useful in this respect.

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[2]   See Loeffler et al. (1975) and Smith and Strens (1976)

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