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LOW-TEMPERATURE OPTICAL STUDIES OF METAL–METAL CHARGE-TRANSFER TRANSITIONS IN VARIOUS MINERALS

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ABSTRACT

The absorption spectra of biotite, chlorite, andalusite, cordierite, and a green and a brown tourmaline, taken from room temperature to helium temperature, enable the temperature-dependences of assigned $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ and $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$ metal–metal charge-transfer (M.M.C.T.) bands to be ascertained. In the 20,000-27,000 cm^{-1} region of the absorption spectra of the andalusite and the two tourmalines, $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ bands increase by approximately 20% on cooling the sample from 293 to 5.5K. This increase is attributed to thermal expansion effects. The intensity of the bands attributed to $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$ charge transfer in the 14,000-18,000 cm^{-1} region of the spectra of the biotite, chlorite, and cordierite is nearly doubled when the sample temperature drops from room to helium temperature. This increase is explained in terms of thermal depopulation of one, or more than one electronic level, close to the ground state of the $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$ transition.

SOMMAIRE

Les spectres d'absorption de la biotite, de la chlorite, de l'andalousite, de la cordiérite et de deux variétés de tourmaline, l'une verte et l'autre brune, pris à diverses températures entre la température ambiante et celle de l'hélium liquide, permettent d'établir comment varient en fonction de la température les bandes de transfert de charge métal-métal $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ et $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$. Les bandes $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ des spectres d'absorption de l'andalousite et des deux tourmalines, situées entre 20,000 et 27,000 cm^{-1}, augmentent d'environ 20% quand on refroidit l'échantillon de 293 à 5.5K; ceci est dû aux effets d'expansion thermique. Les bandes attribuées au transfert de charge $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$, échelonnées entre 14,000 et 18,000 cm^{-1} des spectres de la biotite, de la chlorite et de la cordiérite ont leur intensité presque doublée au refroidissement de la température ambiante à celle de l'hélium. Cette augmentation s'explique par la dépopulation thermique d'un niveau électronique, ou de plusieurs de ces niveaux, près de l'état fondamental de la transition $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$.

(Traduit par la Rédaction)

INTRODUCTION

Assignments of metal–metal charge-transfer (M.M.C.T.) transitions in the optical spectra of minerals have chiefly involved the two transition-metal ions, iron and titanium. These ions give rise to two main types of transfer, one of a homovalent nature (Allen & Hush 1967) involving the transfer of an electron between two valence states of the same kind of cations (*viz.* $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$ and $Ti^{3+}+Ti^{4+}\rightarrow Ti^{4+}+Ti^{3+}$), and the other is heterovalent in character (Allen & Hush 1967) and involves the valence states of two different kinds of cations (*viz.* $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ and $Fe^{2+}+Ti^{3+}\rightarrow Fe^{3+}+Ti^{2+}$). For both types of charge transfer in minerals the cations involved are usually, but not always, situated in edge-sharing octahedral sites. Exceptions include cordierite, in which charge transfer occurs between Fe^{2+} and Fe^{3+} in octahedral and tetrahedral sites respectively (Faye *et al.* 1968), these sites sharing a single edge with each other. In the optical spectra of some minerals (*e.g.* tourmaline and andalusite) previously assigned $Ti^{3+}+Ti^{4+}\rightarrow Ti^{4+}+Ti^{3+}$ transitions [Faye & Harris 1969 (andalusite); Manning 1968 (brown tourmaline); Faye *et al.* 1968 (green tourmaline)] have been re-assigned to $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ transitions [Dowty & Clark 1973 (andalusite); Faye *et al.* 1974 (brown and green tourmalines)], due to the absence of Ti^{3+} in these minerals, and to the author's knowledge no conclusive $Fe^{2+}+Ti^{3+}\rightarrow Fe^{3+}+Ti^{2+}$ assignment has been made in minerals.

Optical bands attributed to $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$ transitions in minerals have been found mainly in the 12,000 to 18,000 cm^{-1} region, whereas $Fe^{2+}+Ti^{4+}\rightarrow Fe^{3+}+Ti^{3+}$ and $Ti^{3+}+Ti^{4+}\rightarrow Ti^{4+}+Ti^{3+}$ transitions have generally been assigned in the 16,000 to 25,000 cm^{-1} region. In some minerals (*e.g.* sapphire) M.M.C.T. transitions involving the above ions have been found outside these regions (Ferguson & Fielding 1971); Loeffler *et al.* (1975) have given a comprehensive list of charge-transfer assignments in minerals.

Previous studies of the temperature-dependence of M.M.C.T. bands in minerals have been confined largely to measurements of spectra at room and liquid-nitrogen or helium temperatures. In one such study, Ferguson & Fielding (1971) showed that the $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ band at 11,500 cm^{-1} in the $E \perp c$ spectrum of blue sapphire increased in intensity on cooling the sample from 293 to 10K, whereas the $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ band at 17,800 cm^{-1} (also in the $E \perp c$ spectrum) showed little variation over the same temperature range. This was confirmed by Smith & Strens (1976), who also found that the $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ bands assigned at 14,100, 14,300 and 17,600 cm^{-1} in the spectra of biotite (Faye 1968), chlorite (Faye 1968) and cordierite (Faye *et al.* 1968) respectively increased in intensity on decreasing the sample temperature from 293 to ~100K. Previous optical measurements of chlorite at 293 and 77K (White & Keester 1966) showed similar results.

The present work extends these low-temperature studies of mineral spectra, presents the first detailed results on the temperature-dependence of $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ and $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ M.M.C.T. transitions in minerals, and discusses possible physical processes which may give rise to these results.

EXPERIMENTAL DETAILS

Specimens

The andalusite and green tourmaline samples were obtained from Minex Lapidary, Melbourne. The biotite and brown tourmaline samples were kindly provided by Mr. D. McColl, museum curator of the Bureau of Mineral Resources, Canberra. Dr. R. G. J. Strens provided the chlorite and cordierite specimens. The minerals came from the following localities: andalusite from Brazil; biotite from Dinkum No. 1 mine, Plenty River, Northern Territory, Australia; brown tourmaline from Yinnetharra, Western Australia; chlorite from Zillerthal, Austria; cordierite (sekaninaite) from Dolni Bay, Czechoslovakia. The source of the green tourmaline is unknown.

Analyses of the chlorite and cordierite specimens were known from previous studies (Smith & Strens 1976). The other minerals were analyzed with an electron microprobe fitted with a lithium-drifted silicon detector, as described in Reed & Ware (1973). Titanium was not detected in the green tourmaline and andalusite samples with this method of analysis, and it was necessary to re-examine the andalusite specimen by emission spectroscopy and the green tourmaline by standard electron microprobe techniques. Partial analyses of the minerals are shown in Table 1.

TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS

Mineral	Transition	Configuration (1)	FeO conc. (wt%)	TiO_2 conc. (wt%)	Polarization	Room Temp $\bar{\nu}(cm^{-1})$	$\frac{\text{Band Intensity (5K)}}{\text{Band Intensity (293K)}}$
Chlorite	$Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$	ESO	5.26	0.16	Unpolarized basal section	14,300 (14,300 + 17,000)	~1.95 (~1.83)
Biotite	"	ESO	19.89	2.01	Unpolarized basal section	14,100 (14,100 + 16,300)	~2.18 (~2.08)
Cordierite	"	ESOT	12.05 FeO 4.21 Fe_2O_3 (2)	0.7	E ∥ b(γ)	17,600	~1.76
Sapphire	"	ESO	0.8	not given	E ⊥ c	11,500	~1.2 $\frac{I_{10K}}{I_{RT}}$ (5)
"	$Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$	"	"		"	17,800	~1 "
Andalusite	"	ESO	0.32	0.0033 (3)	E ∥ c	20,800	~1.19
Tourmaline (dravite)	"	ESO	0.35	0.88	E ⊥ c	22,700	~1.23
Tourmaline (elbaite)	"	ESO	5.36	0.065 (4)	E ⊥ c	24,600	~1.25

1. ESO edge-sharing octahedra; ESOT octahedron edge-sharing with tetrahedron.
2. Cordierite is the only sample for which the Fe_2O_3 concentration is known.
3. Titanium concentration detected by emission spectroscopy.
4. Titanium concentration detected by electron microprobe fitted with crystal spectrometer. (N.B. The other concentrations given for the andalusite, biotite, and the tourmaline samples were detected with an electron microprobe fitted with a lithium drifted silicon detector.)
5. Measured from Figure 3 of Ferguson and Fielding 1971. No accurate resolution could be made due to the size of the reproduced spectra.

For Band Intensity (5K) *read* Band Intensity (5.5K).

Measurements and resolution of spectra

Sections cut parallel to the *c* axis were obtained from large single crystals of andalusite, and from the green and brown tourmalines. The *c* axis was readily identifiable from the external morphology of the crystals and from examination with a polarizing microscope. The sections were thinned for spectral measurements and polished in the standard manner.

Utilizing the distinctive pleochroism of cordierite, a *b–c* section was obtained from the same single crystal as other cordierite specimens studied by Smith & Strens (1976). The correct orientation of the section used here was confirmed by measurements of polarized spectra.

Basal sections were cleaved from a book of biotite and a sample of uniform color and appropriate thickness was chosen for measurement. The basal section of chlorite used in this study is the one previously measured by Smith & Strens (1976). The sample was thinned slightly and repolished.

Absorption spectra were measured with a Cary 17 spectrophotometer. With the exceptions of biotite and chlorite, sample measurements were made with polarized light obtained from matched Glan-Thompson prisms inserted in the reference and sample beams of the spectrophotometer. The room-temperature spectrum of each mineral section was compared with the corresponding spectrum of a similar sample measured previously by Faye (1968) [biotite and chlorite], Faye *et al.* (1968) [cordierite], Faye & Harris (1969) [andalusite] and Faye *et al.* (1974) [brown and green tourmalines]. No noticeable differences in spectral features were detected in these comparisons.

Variation of sample temperature was achieved using a helium flow-tube technique in which a variable flow of helium gas was passed over the sample, enabling it to be cooled from room temperature to as low as 5.5K. The gas flow was controlled by varying the voltage on a carbon resistor inserted in a helium dewar. Temperatures could be stabilized to within ±5K. The sample was mounted on a stainless-steel holder inserted in the flow tube. Temperatures from 293 to 70K were measured using a copper-constantan thermocouple with an ice-junction; from 70 to 5.5K, a carbon resistor calibrated from 100 to 4.2K was employed. Both temperature probes were near the sample to ensure that measured temperatures closely approximated sample temperatures. The use of two temperature probes made it necessary to employ two sample holders, one in conjunction with the thermocouple, and the other with the resistor. Care was taken to ensure that sample position and orientation were preserved in changing the sample from one holder to the other. Spectra measured at ~70K using the thermocouple and the resistor were identical, and little error was involved in remounting the sample. Care was also taken to ensure that the sample/sample beam geometry was the same at all measured temperatures with the sample beam always central to the specimen. Where thermal contraction of the holder resulted in slight changes of sample position, the appropriate adjustments were made.

The measured spectra were converted to the linear energy scale using a Hewlett Packard 9825A calculator in conjunction with H.P. 9862A plotter and H.P. 9864A digitizer attachments. A simple program was used for this conversion. The calculator was then reprogrammed to generate a number of Gaussian waveforms which were superimposed on each redrawn spectrum. By varying the number, heights, widths, and positions of these Gaussian curves, a fit to each spectrum was obtained. For all spectra, a Gaussian background was assumed but was chosen to be fairly similar to a visually-judged background. For a set of resolved spectra, that is, the spectrum of the same sample measured at various temperatures, the areas of the band of interest (*e.g.* the 22,700 cm^{-1} band in brown tourmaline) were determined and normalized to the area of the band resolved from the corresponding 5.5K spectrum. By means of a simple program, areas were measured using the H.P. calculator and digitizer.

At all measured temperatures, reasonable one-band fits were obtained for the 20,800, 17,600 and 22,700 cm^{-1} bands in the polarized spectra of andalusite, cordierite and brown tourmaline, respectively (Figs. 1a, 3c and 5c), there being no necessity to generate extra components which would have a marked effect on measurements of areas of these bands. For chlorite and biotite, it was necessary to fit four bands to the spectra in the 5,000 to 21,000 cm^{-1} region (Figs. 5a,b). Although, without curve resolving, bands at 9,000, 11,000 and 14,000 cm^{-1} are apparent in biotite and chlorite spectra (Figs. 3a and 3b), the bands in the 16,300 to 17,000 cm^{-1} region of the spectra are not so readily observable. Smith & Strens (1976) also detected bands at 16,300 to 17,000 cm^{-1} in biotite and chlorite with a Dupont 310 curve resolver and tentatively assigned them to $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ charge transfer involving the higher lying t_{2g} orbitals of the Fe^{3+} acceptor ion. However, whether these bands are real or result from methods of curve resolution is uncertain. We note that, in both chlorite and biotite, the resolved 16,300 to 17,000 cm^{-1} bands appear to increase in intensity on cooling. Resolution of the green tourmaline spectra (Fig. 5d) resulted in the generation of a band at 17,600 cm^{-1} which, to a minor degree, affected measurements of intensity of the 24,600 cm^{-1} band. Although this band (previously resolved and attributed to $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ charge transfer by Faye *et al.* 1974) is not obvious at room temperature, it becomes clearly visible on cooling to 5.5K (Fig. 1c).

At temperatures lower than 50K, a minor band was detected at ~26,000 cm^{-1} in the $E \perp c$ brown tourmaline spectra. The origin of this band is unknown and its intensity was so small that it is visible only on experimental charts and not on the smaller scale of Figure 5c. Because of the low intensity of the band, it was difficult to resolve and had little or no effect on the results obtained for brown tourmaline.

As might be expected, it was found that resolution of a spectrum was extremely dependent on the Gaussian background assumed for the spectrum. Also, for any set of spectra, readjustment of the background was made at each measured temperature since the spectral absorption edge retreated to higher energies on cooling of the sample. In this study, it is both the choice of background and movement of background with temperature which are regarded as the major sources of error in measuring band intensities. On this basis, the error bars in Figures 2a, b, c and 4a, b, c have been estimated.

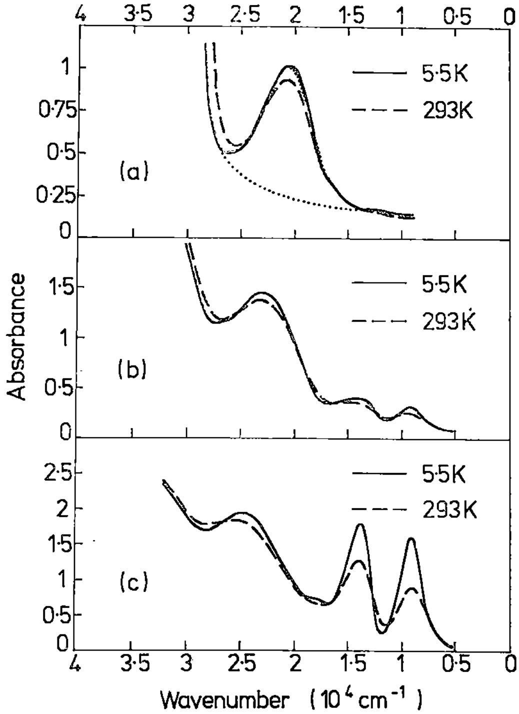

FIG. 1. (a) $E||c$ polarized spectrum of andalusite, specimen thickness 0.88 mm; (b) $E \perp c$ polarized spectrum of brown tourmaline, specimen thickness 0.38 mm; (c) $E \perp c$ polarized specrum of green tourmaline, specimen thickness 0.57 mm. The background and resolution of the andalusite spectrum measured at 5.5K are indicated by dotted lines (top diagram).

RESULTS AND DISCUSSION

Figure 1a shows the 20,800 cm^{-1} band in the $E||c$ polarized spectrum of an andalusite measured at 293 and 5.5K. The temperature-dependence of the integrated intensity of the 20,800 cm^{-1} band (reassigned from a $Ti^{3+}+Ti^{4+} \rightarrow Ti^{4+}+Ti^{3+}$ to a $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ transition—Dowty & Clark 1973; Smith & Strens 1976) is displayed in Figure 2a and it is seen that the band increases in intensity by approximately

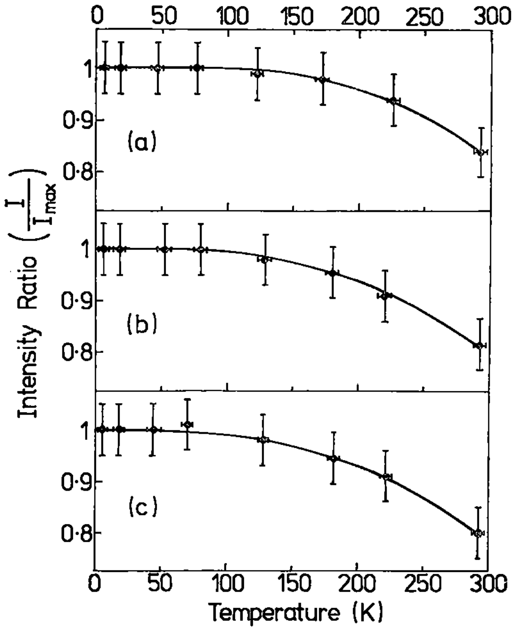

FIG. 2. The temperature variation of the integrated intensity of: (a) 20,800 cm^{-1} band in the $E||c$ spectrum of andalusite; (b) 22,700 cm^{-1} band in the $E \perp c$ spectrum of brown tourmaline; (c) 24,600 cm^{-1} band in the $E \perp c$ spectrum of green tourmaline. In all cases, the integrated band intensity (I) is normalized to the integrated band intensity measured at 5.5K (I_{max}). The full curves represent experimental fits to the results obtained.

20% on cooling from 293 to 5.5K. Similar results (Figs. 2b,c) were obtained for the intensity/temperature variations of the 22,700 and 24,600 cm^{-1} bands in the $E \perp c$ spectra of a brown and green tourmaline, respectively. As with the 20,800 cm^{-1} andalusite band, both the 22,700 and 24,600 cm^{-1} tourmaline bands have been reassigned to $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$ charge-transfer transitions (Faye *et al.* 1974). Figure 1b shows measurements at 293 and 5.5K of the $E \perp c$ spectrum of the brown tourmaline, whereas similar measurements for the $E \perp c$ spectrum of the green tourmaline are in Figure 1c.

Measurements, at room and helium temperatures, of the unpolarized spectrum of a basal section of chlorite (Fig. 3a) show that decrease in temperature has a more pronounced effect on the band at 14,300 cm^{-1} previously assigned to the $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge-transfer transition (Faye 1968). In fact, the integrated intensity of the band increased by a factor of approximately two in cooling to helium temperatures (Fig. 4a). Similar results (Figs. 4b,c) were obtained for the bands at 14,100 and 17,600 cm^{-1} in the unpolarized and $E \| b$ polarized spectra of biotite an dcordierite, respectively. Again, both bands have been previously assigned to the $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ charge-transfer transition (Faye 1968–biotite; Faye *et al.* 1968–cordierite). Figure 3c shows the $E \| b$ spectrum of the cordierite measured at 293 and 5.5 K, and Figure 3b displays similar measurements made for the unpolarized spectrum of the basal sec-

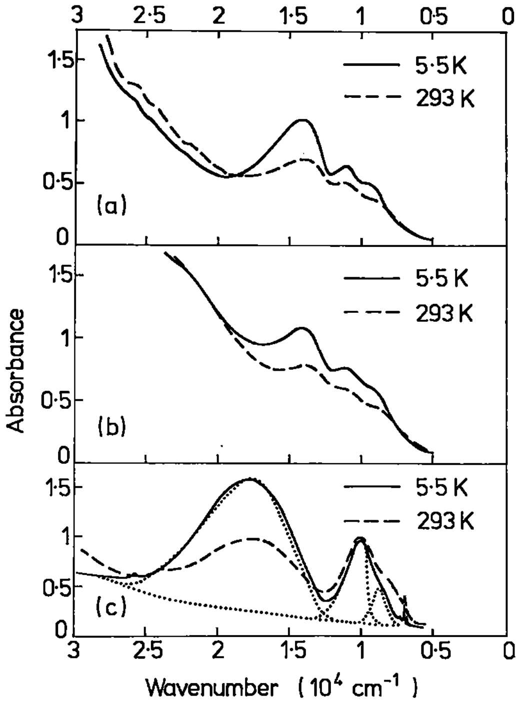

FIG. 3. (a) Unpolarized spectrum of basal section of chlorite, specimen thickness 0.16 mm; (b) unpolarized spectrum of basal section of biotite, specimen thickness 0.09 mm; (c) $E \| b(\gamma)$ polarized spectrum of cordierite, specimen thickness 0.96 mm. The background and resolution of the cordierite spectrum measured at 5.5K are indicated by dotted lines (bottom diagram).

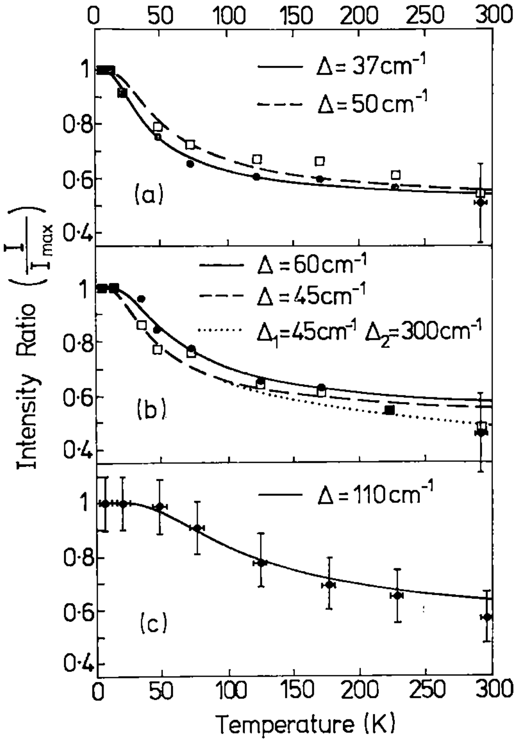

FIG. 4. The temperature variation of: (a) integrated intensity of 14,300 cm^{-1} band (open squares) and sum of integrated intensities of 14,300 and 17,000 cm^{-1} bands (full circles) in the unpolarized spectrum of chlorite; (b) integrated intensity of 14,100 cm^{-1} band (open squares) and sum of integrated intensities of 14,100 and 16,300 cm^{-1} bands (full circles) in the unpolarized spectrum of biotite; (c) integrated intensity of 17,600 cm^{-1} band in the $E \| b$ spectrum of cordierite. In all cases the integrated band intensity or sum of integrated band intensities (I) is normalized to the intensity measurements made at 5.5K. The full and dashed lines show plots of the equation $1/(1+e^{-\Delta/kT})$ with the values of Δ indicated in the figures. The dotted line (middle diagram) shows the plot of the equation $1/(1+e^{-\Delta_1/kT}+e^{-\Delta_2/kT})$ with Δ_1 and Δ_2 equal to 45 and 300 cm^{-1} respectively. For clarity, only one error bar of typical magnitude is shown in the top and middle diagrams.

tion of the biotite. A summary of experimental results is in Table 1.

As pointed out by Ferguson & Fielding (1972), it seems unreasonable to attempt to explain M.M.C.T. band-intensity/temperature variation simply in terms of increased orbital overlap due to thermal contraction of the crystal. If this were so, then similarly polarized $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ and $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ transitions in the spectrum of a mineral would be expected to display a similar temperature variation, and results obtained with sapphire (Ferguson & Fielding 1971) and tourmaline (Smith, unpubl. data) show that this is not the case.

It is suggested here that thermal contraction/increased overlap (*i.e.* increased transition probability) is the main reason for the rather small increase on cooling of the intensities of the $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ bands, but is only a minor factor in the large intensity increases of $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ bands on cooling from room to helium temperatures. In agreement with Ferguson & Fielding (1972), it is thought that the intensity/temperature variation of $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ bands might be better explained in terms of the thermal depopulation of the ground state, because of the presence of nearby levels.

Assuming the existence of one level close to the ground state and a single excited state in the 12,000 to 18,000 cm^{-1} range, with the transition from the ground state to the excited state allowed and the transition from the level close to the ground state to the excited state forbidden, then the intensity/temperature variation of the 14,300 cm^{-1} $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ band in chlorite might be fitted to the thermal population of the ground state obtained from Boltzmann statistics. This curve is of the form $1/(1+e^{-\Delta/kT})$ and in Figure 4a is shown for two values of Δ, where Δ is the difference in energy between the ground state and the level close to the ground state. For $\Delta=37$ cm^{-1}, the curve is fitted to the temperature variation of the sum of the integrated intensities of the chlorite bands resolved at 14,300 and 17,000 cm^{-1} (Fig. 5a). This assumes that the resolved 17,000 cm^{-1} band is not real, but arises from our method of curve resolving. However, if a band is in fact present at 17,000 cm^{-1}, then a two-level Boltzmann fit to the temperature variation of the 14,300 cm^{-1} band alone requires Δ to be equivalent to ~50

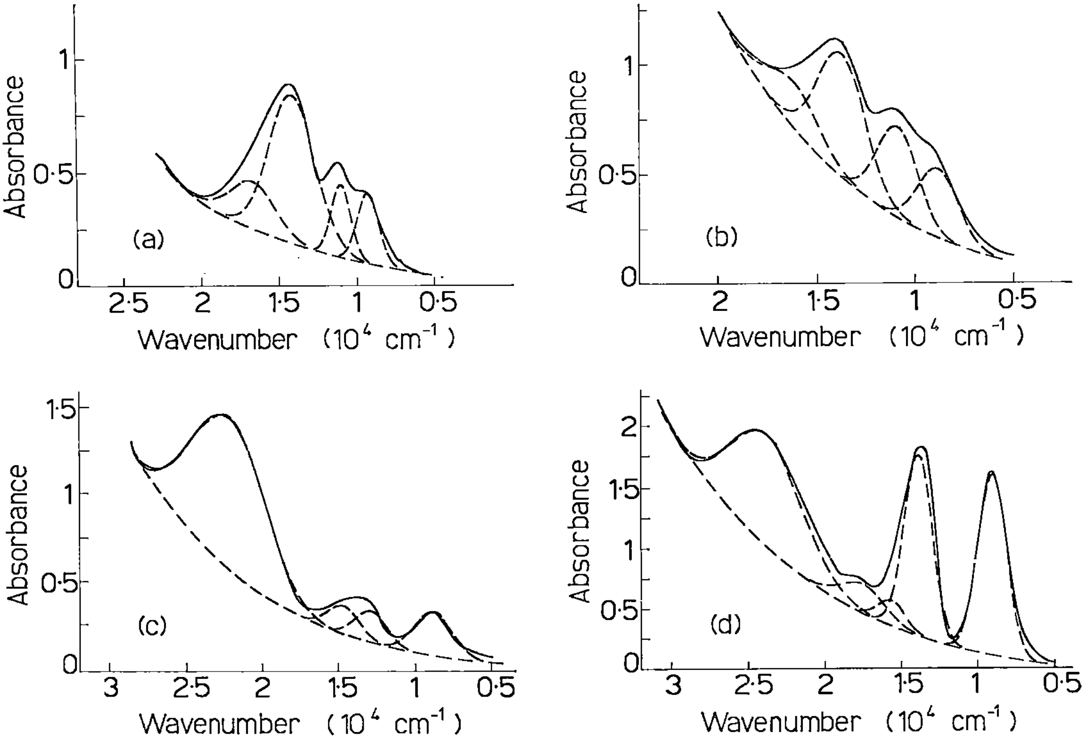

FIG. 5. The background and resolution of: (a) unpolarized spectrum of basal section of chlorite; (b) unpolarized spectrum of basal section of biotite; (c) $E \perp c$ polarized spectrum of brown tourmaline; (d) $E \perp c$ polarized spectrum of green toumaline. The spectra were measured at 5.5K.

cm^{-1} (Fig. 4a). Similar curves involving the above equation can also be drawn for biotite and cordierite and are shown in Figures 4b and 4c respectively. From Figure 4c it is seen that $\Delta =$ 110 cm^{-1} gives a reasonable fit to the temperature-dependence of the intensity of the 17,600 cm^{-1} $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ band in cordierite. For biotite, as with chlorite, we again have the problem of deciding on the feasibility of a real band in the ~16,300 to 17,000 cm^{-1} region (Fig. 5b). A fit to the temperature variation of the biotite $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ 14,100 cm^{-1} band alone gives Δ to be approximately 45 cm^{-1}, whereas $\Delta = 60$ cm^{-1} is obtained in fitting the temperature variation of the sum of the intensities of the bands at 14,100 and 16,300 cm^{-1} (Fig. 4b). For both values of Δ, the theoretical fit is poor at high temperatures. This may imply a thermal expansion contribution to the temperature variation of the bands(s), or the existence of more than one energy level close to the ground state. Figure 4b also shows a curve of the form $1/(1+e^{-\Delta_1/kT} + e^{-\Delta_2/kT})$ where Δ_1 and Δ_2 are equal to 45 and 300 cm^{-1} respectively. For this Boltzmann thermal population curve to be a valid fit to the temperature variation of the biotite 14,100 cm^{-1} band, it has to be assumed that only the transition from the ground to the excited state is allowed, whereas transitions from the levels lying close to the ground state to the excited state are forbidden.

Both visual inspection and resolution of the $E \perp c$ spectrum of blue sapphire measured at 293 and 10K by Ferguson & Fielding (1971) show that the band at 17,800 cm^{-1}, assigned by those authors to the $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ charge-transfer transition, has a smaller intensity increase on cooling compared with the minerals measured here (Table 1). This may simply be due to the smaller thermal expansion of sapphire. Alternatively, the low intensity increase of the 17,800 cm^{-1} band on cooling may be due to the smaller cation – cation distance in sapphire (2.79Å in sapphire compared with ~3.1Å in biotite) which has resulted in smaller spectral effects being observed for the thermal expansion of the mineral. The band at 11,500 cm^{-1} in the $E \perp c$ spectrum of sapphire (attributed to $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ charge transfer by Ferguson & Fielding 1971) has a 20% increase on cooling (Table 1). This increase could be accounted for by assuming an energy-level scheme, with the closest level to the ground state lying ~335 cm^{-1} higher in energy. The value of 335 cm^{-1} was derived using the equation $1/(1+e^{-\Delta/kT})$, and assuming the energy-level scheme and selection rules as previously described for biotite, cordierite, and chlorite.

Whether or not $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ M.M.C.T. band intensity/temperature variation can be explained in the above manner is, as yet, uncertain, since the problems involved in calculating charge-transfer energy levels are extremely complex (Loeffler *et al.* 1975; Hush 1967; Robin & Day 1967). The situation is complicated further in that a thermal population explanation makes it necessary to decide on a mechanism which would generate a system of energy levels with the appropriate selection rules. Since the temperature-dependence of some pair-type transitions (Ferguson *et al.* 1967) is similar to that of $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ transitions, and since the temperature variation of the former type of transition is explained by the thermal population of levels which arise from superexchange coupling between pairs of cations, then it is possible that a similar magnetic coupling may be responsible for generating levels which affect $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}+Fe^{2+}$ charge transfer-type transitions. Here, an explanation involving magnetic coupling would be in keeping with the previous suggestion that $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ transitions are subject only to thermal expansion effects. With this heterovalent transition there would be no magnetic coupling between Fe^{2+} and diamagnetic Ti^{4+} (d^0) cations, and the $Fe^{2+}+Ti^{4+} \rightarrow Fe^{3+}+Ti^{3+}$ transition could arise only from one ground-state level with no nearby levels subject to thermal population. Alternatively, the temperature variation of heterovalent and homovalent charge-transfer processes may be the result of the temperature effect on electron–phonon interactions, the nature of these interactions being somewhat vague at present.

Finally, a comment about the temperature variation of bands in the cordierite, biotite, chlorite, and brown and green tourmaline spectra assigned to Fe^{2+} *d-d* transitions. Inspection of Figure 3c shows that the bands at ~8,000 and ~10,000 cm^{-1} in the cordierite spectra, previously assigned to components of the $Fe^{2+}\,{}^5T_2 \rightarrow {}^5E$ transition (Faye *et al.* 1968), shows a large loss in intensity on cooling as might be expected from vibronically-coupled electric dipole *d-d* transitions. However, the brown and green tourmaline spectra show that the bands at ~9,000 and ~14,000 cm^{-1} (Figs. 1b,c), which have been similarly assigned to the $Fe^{2+}\,{}^5T_2 \rightarrow {}^5E$ transition (Wilkins *et al.* 1969; Faye *et al.* 1974) increase in intensity on cooling to helium temperatures. This temperature variation is not that expected from bands due to either forced electric dipole transitions (as shown for cordierite – Fig. 3c) or formally allowed transitions. Spectral bands arising from the latter type of transition would be temperature-independent (Figgis 1966), although possibly losing a certain amount of intensity on cooling due to vibronic contributions. In previous studies Smith & Strens (1976) attempted to explain the temperature variation of the 9,000 and 14,000 cm^{-1} tourmaline bands by suggesting that intensity increases on cooling were due to thermal population of the electronic ground-state component of the non-degenerate $^5T_2$ level. Whether or not this explanation is correct is uncertain. However, close inspection of the biotite and chlorite spectra (Figs. 3a,b) revealed that the bands assigned to Fe^{2+} *d-d* transitions (Faye 1968) at ~9,000 and ~11,000 cm^{-1} also appeared to show an increase in intensity as the temperature of the samples was decreased. In fact, curve analyses of the spectra revealed that resolved 9,000 and 11,000 cm^{-1} bands in both the biotite and chlorite spectra measured at 5.5K were ~20% greater in intensity than resolved bands at similar energies in the corresponding room-temperature spectra. Although the errors in curve analysis are large, these resolved intensity increases of the 9,000 and 11,000 cm^{-1} bands in biotite and chlorite on cooling may well be consistent with the results obtained for the temperature-dependence of the tourmaline near-infrared bands and require a similar physical explanation.

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