Optical and Mössbauer spectra of manganese-bearing phlogopites: Fe^{3+}_{IV}–Mn^{2+}_{VI} pair absorption as the origin of reverse pleochroism

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Abstract

Eight manganese-bearing phlogopites have been studied by means of X-ray powder diffraction, electron microprobe techniques, Mössbauer spectroscopy and single crystal optical absorption spectroscopy. The different types of spectra were measured at room temperature and at liquid nitrogen temperature.

The major differences in sample $3d$-element chemistry are variations in $[Mn^{2+}]/[Fe^{3+}]$ and $[Fe^{3+}_{IV}]/[Fe^{3+}_{VI}]$ ratios. Samples containing Mn^{2+}_{VI} and Fe^{3+}_{VI} are normal pleochroic, while samples containing Mn^{2+}_{VI} and Fe^{3+}_{IV} are reverse pleochroic. These chemical and optical differences are reflected by pronounced variations in the shape and band content of the optical absorption spectra.

The strongly polarized ($E\|X \gg E\perp X$) bands in the optical spectra of the reverse pleochroic samples occur at energies close to those observed for absorption bands in the spectra of synthetic Fe^{3+}_{IV}-phlogopite and natural Mn^{2+}_{VI}- and Fe^{3+}_{VI}-bearing phlogopites, but have molar extinction coefficients up to ~2 orders of magnitude greater than those calculated for corresponding spin-forbidden single ion Fe^{3+}_{IV}- and Mn^{2+}_{VI}-absorptions. These intense absorption bands are assigned to Fe^{3+}_{IV}–Mn^{2+}_{VI} pair transitions.

The ε-values, energies, polarization and concentration dependence of the pair bands are in agreement with assignments to exchange-coupled pair transitions. The majority of the bands display an inverse temperature dependence on sample cooling, which, in terms of pair theory, may be due to a dominance of "cold" band contributions.

Absorption bands in the spectra of the normal pleochroic manganese-bearing phlogopites appear to be due to spin-forbidden single ion Fe^{3+}_{VI}- and Mn^{2+}_{VI}-transitions, but contributions from various types of pair interactions involving Fe^{3+}_{VI} and Mn^{2+}_{VI} cannot be totally excluded.

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Introduction

On the basis of results obtained from chemical analyses, optical absorption spectroscopy and Mössbauer spectroscopy, reverse pleochroism in Fe^{2+}- and Fe^{3+}-bearing phlogopites has been attributed to tetrahedrally coordinated Fe^{3+} (e.g., Faye and Hogarth, 1969, Hogarth et al., 1970, Puustinen, 1973, Shinno and Suwa, 1981 and Farmer and Boettcher, 1981). Manganese-bearing phlogopites showing reverse pleochroism have also been reported and their anomalous pleochroism has been attributed to variations in the manganese content (e.g., Hamberg, 1890).

The optical $E \perp X$ absorption spectrum of a reverse pleochroic manganese-bearing phlogopite ("manganophyllite") has been measured by Burns (1970) and absorption bands at 23,800, 21,400, 19,050 and 14,850 cm^{-1} were attributed to spin-allowed d–d transitions of octahedrally coordinated Mn^{3+}.

To date neither a Mössbauer study nor an intensive optical spectroscopy study has been carried out for manganese-bearing phlogopites. Here we present detailed optical absorption and Mössbauer measurements for a suite of eight chemically characterized samples. From the results obtained, an attempt is made to explain the pleochroism and complex optical absorption spectra of natural manganese-bearing phlogopites.

Experimental

Chemical analyses of the samples were carried out with an ARL-SEMQ electron microprobe. Data were reduced using the MAGIC IV computer program (Colby, 1971). Phlogopite lattice constants were determined by refining powder diffraction data, using metallic Si powder as internal standard.

Mössbauer spectra of all samples were initially recorded at room temperature. Low temperature (77 K) spectra of samples 1, 2 and 3 were also obtained using procedures described by Hålenius et al. (1981). In order to avoid texture effects, the flaky powder samples were mounted at an angle of 54.7° to the incident γ-rays (Ericsson and Wäppling, 1976). Fitting of symmetric absorption doublets to the spectra can therefore be justified. Approximately 0.5–3.0 mg iron/cm³ was present in the powder absorbers.

Optical absorption spectra were recorded in the range 30,000–5,000 cm^{-1} by means of an automated microscope-spectrophotometer (Langer and Frentrup, 1979) using ultrafluars 10× as objective and condenser. The reference point was taken in Araldite or glycerine embedding material. The diameter of the measuring area was 46.7 μm or 53.4 μm. Computer programs were chosen to give slit widths of 100 cm^{-1}. For measurements at low temperature (~100 K) a nitrogen gas flow technique (Smith et al., 1982) was used. The samples were oriented by means of easily identifiable crystal habit and conoscopic interference figures and the sample thicknesses (15–

200±3 μm) were measured using a defocussing technique or by direct measurements using a stereoscopic microscope with a calibrated eye piece. Due to the extremely weak dichroism within the optical Z–Y plane of the phlogopites, unpolarized spectra of (001)-platelets ("$E \perp X$-spectra") and polarized $E \| X$-spectra were measured. Polarized light was obtained using a calcite prism.

Results

Microprobe analyses and compositions of the present phlogopites are summarized in Table 1. On the basis of the results obtained in the present Mössbauer study the presence of ferrous iron in the investigated samples can be excluded. Furthermore, on comparing the spectra of our natural samples with the spectra of a synthetic Mn^{3+}-bearing phlogopite, it may be concluded that the natural samples contain only trace amounts of Mn^{3+} (≤5% of the total manganese content). Therefore, total iron and manganese contents are given as Fe_2O_3 and MnO respectively. The distribution of Fe^{3+} in tetrahedral and octahedral sites has been determined from the chemical analyses in such a way that ferric iron is assigned to the tetrahedral position when this site cannot be fully occupied by Si and Al. The results of this determination are in excellent agreement with the results of the Mössbauer spectroscopy.

In the detailed *X-ray analyses* of the present samples it was found that some of the reflections were split. This feature may indicate complex layering (i.e., layers of different stacking sequences) in the micas. A similar observation on phlogopites has been reported by Shinno and Suwa (1981). Hence, the significance of the calculated X-ray data is reduced. Results of the cell parameters shown in Table 1 have been obtained assuming a simple 1M phlogopite structure. The measured cell volumes increase, as expected, with increasing concentrations of tetrahedrally coordinated ferric iron (Fe_{IV}^{3+}) and octahedrally coordinated manganese (Mn_{VI}^{2+}).

Mössbauer spectra of selected samples are shown in Figure 1. Only Fe^{3+} is present in all the studied phlogopites. The assignment of ferric iron among the available tetrahedral and octahedral sites has been determined from observed isomer shift values (Annersten and Hålenius 1976). At room temperature, isomer shift values for tetrahedral ferric iron are 0.23±0.03 mm/s (relative to metallic iron) in our samples. Values at low temperature are increased by the second order Doppler shift. According to the Mössbauer results, Fe_{IV}^{3+} can be exclusively assigned to samples 2, 4, 6 and 8 (cf. Table 2). Octahedrally coordinated ferric iron (Fe_{VI}^{3+}) is characterized by a larger isomer shift, approximately 0.36±0.02 mm/s, and can be exclusively assigned to samples 1, 5 and 7. Sample 3 was the only sample measured which contained both Fe_{IV}^{3+} and Fe_{VI}^{3+}. The ferric iron populations shown in Table 2, were obtained from computer fitted area ratios of tetrahedral and octahedral quadrupole doublets. The ab-

Table 1. Chemical analyses, compositions and lattice parameters of the studied manganese-bearing phlogopites. Samples 2 and 6 are from Harstigen, Sweden and the additional six samples from Långban, Sweden.

	1	2	3	4	5	6	7	8
SiO_2 (wt-%)	39.4	41.3	39.9	41.1	39.6	41.5	38.0	41.2
Al_2O_3	14.6	9.5	11.5	12.3	15.4	9.3	16.6	11.7
Fe_2O_3	4.4	3.4	3.3	1.2	3.6	3.8	3.0	2.1
TiO_2	0.7	0.0	0.6	0.1	0.6	0.0	0.7	0.0
MnO	3.9	8.4	10.4	1.1	1.1	7.5	2.2	1.7
MgO	22.7	22.9	20.8	27.8	24.8	23.4	24.3	28.0
BaO	1.0	0.0	0.2	1.4	1.5	0.0	1.0	1.5
Na_2O	0.2	0.1	0.1	0.3	0.4	0.1	0.4	0.2
K_2O	10.0	10.5	10.4	10.2	10.0	10.5	10.0	10.3
	96.9	96.1	97.2	95.5	97.0	96.1	96.2	96.7
Cations on the basis of 44 negative charges								
Si	5.60	6.00	5.80	5.82	5.56	6.01	5.45	5.81
Al_{IV}	2.40	1.63	1.97	2.06	2.44	1.59	2.55	1.95
Fe_{IV}^{3+}	-	0.37	0.23	0.12	-	0.40	-	0.22
Al_{VI}	0.04	-	-	-	0.11	-	0.26	-
Fe_{VI}^{3+}	0.47	-	0.13	0.01	0.38	0.01	0.33	-
Ti	0.08	-	0.06	0.01	0.07	-	0.07	-
Mn	0.46	1.03	1.27	0.13	0.13	0.92	0.26	0.20
Mg	4.82	4.96	4.52	5.86	5.20	5.07	5.19	5.88
Ba	0.06	-	0.01	0.08	0.08	-	0.06	0.09
Na	0.07	0.02	0.03	0.09	0.11	0.02	0.11	0.04
K	1.82	1.94	1.92	1.85	1.80	1.95	1.84	1.84
Lattice parameters								
a(Å)	5.329(4)	5.368(9)	5.379(8)	5.32(1)	5.36(1)	5.365(7)	5.299(5)	5.316(9)
b(Å)	9.256(9)	9.285(9)	9.271(9)	9.26(1)	9.32(1)	9.282(9)	9.262(4)	9.285(6)
c(Å)	10.281(9)	10.28(1)	10.318(9)	10.27(1)	10.20(3)	10.312(9)	10.193(9)	10.266(9)
β (°)	99.9(2)	100.0(1)	99.9(2)	99.9(3)	99.5(1)	100.2(1)	99.7(1)	99.7(2)
V(Å³)	499.6	504.6	506.8	498.6	495.5	505.4	493.1	499.4

sorption doublets resulting from Fe_{VI}^{3+} are characteristically broader than the absorption lines arising from Fe_{IV}^{3+}. This may indicate that in phlogopite Fe_{VI}^{3+} is distributed over the two non-equivalent octahedral sites M1 and M2 (Annersten, 1974). Two Fe_{VI}^{3+} patterns were fitted to the spectrum of sample 5 (Table 2), but in order to have the fit converging, the intensities of the two quadrupole doublets had to be constrained to 1:1. No pronounced compositional dependence of the Mössbauer parameters was observed.
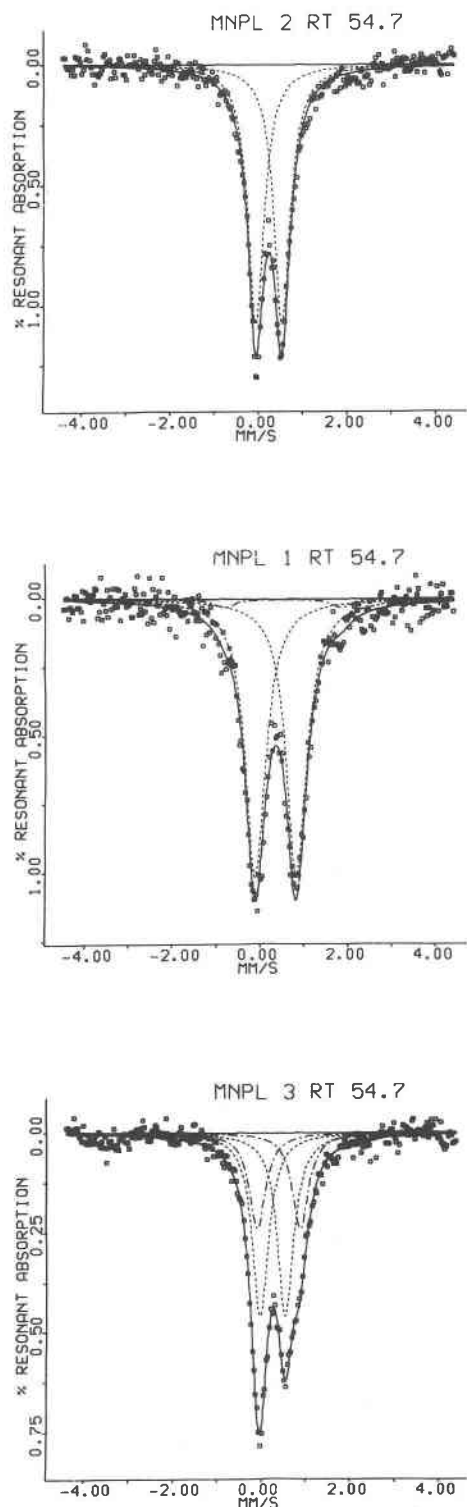
Optical absorption spectra of the present phlogopites can be divided into two groups. Those of *samples 2, 4, 6 and 8 are* dominated by medium to strong absorption bands at 29,100, 27,000, 25,500, 24,800, 23,800, 22,300, 21,300, 19,700, 18,500 and 14,500 cm^{-1}. These samples are reverse pleochroic (R.P.) and the pleochroism is caused by the strong pleochroism of the absorption bands (Fig. 2). The envelope of the spectra of the reverse pleochroic samples displays an inverse temperature dependence (increasing integrated absorption on cooling). This indicates that the majority of the absorption bands have this temperature dependence. Due to the strong overlap between the absorption bands, it is difficult to quantify the increase in integrated absorption for any single absorption band on cooling (Fig. 3).

The absorption spectra of *samples 1, 5 and 7* are characterized by a strong UV edge absorption and show weak bands at ~29,000, ~27,500, 24,600, 23,800, 21,500, ~18,000 and ~15,000 cm^{-1}. These samples are normal pleochroic (N.P.) and the pleochroism is caused by the pleochroism of the UV-absorption edge (Fig. 2).

Sample 3 is weakly reverse pleochroic and the spectrum of this sample shows absorption bands found in the spectra of both previous types.

Table 2. ^{57}Fe Mössbauer parameters of manganese-bearing phlogopites.

Sample	Absorber Temp. (K)	ΔE_Q (mm/s)	IS (mm/s)	Intensity (%)	FWHH (mm/s)	Assignment
1	293	0.94	0.35	100	0.56	Fe_{VI}^{3+}
	77	0.98	0.47	100	0.62	"
2	293	0.59	0.23	100	0.44	Fe_{IV}^{3+}
	77	0.63	0.32	100	0.39	"
3	293	0.56	0.25	58	0.41	Fe_{IV}^{3+}
		0.94	0.38	42	0.51	Fe_{VI}^{3+}
	77	0.63	0.33	62	0.41	Fe_{IV}^{3+}
		0.89	0.54	38	0.50	Fe_{VI}^{3+}
4	293	0.69	0.22	100	0.67	Fe_{IV}^{3+}
5	293	1.22	0.37	50	0.57	Fe_{VI}^{3+}
		0.72	0.35	50	0.57	"
6	293	0.57	0.22	100	0.36	Fe_{IV}^{3+}
7	293	1.02	0.36	100	0.70	Fe_{VI}^{3+}
8	293	0.68	0.22	100	0.36	Fe_{IV}^{3+}

Fig. 1. Room temperature Mössbauer spectra of samples 2, 1 and 3. Sample 2: Fe_{IV}^{3+}, sample 1: Fe_{VI}^{3+} and sample 3: Fe_{IV}^{3+} and Fe_{VI}^{3+}. The fitted quadrupole doublet of very low intensity in the spectrum of sample 1 is due to the presence of minor quantities of hematite.

Isomer shift (IS) relative to metallic iron. Relative errors for IS and ΔE_Q ±0.01 mm/s. Esd for intensities 3.0 %.
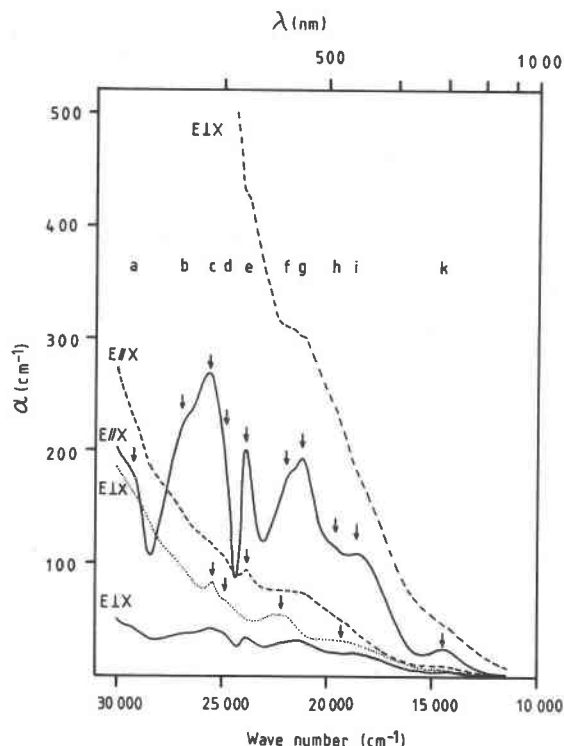
Fig. 2. Room temperature $E \parallel X$ and $E \perp X$ absorption spectra of sample 1 (- - - -), sample 8 (——) and $E \perp X$ spectrum of synthetic Fe_{IV}^{3+}-phlogopite ($\cdots$). α = absorbance/sample thickness (cm). For the reverse pleochroic sample 8, letters a, b, .. and arrows indicate absorption bands assigned in Table 3. Arrows at the spectra of the synthetic sample and the normal pleochroic sample 1 denote bands which occur at the same energies as bands in the reverse pleochroic samples.

In the spectra of the present samples, no absorption bands were observed in the region 11,000–5,000 cm^{-1}.

Discussion

The differences in pleochroism and band content observed for the present phlogopites can obviously be correlated to the distribution of ferric iron. The reverse pleochroic samples 2, 4, 6 and 8 contain exclusively Fe_{IV}^{3+}, the normal pleochroic samples 1, 5 and 7 are Fe_{VI}^{3+}-bearing and the intermediate sample 3 contains Fe_{IV}^{3+} and Fe_{VI}^{3+}. All samples contain manganese.

This information is insufficient to enable us to interpret the complex spectra shown in Figures 2, 3 and 4. To help us to carry out this task, phlogopites containing only Mn_{VI}^{3+} and only Fe_{IV}^{3+} (of the transition metal ions) have been synthesized and investigated by means of electron microprobe, Mössbauer, X-ray powder diffraction and optical absorption techniques. Although a full report on the studies of the synthetic samples will be given at a later date (Ackermann, L., Smith, G. and Cemic, L., Technische Universität Berlin, in prep.), several results are

discussed here and are shown to be crucial in interpreting the optical absorption spectra of the natural samples.

Mn_{VI}^{2+} in phlogopites

An initial assertion is that the present phlogopites contain divalent manganese in octahedral positions (Mn_{VI}^{2+}). One reason for this is that the optical absorption spectra of a synthetic Mn_{VI}^{3+}-bearing phlogopite revealed three, weakly normal pleochroic, broad (half line widths of ~4,000 cm^{-1}) absorption bands of approximately equal intensity ($\varepsilon_{Mn^{3+}}$ ~30–60 $1 \cdot g$-atom$^{-1} \cdot cm^{-1}$) at 22,400, 19,500 and 12,300 cm^{-1}, and no evidence for such a band system has been found in the spectra of our natural samples. Further, the assignment of Mn_{VI}^{2+} in the natural phlogopites is in excellent agreement with cation/site occupancies derived from chemical analyses (Table 1). The other possibilities for location and valence states of manganese in the present samples, Mn_{IV}^{2+} and Mn_{IV}^{3+}, are, as will be demonstrated, completely untenable with regards to interpretations given for the optical spectra.

Reverse pleochroic (R.P.) samples 2, 4, 6 and 8

From the foregoing, these samples contain Fe_{IV}^{3+} and Mn_{VI}^{2+}, and the properties of the bands in their absorption spectra are summarized as follows.

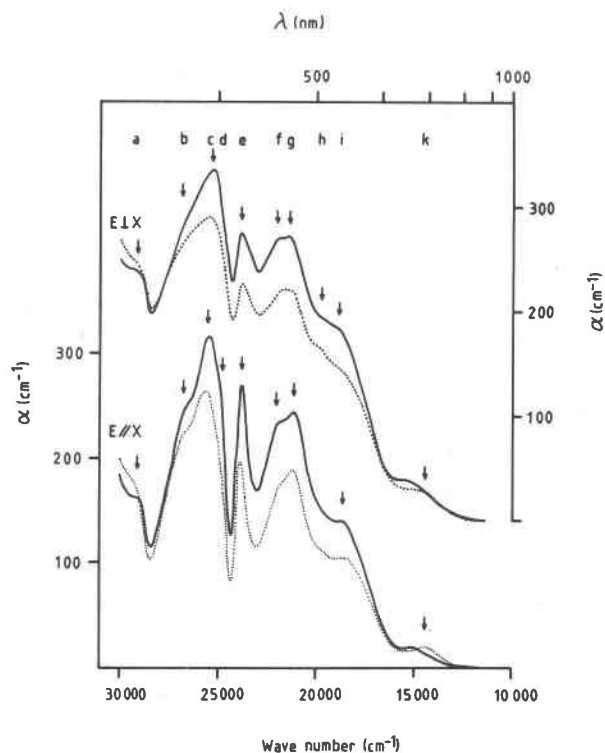A comparison of the spectra of a synthetic Fe_{IV}^{3+}-bearing

Fig. 3. Room temperature ($\cdots$) and low temperature (———) absorption spectra of sample 2 ($E \perp X$) and sample 8 ($E \parallel X$). Letters and α as in Fig. 2.
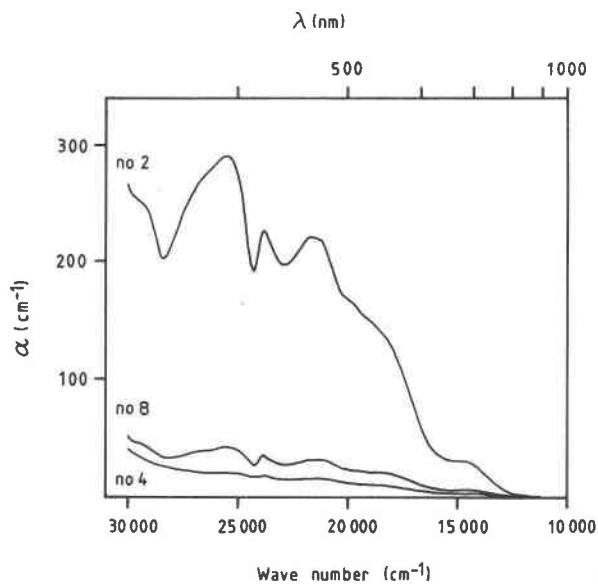
Fig. 4. Room temperature $E \perp X$ absorption spectra of samples 2, 4 and 8, with $[Fe_{IV}^{3+}][Mn_{VI}^{2+}]$ concentration products of [1.23][3.43], [0.44][0.45] and [0.76][0.69] g-atom l^{-1} respectively. α as in Fig. 2.

phlogopite with the composition $K_{1.93}Mg_{6.06}(Si_{5.97}$ $Fe_{2.03})O_{20}(OH)_4$ and the natural R.P. samples (Fig. 2) shows that, in the 16,000–26,000 cm^{-1} range, both spectra have bands at *energies* of 25,500, 24,800, 22,300 and 19,700 cm^{-1}. The latter absorption band in the spectra of the natural samples is only apparent on close inspection (Fig. 2). The absorption features in the spectra of the synthetic phlogopite are attributed to single ion spin-forbidden *d–d* transitions of Fe_{IV}^{3+} and have molar extinction coefficients (*e.g.*, $\varepsilon_{22,300} \sim 2.5$ 1 · g-atom^{-1} · cm^{-1}) in keeping with this interpretation. Hence we may associate the 25,500 (c), 24,800 (d), 22,300 (f) and 19,700 cm^{-1} (h) bands in the spectra of the natural R.P. samples with transitions (not necessarily single ion) involving Fe_{IV}^{3+}. Absorption bands present in the 16,000–26,000 cm^{-1} spectral region of the natural R.P. phlogopites, but which are not observed in the spectrum of the synthetic Fe_{IV}^{3+}-phlogopite, are located at 23,800 (e), 21,300 (g) and 18,500 cm^{-1} (i). These absorption bands in the spectra of the R.P. samples could then reasonably be associated with transitions involving Mn_{VI}^{2+}. An alternative approach to associate absorption bands with Mn_{VI}^{2+} is to compare the spectra of N.P. and R.P. samples. Since Mn^{2+} is common to both types of phlogopite, bands caused by transitions involving Mn_{VI}^{2+} should occur at the same energies. This comparison (Fig. 2) clearly links the 23,800 cm^{-1} (e) band with Mn_{VI}^{2+}, but possible absorptions at 21,300 (g) and 18,500 cm^{-1} (i) in N.P. sample spectra are either too weak or are hidden by other absorption features to be clearly identified and ultimately linked with Mn_{VI}^{2+}. Weak absorption bands at ~29,000, ~27,000 and

~15,000 cm^{-1} are observed in the spectra of the natural N.P. samples and the synthetic Fe_{IV}^{3+}-phlogopite (Fig. 2). These absorption bands may have different origins in the different types of sample and this will eventually make assignments of the absorption bands at 29,100 (a) 27,000 (b) and 14,500 cm^{-1} (k) in the spectra of the R.P. samples difficult (Figs. 2–4).

The absorption bands in the spectra of the R.P. phlogopites have extremely *high intensities*. If these bands, which we have associated with Fe_{IV}^{3+} and Mn_{VI}^{2+}, were assigned to single ion transitions, then for the $E \perp X$-spectrum ($E \| X \gg E \perp X$), the molar extinction coefficients of these bands would be up to two orders of magnitude greater than expected for such transitions (*e.g.*, when assuming Mn_{VI}^{2+} to be the absorbing species, the molar extinction coefficients for the 23,800 cm^{-1} band in the room temperature spectra of sample no. 8 are ~35 ($E \perp X$) and ~200 ($E \| X$) 1 · g-atom^{-1} · cm^{-1}).

Assuming that the optical direction X is perpendicular to (001) and taking α and β to be the angles between metal$_{IV}$–metal$_{VI}$ vector and the optical directions X and $\perp X$ respectively, then the ratio $\cos^2\alpha : \cos^2\beta$ is calculated as 5:1. A qualitative inspection of the spectra of the R.P. samples (Fig. 2) shows that the $E \| X : E \perp X$ intensity ratio of the absorption envelope in the 30,000–10,000 cm^{-1} spectral range is approximately 6:1, which indicates that the majority of the absorption bands in the spectra of the R.P. phlogopites are *strongly polarized* along the Fe_{IV}^{3+}–Mn_{VI}^{2+} vectors. The minor difference between observed and calculated intensity ratio could exist because (i) the exact atomic coordinates for Fe_{IV}^{3+} and Mn_{VI}^{2+} in Mn_{VI}^{2+}, Fe_{IV}^{3+}-bearing phlogopites have not been determined (ii) a deviation of X of only 5 degrees from the assumed direction would produce a $\cos^2\alpha : \cos^2\beta$ ratio equal to the experimentally found value.

Considering possible *concentration correlations* (Fig. 4), it is found that despite the fact that only the spectra of three of the R.P. samples may be reasonably compared (samples 2 and 6 have similar Fe_{IV}^{3+} and Mn_{VI}^{2+} ion concentrations, giving rise to absorption spectra of similar intensity), there is no link between absorption bands associated with Fe_{IV}^{3+} (*e.g.*, at 25,500 cm^{-1}) and single ion Fe_{IV}^{3+}-content. There could be a correlation between intensities of bands associated with Mn_{VI}^{2+} (*e.g.*, at 21,300 cm^{-1}) and single ion Mn_{VI}^{2+} content, but this would not explain why the absorption features in the spectra of the different R.P. phlogopites appear to maintain the same relative intensity. From Figure 4, the only reasonable correlation is that the intensities of the majority of the absorption bands in our R.P. samples are related to the $[Fe_{IV}^{3+}][Mn_{VI}^{2+}]$ concentration product.

Absorption bands resulting from single ion *d–d* transitions either lose intensity or maintain equal absorption areas on sample cooling (Lever, 1968). Although such a *temperature variation* might be argued for the absorption bands at 29,100 (a) and 14,500 cm^{-1} (k) in the spectra of the R.P. samples (Fig. 3), the majority of the absorption

bands in the 30,000–10,000 cm^{-1} spectral region of these samples clearly increase in intensity with decreasing temperature.

We assign the majority of the absorption bands in the spectra of the R.P. manganese-bearing phlogopites to Fe^{3+}_{IV}–Mn^{2+}_{VI} pair transitions which involve the excitation of either Fe^{3+}_{IV} or Mn^{2+}_{VI} (*i.e.*, single excitation process). That pair bands arising from such transitions occur close to the energies of spin-forbidden bands of one or both of the component ions of the pair, and have intensities 1–2 orders of magnitude greater than the single ion spin-forbidden *d–d* absorption bands is well established (*e.g.*, Ferguson *et al.*, 1966) and consistent with this assignment. The polarization of the absorption bands and their intensity variation with the $[Fe^{3+}_{IV}]$ $[Mn^{2+}_{VI}]$ concentration product are also consistent with a pair interpretation. An explanation of the temperature variations for the band intensities is discussed later in the text.

A partial assignment scheme for the absorption bands observed in the spectra of the R.P. manganese-bearing phlogopites is given in Table 3. The decisions as to which ion of the Fe^{3+}_{IV}–Mn^{2+}_{VI} pair is excited stem from previous remarks on band energies linking Fe^{3+}_{IV} and Mn^{2+}_{VI} with absorptions at 25,500 (c), 24,800 (d), 22,300 (f), 19,700 cm^{-1} (h) and 23,800 (e), 21,300 (g), 18,500 cm^{-1} (i) respectively. Actual assignments have been made assuming that the sharp bands at 22,300 (actually split in two components at 22,700 and 22,000 cm^{-1}) and 25,500 cm^{-1} in the spectrum of synthetic Fe^{3+}_{IV}-phlogopite represent the field independent $^6A_1(S) \rightarrow {}^4A_1{}^4E(G)$ and $^6A_1(S) \rightarrow {}^4E(D)$ spin-forbidden transitions in Fe^{3+}_{IV} respectively, and that the sharp absorption band at 23,800 cm^{-1} (e) in the spectra of the R.P. samples has the energy expected for the Mn^{2+}_{VI} field independent $^6A_1(S) \rightarrow {}^4A_1{}^4E(G)$ spin-forbidden transition (Manning 1968). The assignment scheme given in Table 3 is regarded as plausible but not necessarily correct. The spectra are obviously extremely complex and several absorption bands may be hidden. Special difficulties are encountered in assigning absorption bands at 29,100 (a), 27,000 (b) and 14,500 cm^{-1} (k) in the spectra of the R.P. samples since, as mentioned previously, weak bands and shoulders are found near these energies in the spectra of both the synthetic Fe^{3+}_{IV}-phlogopite and the natural N.P. manganese-bearing phlogopites. Further, the 29,100 (a) and 14,500 cm^{-1} (k) bands in the spectra of the R.P. samples could be argued to display a single ion temperature dependence with the added feature that the lower energy absorption shows a decided shift to higher energies on cooling (Fig. 3). However, any attempts to give both bands single ion assignments also have to explain their polarizations and intensities relative to other absorption features with varying Fe^{3+}_{IV} and Mn^{2+}_{VI} contents.

On comparing the spectra (26,000–16,000 cm^{-1}) of a reverse pleochroic, essentially Mn-free, Fe^{2+}_{VI}- and Fe^{3+}_{IV}-bearing phlogopite (Faye and Hogarth, 1969) with the spectra of our Mn^{2+}-bearing R.P. phlogopites, some interesting differences are noted. Absorption bands at 23,800 (e) and 21,300 cm^{-1} (g) are not observed in their spectra, which further supports our assignment of these bands to transitions involving the excitation of Mn^{2+}_{VI}. A prominent absorption band (E $\parallel$ X $\gg$ E $\perp$ X) at 20,300 cm^{-1} in their spectra is not observed in the spectra of our natural R.P. samples or in the spectrum of the synthetic Fe^{3+}_{IV}-phlogpite. Finally, absorption bands at ~25,000, ~22,700 and ~19,200 cm^{-1} (all E $\parallel$ X $\gg$ E $\perp$ X) observed in the spectra of the Mn^{2+}-free phlogopite (Faye and Hogarth, 1969), as well as in our R.P. Mn^{2+}-bearing phlogopites (within 500 cm^{-1}), all exhibit, along with the 20,300 cm^{-1} band, unusually high ε-values when assigned to single ion Fe^{3+}_{IV} (Faye and Hogarth, 1969, made this assignment for absorption bands lying between 24,000–16,000 cm^{-1}). These observations suggest that other M_{VI}–M_{IV} pair interactions (*e.g.*, Fe^{2+}_{VI}–Fe^{3+}_{IV}) could play an important role in the absorption spectra of reverse pleochroic phlogopites.

Normal pleochroic (N.P.) samples 1, 5 and 7

From the Mössbauer spectroscopy of these samples and from a comparison with the optical absorption spectra of the synthetic phlogopites, samples 1, 5 and 7 contain Fe^{3+}_{VI} and Mn^{2+}_{VI}. The E $\perp$ X spectra of these samples show weak bands or shoulders at ~29,000, ~27,500, ~18,000 and ~15,000 cm^{-1}. Only three absorption bands at 24,600, 23,800 and 21,500 cm^{-1} may be clearly identified (Fig. 2). As discussed previously, the band at 23,800 cm^{-1} is associated with transitions involving Mn^{2+}_{VI}. Further, it is reasonable to assume that the

Table 3. Partial assignment scheme for the absorption bands in the spectra of reverse pleochroic manganese-bearing phlogopites.

Energy (cm^{-1})	Assignment	
29,100 (a)	Fe^{3+}_{IV}–Mn^{2+}_{VI}	
27,000 (b)	Fe^{3+}_{IV}–Mn^{2+}_{VI}	
25,500 (c)	*Fe^{3+}_{IV}–Mn^{2+}_{VI}	$^6A_1(S)^6A_1(S) \longrightarrow {}^4E(D)^6A_1(S)$
24,800 (d)	*Fe^{3+}_{IV}–Mn^{2+}_{VI}	" $\longrightarrow {}^4T_2(D)^6A_1(S)$
23,800 (e)	Fe^{3+}_{IV}–*Mn^{2+}_{VI}	" $\longrightarrow {}^6A_1(S)^4A_1,{}^4E(G)$
22,300 (f)	*Fe^{3+}_{IV}–Mn^{2+}_{VI}	" $\longrightarrow {}^4A_1,{}^4E(G)^6A_1(S)$
21,300 (g)	Fe^{3+}_{IV}–*Mn^{2+}_{VI}	" $\longrightarrow {}^6A_1(S)^4T_2(G)$
19,700 (h)	*Fe^{3+}_{IV}–Mn^{2+}_{VI}	" $\longrightarrow {}^4T_2(G)^6A_1(S)$ or ${}^4T_1(G)^6A_1(S)$
18,500 (i)	Fe^{3+}_{IV}–*Mn^{2+}_{VI}	" $\longrightarrow {}^6A_1(S)^4T_1(G)$
14,500 (k)	Fe^{3+}_{IV}–Mn^{2+}_{VI}	

*Denotes which ion undergoes excitation. (a),(b),... refer to bands in Figs. 2 and 3.

bands at 24,600 and 21,500 cm^{-1} are associated with transitions involving Fe_{VI}^{3+}. This interpretation is consistent with the observation that the 23,800 cm^{-1} band increases in intensity relative to the other two absorption bands with increasing $[Mn_{VI}^{2+}]/[Fe_{VI}^{3+}]$ concentration ratio. Although our range of transition metal ion content is small and the absorption bands lie on a strong UV-absorption bacground, it appears that the intensities of these three bands could vary linearly with single ion concentrations. The three absorption bands appear not to be strongly polarized ($E \perp X > E \parallel X$) (Fig. 2). The evidence available suggests that the absorption bands at 24,600, 23,800 and 21,500 cm^{-1} in the spectra of samples 1, 5 and 7 should be assigned to single ion spin-forbidden transitions of Fe_{VI}^{3+}, Mn_{VI}^{2+} and Fe_{VI}^{3+} respectively. However, it is a puzzling feature that, with a single ion assignment, the molar extinction coefficients for the 23,800 and 21,500 cm^{-1} bands in the $E \perp X$ and ($E \parallel X$) spectra are $\varepsilon_{Mn_{VI}^{2+}} \sim 7$ (4) $1 \cdot$ g-atom$^{-1} \cdot$ cm^{-1} and $\varepsilon_{Fe_{VI}^{3+}} \sim 15$ (10) $1 \cdot$ g-atom$^{-1} \cdot$ cm^{-1} respectively. Normal extinction coefficients for spin-forbidden bands due to these ions and at these energies are $\varepsilon_{Mn_{VI}^{2+}}$ 0.2–0.4 $1 \cdot$ g-atom$^{-1} \cdot$ cm^{-1} and $\varepsilon_{Fe_{VI}^{3+}}$ 1–3 $1 \cdot$ g-atom$^{-1} \cdot$ cm^{-1} (*e.g.*, Manning, 1968 and Faye, 1968). It is certainly possible that the large ε-values result from an overestimation of absorbance values caused by our approximation for the background absorption. Nevertheless, since Fe_{VI}^{2+}–Fe_{VI}^{3+} pair interactions have been proposed for other minerals including biotite (Smith *et al.*, 1980), the possibility that Fe_{VI}^{3+}–Mn_{VI}^{2+}, Fe_{VI}^{3+}–Fe_{VI}^{3+} or Mn_{VI}^{2+}–Mn_{VI}^{2+} pair interactions play a role in the $E \perp X$ spectrum of our N.P. phlogopite samples is not very easily eliminated. Trace concentrations of Fe_{IV}^{3+}, which would not be detectable by Mössbauer spectroscopy, could be responsible for the enhanced band intensities in the $E \parallel X$ spectra of the N. P. Mn^{2+}-bearing phlogopites. If traces of Fe_{IV}^{3+} were present in the N.P. samples, the observed enhanced intensities of the bands in the $E \parallel X$-spectra would be caused by Fe_{IV}^{3+}–M_{VI} pairs. However, the absence of the dominating Fe_{IV}^{3+}–Mn_{VI}^{2+} pair band at 25,000 cm^{-1} in the $E \parallel X$-spectra of the N.P. phlogopites suggest that the concentration of Fe_{IV}^{3+}–Mn_{VI}^{2+} pairs is very low in these samples, and the cause for the enhancement of the band intensities in $E \parallel X$ has to be looked for elsewhere. Temperature dependence measurements of the $E \perp X$ spectrum of sample 1 proved inconclusive.

Mechanism of Fe_{IV}^{3+}–Mn_{VI}^{2+} pair interactions in Mn^{2+}-bearing phlogopites, temperature variations and general comments concerning pair bands in minerals

As a result of their complex structure and considerable and varied cation concentrations, minerals, unlike simple oxides and fluorides, invariably give rise to complex and broad band spectra and are not prone to display optical fine structure. This can make it very difficult to define the nature of interacting processes observed in mineral spectra and, consequently, to explain features (*e.g.*, band

intensity variations in relation to temperature variations) associated with these processes.

Ferguson and Fielding (1971, 1972) were able to conclusively confirm the presence of Fe^{3+}–Fe^{3+} pairs in sapphire from measurements of optical absorption spectra at room temperature and liquid helium temperature. In particular, they were able to demonstrate fine structure for the assigned $^6A_1(S)^6A_1(S) \rightarrow {}^4A_1,{}^4E(G)^6A_1(S)$ pair band and show how the fine structure obeyed spin-selection rules down to 4.2 K. For absorption bands resulting from pair transitions involving field independent energy levels and which also obey the spin-selection rule, $\Delta S = 0$, a decrease in integrated band absorption on cooling is predicted. However, the assigned Fe_{IV}^{3+}–$MnFe_{VI}^{2+}$ pair bands involving transitions to $^6A_1(S)^4A_1$, $^4E(G)$ and $^6A_1(S)^4E(D)$ pair levels (Table 3) in the spectra of R.P. Mn^{2+}-phlogopites increase in integrated absorption on cooling down to 100 K (Fig. 3). Hence, unless dramatic reversals of the band temperature dependencies take place below 100 K, we are unable to explain the temperature variations for absorption bands in the spectra of these phlogopites in terms of this simple exchange coupled pair theory.

Possibly more relevant to the case of R.P. manganese phlogopites, and perhaps minerals in general, is an early publication by Lohr and McClure (1968). In discussing Mn^{2+} pair interaction in various salts they described them as spin-wave transitions, which is a simultaneous transition, where one ion of the pair undergoes an electronic *d–d* transition (exciton) and the other ion undergoes a spin-deviation (magnon). This process will conserve the total spin projection. The described type of interaction will affect not only the intensities of absorption bands occurring at the energies of field-independent transitions, *e.g.*, $^6A_1(S) \rightarrow {}^4A_1,{}^4E(G)$, but also bands at energies of transitions which involve a change in orbital configuration (*e.g.*, $^6A_1(S) \rightarrow {}^4T_1(G)$). Further Lohr and McClure (1968) considered how the temperature variation of a spectral pair feature will be dependent on whether "cold bands" (exciton + magnon transition) or "hot bands" (exciton-magnon transition) provide the greater contributions to the feature. Following Lohr and McClure (1968) it might therefore be suggested that the inverse temperature dependence displayed by the majority of the features in the spectra of R.P. Mn^{2+}-bearing phlogopites primarily results from "cold bands" providing the greater contributions' to the features. Later studies by Fujiwara and Tanabe (1972), Fujiwara *et al.* (1972), Shinagawa and Tanabe (1971) and Ono and Fuchikama (1977) should also be relevant to the spectra of R.P. Mn^{2+}-phlogopites but, at present, we find such studies to sophisticated for our purposes.

Table 4 compares the properties of assigned pair bands in some mineral spectra. It is seen that the effects observed in the spectra of the R.P. Mn^{2+}-bearing phlogopites could be the "spin-forbidden counterpart" of pair effects observed in tourmaline and biotite spectra, and

Table 4. Comparison of properties of pair bands in some mineral spectra.

Mineral / Ion pair	Band energy	Polarization	Intensity	Temperature dependence	Concentration dependence	Reference
Tourmaline, biotite Fe_{VI}^{2+} - Fe_{VI}^{3+}	That of single ion spin-allowed Fe_{VI}^{2+}-absorptions	Along Fe_{VI}^{2+}-Fe_{VI}^{3+} vectors	1 order of magnitude greater than that of single ion absorptions	Inverse down to 10 K	Non-linear versus FeO-concentration	Smith 1978a, 1978b Smith et al. 1980
Mn^{2+}- phlogopites Fe_{IV}^{3+} - Mn_{VI}^{2+}	That of single ion spin-forbidden Fe_{IV}^{3+}- and Mn_{VI}^{2+}- absorptions	Along Fe_{IV}^{3+}-Mn_{VI}^{2+} vectors	2 orders of magnitude greater than that of single ion absorptions	Inverse down to 100 K	$[Fe_{IV}^{3+}][Mn_{VI}^{2+}]$	This work
Hydroxy Fe-sulfates Fe_{VI}^{3+} - Fe_{VI}^{3+} (?)[*]	That of single ion spin-forbidden Fe_{VI}^{3+}-absorptions	Along Fe_{VI}^{3+}-Fe_{VI}^{3+} vectors and planes	1-2 orders of magnitude greater than that of single ion absorptions	(?)[**]	(?)	Rossman 1975
Sapphire [***] Fe_{VI}^{3+} - Fe_{VI}^{3+}	That of single ion spin-forbidden Fe_{VI}^{3+}-absorptions	(?)	1 order of magnitude greater than that of single ion absorptions	As predicted down to 4.2 K	$[Fe^{3+}]^{1.7}$	Ferguson & Fielding 1971, 1972 Krebs & Maisch 1971

[*] Intensity enhanced and strongly polarized absorption bands were not explicitly assigned to Fe_{VI}^{3+}-Fe_{VI}^{3+} pairs, but their intensity enhancement was "associated with antiferromagnetic exchange coupling of the ferric ions".

[**] The absorption band at 830 nm (12,050 cm^{-1}) in the copiapite spectrum decreases in integrated intensity on cooling to liquid nitrogen temperature (G.R. Rossman, pers. comm.). No information on the temperature dependence of other bands in these mineral spectra is at present available.

[***] For sapphire, the properties of pair bands resulting from single excitation processes are quoted.

that the same interaction mechanism may be operating in these minerals. Further work is, of course, required to substantiate this proposal.

Finally, the complex nature of most mineral structures make them likely hosts for a great variety of pair interactions, some of which may be readily seen in optical absorption spectra. Clearly, anomalously high band intensity and Beer's law failure are critical parameters in detecting these interactions. It is suggested that pair bands lying at the energies of spin-forbidden transitions may be located in the UV and visible regions of viridine (23,300 cm^{-1} band, Smith et al., 1982), chloritoid (24,000 cm^{-1} band, Hålenius et al., 1981) and yoderite (25,500 cm^{-1} band, Langer et al., 1982). In these minerals, bands at the energies of spin-forbidden transitions have unusually high molar extinction coefficients, when attributed to single ion, and display "non-single ion" (i.e., inverse) temperature dependencies. In the light of the results of Lohr and McClure (1968), the temperature dependence criteria must however be applied with some caution.

Conclusions

Reverse pleochroism in Mn^{2+}-bearing phlogopites is caused by strongly polarized ($E\|X \gg E\perp X$) absorption bands arising from transitions between energy levels of Fe_{IV}^{3+}–Mn_{VI}^{2+} ion pairs. These absorption bands occur at energies close to those of spin-forbidden single ion d–d bands of Fe_{IV}^{3+} and Mn_{VI}^{2+} in phlogopite. The ε-values of the pair bands are up to ~2 orders of magnitude higher than the ε-values of spin-forbidden single ion d–d bands of Fe_{IV}^{3+} and Mn_{VI}^{2+}. The inverse temperature dependence of the majority of the pair bands may be in accordance with a theory for exchange-coupled pair transitions. Reverse pleochroic Mn^{2+}-bearing phlogopites may show effects which are the "spin-forbidden counterpart" of Fe^{2+}–Fe^{3+} pair transitions in tourmaline and biotite.

Possible Fe_{VI}^{2+}–Fe_{IV}^{3+} pair absorption in phlogopites is suggested from comparison between spectra of manganese free, reverse pleochroic Fe_{VI}^{2+}-, Fe_{IV}^{3+}-bearing phlogopite and the present reverse pleochroic Mn^{2+}-bearing phlogopites.

Absorptions in normal pleochroic Mn^{2+}-bearing phlogopites appear to be due to single ion spin-forbidden Mn_{VI}^{2+} and Fe_{VI}^{3+}, but possible M_{VI}–M_{VI} ion pair interactions cannot be completely discounted in the interpretation of the spectra.

No spectral evidence for the presence of Mn^{3+} ions in the present samples has been obtained.

Acknowledgments

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