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Electronic absorption spectra of Fe^{2+} ions in oxygen-based rock-forming minerals at temperatures between 297 and 600 K

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Abstract Polarized electronic single crystal spectra of natural Fe^{2+} ion-bearing oxygen-based minerals, in which ferrous ions enter octahedral sites of different symmetry and distortion (olivine, cordierite, ortho- and clinopyroxene, amphibole), eightfold sites in garnet (almandine) and clinopyroxene (M2), and tetrahedral sites in spinel, were studied at temperatures from 300 to ca. 600 K. In the minerals studied, the spin-allowed bands of Fe^{2+} display rather variable temperature behaviour. In most cases, due to the thermal expansion of the Fe^{2+}-bearing polyhedra, bands shift to lower energies upon increasing temperature, though there are some exceptions to this rule: in cases of other than sixfold octahedral or close to octahedral coordination, in almandine and spinel the bands shift to higher energies, which can be explained by an increase in distortions of the Fe^{2+}-bearing polyhedra. Splitting of the excited ^5E_g-level of Fe^{2+} ions usually, but not always, increases with temperature, reflecting thermally induced increase in distortion of the Fe^{2+}-bearing sites in the minerals studied. Integral intensities of the bands in question do not always obey the general rule, according to which intensity should increase with temperature, when the $3d^N$-centred site is centrosymmetric, or should remain unchanged when the $3d^N$ site lacks an inversion centre. The experimental results show that the response of the characteristics of absorption bands such as width, intensity and energy caused by *dd* transitions of Fe^{2+} in oxygen-based minerals to increasing temperature is not always uniform and is at variance with expectation. This temperature dependence cannot be used directly to solve band assignment problems, as earlier proposed in the literature.

Key words Fe^{2+}-bearing silicates and oxides · *dd* transitions · Temperature dependence

Introduction

The absorption bands observed in the UV/VIS/NIR spectra of oxygen-based minerals are caused by various electronic excitation mechanisms: (1) ligand-metal charge transfer, (2) metal–metal charge transfer, (3) *dd* transitions of $3d^N$ ions in the available structural sites. Such *dd* transitions of type (3) may be either spin-allowed or spin-forbidden, and both may be influenced by exchange-coupled-pair effects (ECP). Considering that all the above-mentioned excitations may occur along-side each other, and various $3d^N$ ions may be present in natural crystals, then proper band assignment is a difficult task and as many as possible identifying characteristics are needed. Characteristic temperature dependencies may contribute to solve the problems involved.

Recent papers presented temperature dependencies of metal–metal charge-transfer bands (Taran and Langer 1998), exchange-coupled-pair influenced *dd* transitions in $Fe^{2+}Fe^{3+}$ pairs (Taran et al. 1996) as well as spin-allowed and spin-forbidden bands of Cr^{3+} (Taran et al. 1994) and Fe^{3+} (Taran and Langer 2000), respectively. Though a number of regularities were detected, *dd* transitions of different $3d^N$ ions may not show the same temperature response for all N. Therefore, this paper presents results of a study of the temperature effect on *dd* bands of $3d^6$-configurated Fe^{2+} incorporated in various structural matrices. The iron-bearing minerals studied here were selected such that exchange-coupling effects between *dd* transitions of Fe^{2+} and Fe^{3+} possibly present in neighbouring polyhedra, the so-called ECP effects, are avoided if possible. When ECP effects occur, then the temperature behaviour of the *dd* bands

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themselves is strongly disturbed (Taran et al. 1996). However, in minerals this effect is rare when compared with IVCT phenomena: any Fe^{2+}–Fe^{3+} intervalence charge transfer, $Fe^{2+}Fe^{3+}$–CT, possibly present in the minerals studied here, will not interfere with the Fe^{2+} *dd* bands to be studied, as there occurs only a simple overlapping of both, which can be analyzed, an effect which is restricted to the rare cases where the polarization of CT and *dd* bands is the same.

Experimental

The mineral crystals for investigation (Table 1) were prepared as oriented transparent self-supporting platelets, polished from both sides. A micrometer screw was used to measure the thickness of the plates. Orientations were confirmed by conoscopic observation to be always within 5° of the exact ones.

Electronic spectra were measured in the range ca. 33 000–2500 cm^{-1} with a single-beam microspectrophotometer constructed on the basis of a SpectraPro-275 triple-grating monochromator, polarizing mineralogical microscope MIN-8 and IBM PC 486. The principal optical scheme of the instrument is similar to that described by Taran and Platonov (1988). The diameter of the measuring spot did not exceed 500 μm. A miniature electric furnace with an electronic control device, providing a temperature stability of ± 0.5 K [to register spectra at temperature (T) from 300 to 600 K] was attached to the spectrophotometer.

The spectra of minerals displaying bands below ca. 5000 cm^{-1} (spinel, almandine and amphibole) were measured from 7000 to 3500 cm^{-1} by means of a Fourier transform interferometric spectrometer (Bruker IFS 66) with KBr beam-splitter and attached IR microscope. The microscope was equipped with mirror optics, a polarizing foil, an LN_2-cooled MCT detector and a heating table (Lincam FTIR 600), which allowed measurement of spectra at elevated temperatures; 200 scans were averaged for each measurement.

The spectra were normalized to a thickness of 1 cm. The resultant linear absorption coefficient (cm^{-1}) was then plotted versus the wavenumber. Curve deconvolution and determination of band characteristics were performed with the Peakfit 4.0 (Jandel Scientific) software. Band shapes as well as backgrounds in the range of the absorption edge were assumed to be Gaussian.

Microprobe analyses were performed on the same crystal slabs using the methods described earlier (Taran et al. 1994), and some samples were studied by wet chemical analysis (Table 1).

Results and discussion

At ambient conditions, electronic spectra of all minerals studied closely resemble those of previously published studies. They consist of an intense high-energy edge, which is believed to be caused by UV ligand-metal charge transfer electronic transitions $O^{2-} \rightarrow Fe^{3+}$ and/or $O^{2-} \rightarrow Fe^{2+}$, weak narrow spin-forbidden bands of Fe^{2+} and a system of broad, intense bands in the NIR, caused by spin-allowed *dd* transitions in Fe^{2+} ions. In most cases, Fe^{2+} ions enter more than one structural position, giving rise to a set of overlapped NIR bands with intensity ratios regulated by actual intracrystalline distribution of Fe^{2+} ions among the inequivalent sites and selection rules for electronic transitions in them. Besides, in the visible range, the clinopyroxene, amphibole, cordierite and sekaninaite spectra display an intense broad pleochroic band in the range $\sim$14 000 cm^{-1} to $\sim$17 000 cm^{-1} caused by Fe^{2+}/Fe^{3+} IVCT (e.g. Burns 1993).

Upon increasing temperature, T, the high-energy absorption edge shifts to lower energy, whereas the intensity of Fe^{2+}/Fe^{3+} IVCT bands profoundly decrease, an effect that was investigated recently by Taran and Langer (1998). Spin-forbidden bands of Fe^{2+} markedly broaden and decrease in peak intensity, approximately maintaining their integral intensities.

Spin-allowed bands of Fe^{2+} in different minerals studied here display a variable temperature behaviour. In general, due to the thermal expansion of Fe^{2+}-bearing polyhedra and thus a decrease in the crystal-field strength, Dq, the bands shift to lower energies at increasing T, though there are exceptions to this tendency. Low symmetry splitting of the excited ^5E_g-level of Fe^{2+} usually, but not always, increases with temperature, reflecting a thermally induced increase in the distortion. Integral intensities of the bands do not always obey a general rule whereby the intensity of bands of $3d^N$ ions in centrosymmetric positions should increase on rising temperature, or remain unchanged on a lack of centrosymmetry (e.g. Bersuker 1996).

Olivine $(Mg, Fe)_2SiO_4$

Weak high-energy edge and an absence of Fe^{2+}/Fe^{3+} IVCT band makes curve fitting of olivine spectra simple and reliable compared with most of the other minerals studied here. For this reason, we were able to study the

Table 1 Chemical compositions of the minerals studied

Sample	Crystal chemical formula
Olivine[a]	$(Mg_{1.86}Fe_{0.10}Mn_{0.01}Ca_{0.02})^{[6]}$ SiO_4
Orthopyroxene[b]	$(Mg_{1.63}Fe_{0.27}Ca_{0.04}Al_{0.02})^{[6]}$ $Si_{1,97}Al_{0.03}O_6$
Clinopyroxene[b]	$(Ca_{0.84}Na_{0.12}Fe_{0.01})^{[8]}$ $(Mg_{0.91}Fe_{0.07}Cr_{0.02})^{[6]}$ $Si_{2.03}O_6$
Amphibole[b]	$(Na_{0.11}K_{0.01})^{[10]}$ $(Ca_{1.79}Mn_{0.02}Mg_{0.19})^{[6]}$ $(Mg_{4.13}Fe^{2+}_{0.59}Al_{0.14})^{[6]}$ $Si_{7.98}Al_{0.02}O_{22}(O, OH)$
Cordierite[a]	$(Ca_{0.2}Na_{0.4}K_{0.1})^{Channel}$ $(Mg_{1.73}Fe_{0.24}Mn_{0.01})^{[6]}Al_{3,97}Si_{4.97}O_{18} \times 0.13H_2O$
Sekaninaite[a]	$(K_{0.004}Na_{0.15}Ca_{0.09})^{Channel}(Mg_{0.15}Fe^{2+}_{1.64}Mn^{2+}_{0.08}Ti_{0.003})^{[6]}$ $[Fe^{3+}_{0.08}Al_{3.97}Si_{4.96}O_{18}] \times 0.72H_2O$
Almandine[b]	$(Fe^{2+}_{2.35}Mn^{2+}_{0.06}Mg_{0.42}Ca_{0.07})^{[8]}$ $(Al_{2.00})^{[6]}$ $[Si_{1.01}O_4]_3$
Spinel[b]	$Mg_{1.01}Al_{1.99}O_4$

[a] Wet chemical analysis

[b] Microprobe; all iron is calculated as FeO

temperature behaviour of spin-allowed bands of Fe^{2+} in olivine spectra in detail.

In the olivine structure (e.g. Birle et al. 1968), Fe^{2+} ions are nearly statistically distributed over two unequivalent octahedral positions M1 and M2 of different point symmetries, $\bar{1}$ and *m*, respectively, and dimensions. The mean ligand-metal distance in M1 octahedron varies from 2.10 Å in forsterite (Mg_2SiO_4) to 2.16 Å in fayalite (Fe_2SiO_4), while the M2 site varies from 2.12 to 2.18 Å, respectively.

In the spectra of the olivine studied (Fig. 1), four broad, intense bands, a, b, c and d, in the range 12 000 to 7000 cm^{-1} are caused by spin-allowed *dd* transitions derived from $^5T_{2g} \rightarrow {}^5E_g$ of Fe^{2+} in M1 and in M2. The low intensity of the UV edge, when compared with many other olivines of different origins described elsewhere, suggests a relatively low content of Fe^{3+} in the sample (0.07 wt% of Fe_2O_3). At the maximal *T* applied (600 K), the edge, though increased, still remains far too weak to overlap the spin-allowed *dd* bands a to d. Thus, the curve fitting of the olivine spectra (Fig. 2) was much more reliable compared to the other minerals studied.

For Fe^{2+} in M2 positions, the energy level scheme proposed by Runciman et al. (1973a) seems to be the most reliable. They attributed the intense bands of b around 9540 cm^{-1} (Z > Y) and c $\sim$9100 cm^{-1} (Y-polarization) (cf. Fig. 1, Table 2) to electronic *dd* transitions from the ground state A_1 of Fe^{2+} (M2) to excited B_1 and A_1 levels, derived from the ^5E_g state, split by the low-symmetry crystal field, approximated as *mm*2.

A pair of weaker bands, a and d, clearly seen as shoulders at $\sim$11 800 and $\sim$8050 cm^{-1} in XY and YZ polarization, may be assigned in accordance with Burns (1970, 1974, 1993), to spin-allowed *dd* transitions $^5T_{2g} \rightarrow {}^5E_g$ of Fe^{2+} in M1 sites. The splitting is caused by low symmetric field $\bar{1}$, that lifts the degeneracy of the exited ^5E_g- as well as the ground $^5T_{2g}$ levels. Note that although the a band is not fully resolved in the Z-polarized spectrum (Fig. 1), the curve resolution reveals a relatively strong Z component (Fig. 2) with energy and half-width rather close to those in X and Y polarization (Table 2).

Low intensities of Fe^{2+}(M1) bands, a and d, when compared with those of Fe^{2+}(M2), b and c (cf. Table 2), are due to the centrosymmetric character of the M1 position (point group $\bar{1}$), that causes the spin-allowed *dd* transitions of Fe^{2+}(M1) to be forbidden as dipole–dipole ones by symmetry selection rules. At *T* higher than absolute zero, the rules can be partly relaxed because of odd vibrations of metal–oxygen bonds in coordination octahedra, which mix *d* states with states of the opposite parity, *p* state of Fe^{2+}, for instance. Indeed, on increasing *T*, integral intensities of the bands markedly rise when compared with the M_2 bands (Table 2). Thus, at 600 K, integral intensities of bands a and d averaged over all three polarizations rise by a factor of 1.7 and 1.5, respectively, which is obvious from both visual observation (Fig. 1) and curve deconvolution. As to the bands b and c of Fe^{2+} in the non-centrosymmetric position M2, the deconvolution shows that their integral intensities remain nearly constant (Table 2). The observed temperature behaviour of the intensities of bands a to d are, therefore, consistent with the assignment to electronic spin-allowed transitions of Fe^{2+} in the two sites, M1 and M2, of different symmetry.

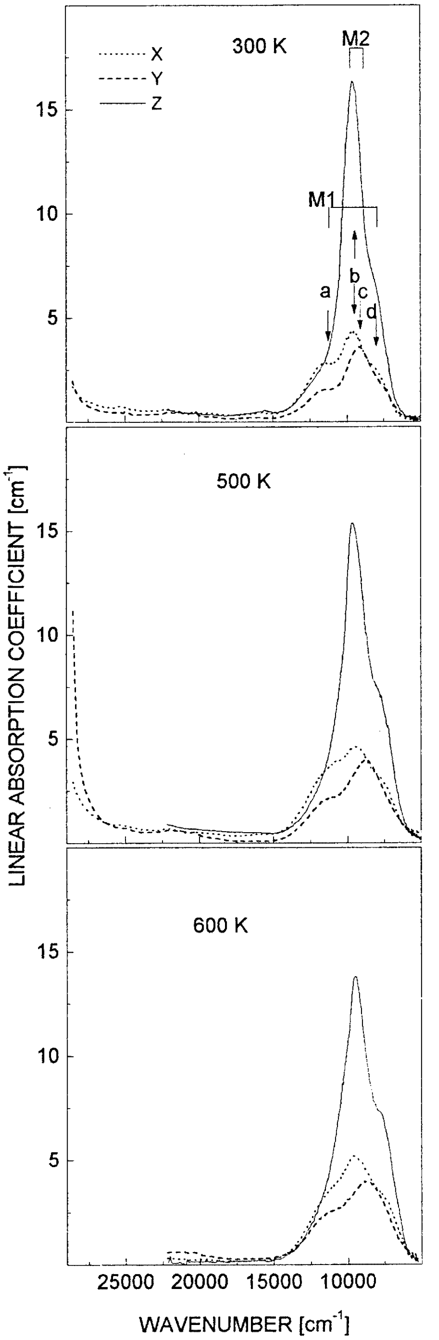

Fig. 1 Polarized single-crystal spectra of olivine (Table 1) at different temperatures

On increasing temperature, all spin-allowed *dd* bands, a, b, c and d, shift to lower energies (Fig. 3), displaying thermal expansion of the coordination octahedra M1 and M2 occupied by Fe^{2+}. An estimation of the local thermal expansion coefficient, α_{loc}, of $Fe^{2+}(M1)O_6$ and

$Fe^{2+}(M2)O_6$ is possible by evaluating the temperature shifts of the barycenters of bands a and d or b and c, respectively, a procedure which assumes that the $^5T_{2g}$ ground state of Fe^{2+} is not split. This assumption will not greatly influence the α_{loc} value, as the ground-state splitting is small and not expected to strongly change with T. The results of the estimation are $\alpha_{loc} \approx 1.14 \times 10^{-5}\ K^{-1}$ for M1 and $\alpha_{loc} \approx 0.87 \times 10^{-5}\ K^{-1}$ for M2. These spectroscopic values are in the same order of magnitude, though characteristically lower than those obtained from the crystal averaging methods of X-ray diffraction yielding $1.93 \times 10^{-5}\ K^{-1}$ or $1.26 \times 10^{-5}\ K^{-1}$ for M1 and $1.72 \times 10^{-5}\ K^{-1}$ or $1.50 \times 10^{-5}\ K^{-1}$ for M2 in forsterite- or fayalite-rich olivine, respectively (Lager and Meager 1978). The sign of the difference is in accord with recent observations on differences between results of crystal averaging structure analysis and local methods (Langer 2001). The difference may, at least in part, be due to the above neglect of Fe^{2+} ground-state splitting.

As seen in Fig. 3 and Table 2, the temperature-induced shifts are different for bands a to d, so that the splitting of the ^5E_g state increases for both Fe^{2+}(M1) and Fe^{2+}(M2), showing that distortions of both sites increase. This conclusion is consistent with results of high-temperature X-ray structure refinement on hortonolite by Brown and Prewitt (1973), who found that distortions of both sites, M1 and M2, increase with T. The ^5E_g splitting of Fe^{2+}(M2) increases at a stronger rate than that of Fe^{2+}(M1) (Fig. 3), which may be caused by a displacement of the M2 cations from the "centroid" of the octahedra with increasing temperature (Lager and Meager 1978).

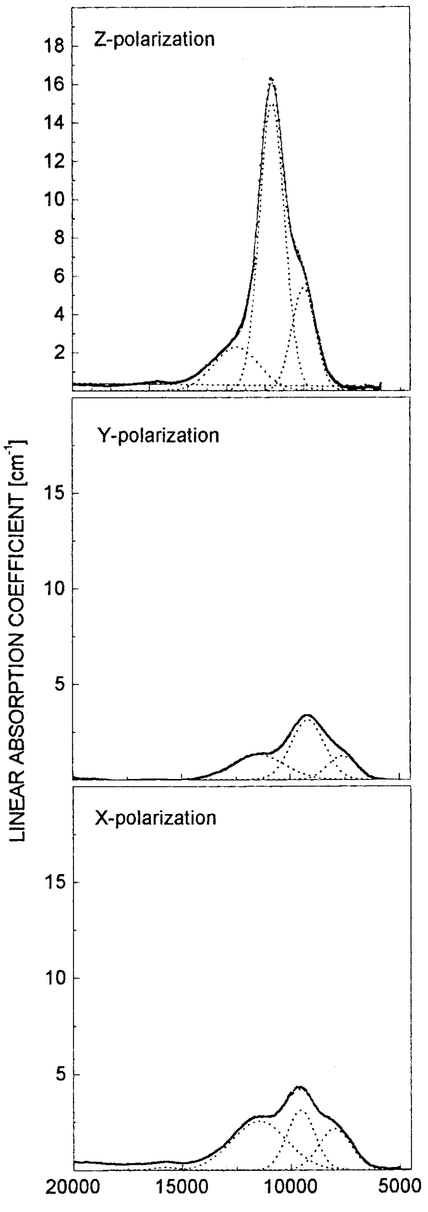

Fig. 2 Band analyses of the NIR band system in polarized olivine spectra at room temperature

Orthopyroxene (Mg, Fe)SiO_3

In the orthopyroxene structure (e.g. Morimoto and Koto 1969), Fe^{2+} ions are distributed over two unequivalent octahedral positions, M1 and M2, with a strong preference for M2 (Ghose 1965). Both the octahedra have point symmetry 1. The M1 site is smaller and much less distorted than M2, and is frequently regarded as a regular octahedron: in terms of mean-squares relative deviation from the average,

Table 2 Energy (ν), half width ($\Delta\nu_{1/2}$) and integral intensity at room temperature (A_0) of spin-allowed bands a, b, c and d of Fe^{2+} ion in olivine spectra as obtained by curve fitting. Temperature responses of energy ($d\nu/dT$), half-width ($d\Delta\nu_{1/2}/dT$) and integral intensity, A, relative to A_0, $1/A_0 \cdot dA/dT$, are all averaged over three polarizations X, Y and Z

Site	Band	Polarization	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	A_0, cm^{-2}	$d\nu/dT$, cm^{-1} K^{-1}	$d\Delta\nu_{1/2}/dT$, cm^{-1} K^{-1}	$1/A_0 \cdot dA/dT$, 10^{-3} K^{-1}
M1	a	X	11451	2554.7	8138.4	−1.07	1.24	2.2
		Y	11463	2408.6	3992.6			
		Z	11483	2338.8	6654.8			
	d	X	7981.8	1477.5	3975.4	−0.99	1.88	1.6
		Y	7591.5	1344.9	2085.8			
		Z	7987.3	1235.5	8313.1			
M2	b	X	9536.2	1290.4	5027.8	−0.55	0.80	−0.3
		Y	–	–	–			
		Z	9621.3	1305.8	24 565			
	c	X	–	–	–	−1.13	1.41	0.4
		Y	9178.3	1534.4	6011.8			
		Z	–	–	–			

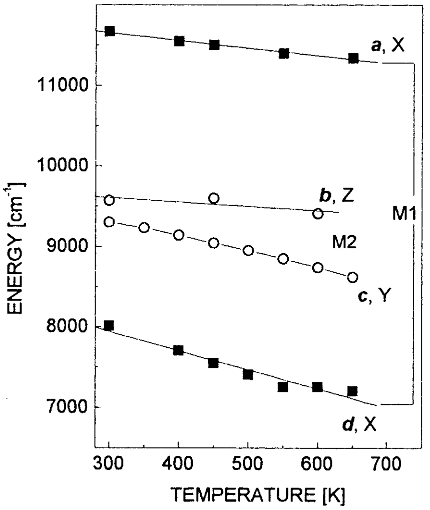

Fig. 3 Energy shift with temperature of bands a and d in **E**||X, caused by *dd* transition of Fe^{2+}(M1) in olivine and bands b and c in **E**||Y and **E**||Z, respectively, caused by Fe^{2+}(M2)

$\Delta = \frac{1}{6}\cdot\sum_{i=1}^{6}[(R_i - \bar{R})/\bar{R}]^2$, where R_i is distance from the central atom to the *i*-th oxygen ion in the octahedron and $\bar{R}$ is the average bond length in Å (Brown and Shannon 1973), Δ_{M1} = 0.00041 and Δ_{M2} = 0.00918. The M2 site symmetry is usually approximated as *mm*2 (Runciman et al. 1973b; Goldman and Rossman 1977a), with the pseudo-twofold axis lying in or close to the *bc* plane, making an angle of ~22° with the *c* axis (Ghose 1965).

In the room temperature (RT) spectra of our orthopyroxene (Fig. 4), the bands attributed to spin-allowed *dd* transitions in both Fe^{2+}(M1) and Fe^{2+}(M2) ions are clearly discernable. According to the convincing interpretation (e.g. Runciman et al. 1973b; Goldman and Rossman 1977a; Steffen et al. 1988), a pair of strong broad bands a ($X \gg Y \geq Z$) and d ($Y > Z > X$) at ~11 100 cm^{-1} and ~5460 cm^{-1}, respectively, are caused by electronic transitions from the ground to the excited ^5E_g level of Fe^{2+}(M2), split by the low-symmetry crystal field. As for the transitions in Fe^{2+}(M1), one may find some divergences in literature (e.g. Burns 1966; Bancroft and Burns 1967; Goldman and Rossman 1977a; Rossman 1980; Steffen et al. 1988). We suppose here that these transitions are displayed by the Z-polarized shoulder c ~8640 cm^{-1} and band b around 11 000 cm^{-1}, occurring in Y polarization probably together with and partly hidden by a stronger Y-polarized component of the a band of Fe^{2+}(M2) (Steffen et al. 1988). The low intensities of the Fe^{2+}(M1) bands b and c are due to a comparatively low distortion of the site, and the above-mentioned strong preference of Fe^{2+} for M2.

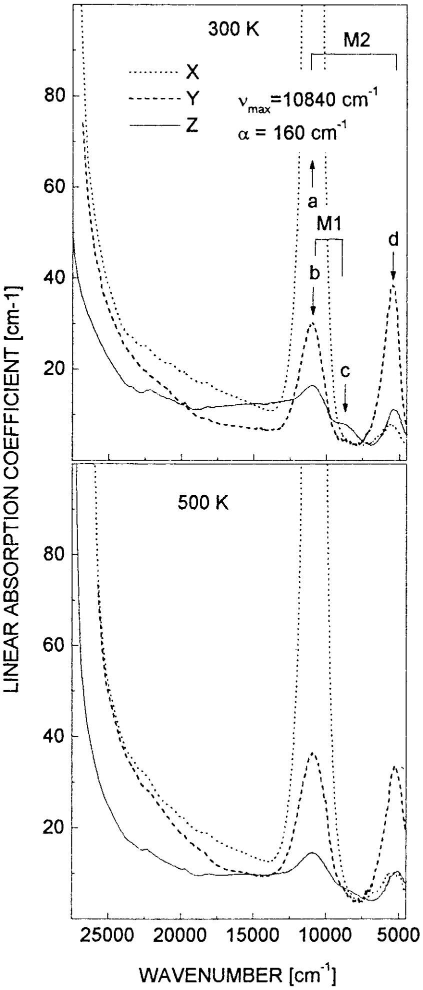

Fig. 4 Polarized single-crystal spectra of orthopyroxene (Table 1) at two temperatures

On increasing *T*, the intensity of the Z-polarized component of the a band does not change significantly. In X polarization, where the a band is of the maximum intensity (α = 160 cm^{-1}, Fig. 4), it slightly shifts to lower energies and broadens upon heating. The Y-polarized b band displays some enhancement of both linear and integral intensities. All differently polarized components of the d band show slight decreases of linear intensities accompanied by broadening of the bands, so that their integral intensities remain nearly unchanged.

The most pronounced feature is that the c band, caused by Fe^{2+}(M1), strongly decreases with *T*, almost disappearing at ca. 500 K (Figs. 4, 5). This certainly cannot be caused by a redistribution of Fe^{2+} ions between M1 and M2 sites, or their oxidation to Fe^{3+} on heating. To elucidate the *T* behaviour of the band, curve fitting of Z-polarized spectra measured in the range 5000–10 500 cm^{-1} was made. In this procedure we assumed that only three bands, namely, a Z-polarized component of the a band (the low-energy wing of it), c and d, contribute to this part of the spectrum. Contributions of other features were neglected (e.g. possible small contributions of the tail of the UV edge and of the low-energy wing of the Fe^{2+}/Fe^{3+} IVCT band (Steffen et al. 1988). Deconvolution of the Z spectrum above 10 500 cm^{-1} failed due to a complicated shape of the $\alpha = f(\nu)$ curve (cf. Fig. 4).

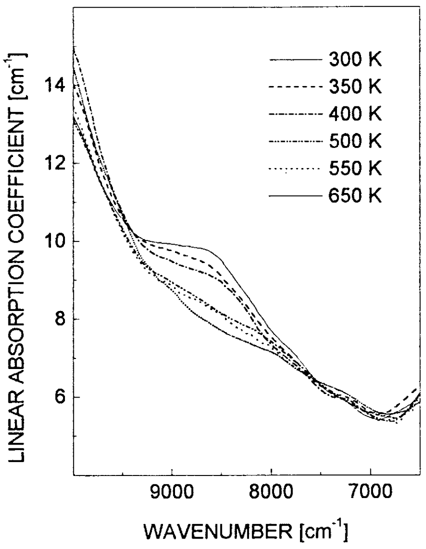

Fig. 5 Temperature dependence of band c in the Z-polarized orthopyroxene spectrum

By fitting, the c band shifts without any significant broadening from 8640 to 8100 cm^{-1} ($dv/dT \approx -1.54$ cm^{-1} K^{-1}), its integral intensity decreases by a factor of 0.48. Such a strong inverse temperature dependence of intensity is entirely untypical for an ordinary spin-allowed *dd* band, which the *b* band undoubtedly is (e.g. Goldman and Rossman 1977a; Rossman 1980; Steffen et al. 1988; Ross and Sowerby 1999). As M1 is frequently regarded as an almost regular octahedron, the intensity of spin-allowed *dd* bands of Fe^{2+}(M1) should increase upon heating or, at least, remain constant, but not decrease. Note that a rather similar temperature-induced intensity loss was found for bands of quite a different nature, namely, those of Fe^{2+}/Fe^{3+} IVCT (e.g. Taran and Langer 1998), and exchange-coupled $Fe^{2+}Fe^{3+}$ pairs (Taran et al. 1996). However, it is doubtful whether the c band can be reassigned to one of these two types. First, its energy is too low (~8640 cm^{-1}) when compared with energies of all known Fe^{2+}/Fe^{3+} IVCT transitions in minerals (9700–18 900 cm^{-1}; Burns 1993). Moreover, the Fe^{2+}/Fe^{3+} IVCT band between Fe^{2+}(M1) and Fe^{3+}(M1) has been identified at ~12 500 cm^{-1} in Z-polarized spectra of synthetic ferrosilite (Steffen et al. 1988). Second, the intensity of the c band changes considerably at thermal disordering of Fe^{2+} between M2 and M1 sites (850 °C in vacuum: Goldman and Rossman 1979), which indicates that it can hardly be caused by exchange-coupled $Fe^{2+}Fe^{3+}$ pairs, but rather justifies its *dd* transition origin.

As seen from Fig. 4, band b in the Y spectra, which is likely to be caused, at least partly, by the second split component of the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe^{2+}(M1) (Steffen et al. 1988), increases in intensity at rising *T* and shifts slightly to lower energies ($dv/dT \approx -0.4$ cm^{-1} K^{-1}), indicating, together with the low-energy shift of the c band, a thermal expansion of the site. This increase in intensity of the b band in combination with the profound decrease of the c band provides evidence for a possible redistribution of the intensity between these two components of the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe^{2+}(M1). Such redistribution may be caused by a strong change in Fe^{2+}(M1)-site distortion on heating, which, in turn, changes the existing selection rules of electronic transitions. However, no structural data exist which could support this supposition, so far.

The bands a and d also shift to lower energies upon increasing temperature, thus showing the temperature-induced expansion of Fe^{2+}(M2) site. The values of dv/dT are ca. −0.5 cm^{-1} K^{-1} for the *a* band and ca. −1.1 cm^{-1} K^{-1} for the d band. Therefore, the ^5E_g splitting increases, which proves that the distortion of the Fe^{2+}(M2) octahedra increases at elevated temperatures.

Clinopyroxene $Ca(Mg, Fe)Si_2O_6$

In the clinopyroxene structure (e.g. Cameron et al. 1973) there are two cationic sites, M1 and M2, of different distortion which can accommodate Fe^{2+} ions. The M2 site is nominally filled by Ca ions so that most Fe^{2+} enters the M1 site, replacing Mg ions. This position, M1 ($\Delta_{M1} \sim 0.0003$, depending on composition), is similar by dimension and symmetry to the M1 site of the orthopyroxene structure. The M2 site of clinopyroxene is considerably larger and more distorted, with variable coordination number which changes from eight to six, depending upon M2-cation radius and definition of next neighbours. In our sample, which is close to the diopside–hedenbergite composition (Table 1), the M2 site should be of eightfold coordination.

In RT spectra of the clinopyroxene (Fig. 6), bands attributed to both Fe^{2+}(M1) and Fe^{2+}(M2) (Burns 1993), are clearly seen. A pair of more intense bands, b (Y polarization) and d (X > Z) at ~9770 and ~4400 cm^{-1}, respectively, are assigned to spin-allowed *dd* transitions of Fe^{2+}(M2) entering M2 position in small amounts, and replacing Ca^{2+} (Burns 1993). Much weaker bands a (X ≈ Z) and c (Z > X) at ~10 000 and ~8700 cm^{-1}, are attributed to the *dd* transitions in Fe^{2+}(M1). Lower splitting and lower intensities of these bands compared with those of Fe^{2+}(M2) are due to the M1 site being more regular than the M2.

Although the M1 octahedron is usually considered nearly regular, at elevated temperatures, intensities of bands a and c, caused by Fe^{2+}(M1), do not change considerably. This is consistent with the lack of 1 in the M1 site, which causes the intensity of the *dd* transitions to be independent of temperature.

Both linear and integral intensities of Fe^{2+}(M2) bands b and d decrease a little with temperature, which most probably indicates that at least a part of the intensity of bands b and d is caused by exchange-coupled interaction of Fe^{2+}(M2) with neighbouring Fe^{3+} ions, consistent with the high-pressure spectroscopic study of clinopyroxene by Taran and Langer (1998).

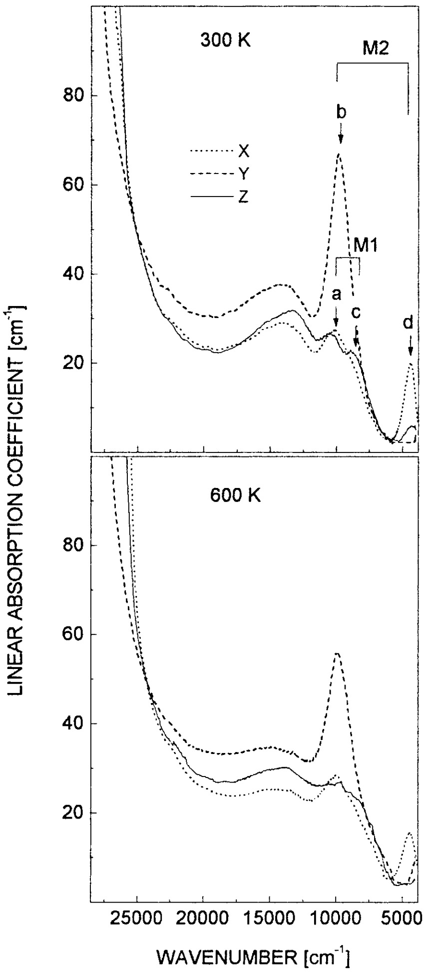

Fig. 6 As Fig. 4, but for clinopyroxene (Table 1)

Bands a, b and c shift to lower energies while the d band shifts slightly to higher energy. One may, therefore, suggest that on heating the distortion of Fe^{2+}(M1) octahedra increases, whereas that of Fe^{2+}(M2) polyhedra decreases. This temperature effect on the Fe^{2+}(M2) polyhedra may be due to the fact that at high temperature, two oxygens out of eight move away so that the coordination of the M2 site in the clinopyroxene structure is gradually changed to six (Cameron et al. 1973).

Amphibole $A_{0\text{-}1}\ B_2C_5T_8O_{22}(OH,\ F,\ O^{2-})_2$

In calcic amphiboles, the A position may be partly filled by Na^+ and K^+, the B position contains Ca^{2+}, Na^+, Mn^{2+}, Fe^{2+} and Mg^{2+}, the C position – Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Ti^{4+}, Cr^{3+} and the T position – Si^{4+} and Al^{3+}. The cations of the C position, including Fe^{2+}, are distributed over three non-equivalent octahedral sites M1, M2 and M3, which are close in dimensions and point symmetries, 2, 2 and 2/*m*, respectively. The B cations are accommodated in the M4 site, which is a comparatively large, strongly distorted polyhedron with point symmetry 1 (e.g. Hawthorne 1983).

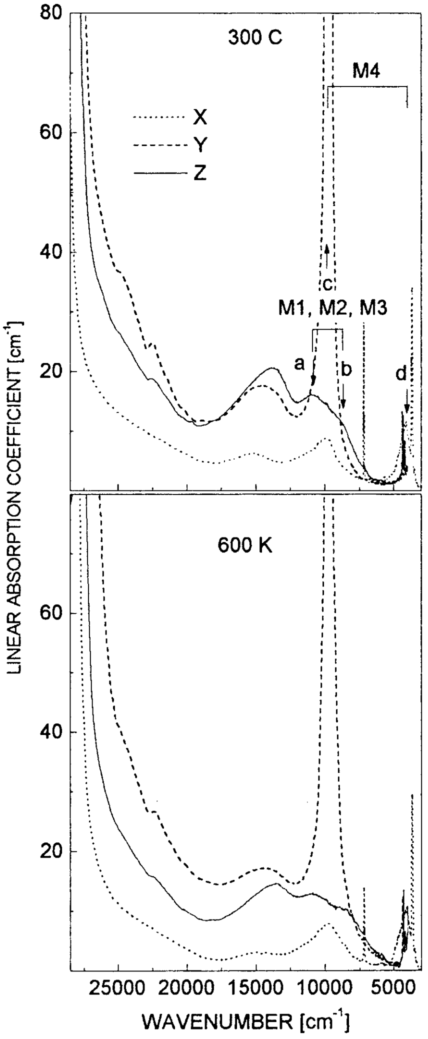

Fig. 7 As Fig. 4, but for a calcium amphibole (Table 1)

In the RT spectra of the Ca-amphibole studied (Fig. 7), a pair of bands c ($Y \gg X$) and d (X) at around 10 000 cm^{-1} and 4050 cm^{-1}, respectively, are attributed to Fe^{2+}(M4) (Goldman and Rossman 1977b). Another pair, a and b, are caused by the spin-allowed *dd* transition derived from $^5T_{2g} \rightarrow {}^5E_g$ of Fe^{2+} in M1, M2 and M3 sites (Goldman and Rossman 1977b; Burns 1993). An intense sharp line at 7140 cm^{-1} and a much weaker one at 10 530 cm^{-1}, both in X polarization, as well as a line system around 4400 cm^{-1} (YZ), are probably caused by overtones and combination vibrations of OH groups. A broad X-polarized band with maximum at around 15 200 cm^{-1} has a characteristic fine structure and is undoubtedly caused by the spin-allowed $^4A_{2g} \rightarrow {}^4T_{2g}$ transition in Cr^{3+} (cf. Hawthorne 1983). The second spin-allowed transition of Cr^{3+}, $^4A_{2g} \rightarrow {}^4T_{1g}$, is overlapped by the UV absorption edge, and is thus displayed as a vague X-polarized envelope on the wing of the edge (Fig. 7).

Due to the strong decrease in intensity upon the raising temperature of the Y-, Z-polarized Fe^{2+}/Fe^{3+}

IVCT band at $\sim$14 000 cm^{-1}, and due to a concomitant increase in the absorption edge, the resulting temperature effect shows a drastic change in the configuration of the spectra (Fig. 7). On the other hand, the intensities of all bands, a–d, do not change significantly, which is consistent with the low symmetry of the M1-M4 sites, while their energies mostly decrease. The c band (X-polarized component) shows the strongest shift $d\nu/dT$ = 2.3 cm^{-1} K^{-1} in the temperature range 300–600 K, whereas the energy of the d band remains almost unchanged. Therefore, we can expect that the dimension and distortion of Fe^{2+}(M4) octahedra are not strongly altered upon heating, in contrast to M1-M3 which expand and probably become more distorted.

Cordierite (Mg, Fe)$_2$Al$_4$Si$_5$O$_{18}$ · nX^{chan} and sekaninaite Fe$_2$Al$_4$Si$_5$O$_{18}$ · nX^{chan}

The structure of cordierite and sekaninaite have been obtained or refined by Hochella et al. (1979). In polarized single-crystal spectra of cordierite and sekaninaite (Fig. 8a and b, respectively) a series of sharp lines around 8700, 7090, 6780 and 5260 cm^{-1} are overtones and combination vibrations of channel molecules of H_2O (e.g. Goldman et al. 1977). A very broad and intense band at $\sim$17 300 cm^{-1}, which causes the characteristic violet colour and strong pleochroism of these minerals, is interpreted as a Fe^{2+}/Fe^{3+} IVCT transition (Farrel and Newnham 1967; Faye et al. 1968; Goldman et al. 1977). According to the Goldman et al. (1977) interpretation, the three broad differently polarized bands, a, b and c (Fig. 8), in the range 11 000–8000 cm^{-1} are caused by the spin-allowed *dd* transitions of Fe^{2+}. A different ratio of the band intensities of different samples (cf. Fig. 8a and b) provides evidence that Fe^{2+} ions entered at least two different structural positions. One is seen as band a, the other as band b and c, which keep their intensity ratios from sample to sample, belonging therefore to the same absorption centre. The low-energy shift of all the bands in the sekaninaite spectra as compared with those of cordierite is due to the larger metal-ligand distances in the iron-rich sekaninaite. Quite in agreement with Goldman et al.'s (1977) observations, on the low-energy wing of band a (Y and Z polarization) in the sekaninaite spectra, there are distinct shoulders, which are absent in cordierite.

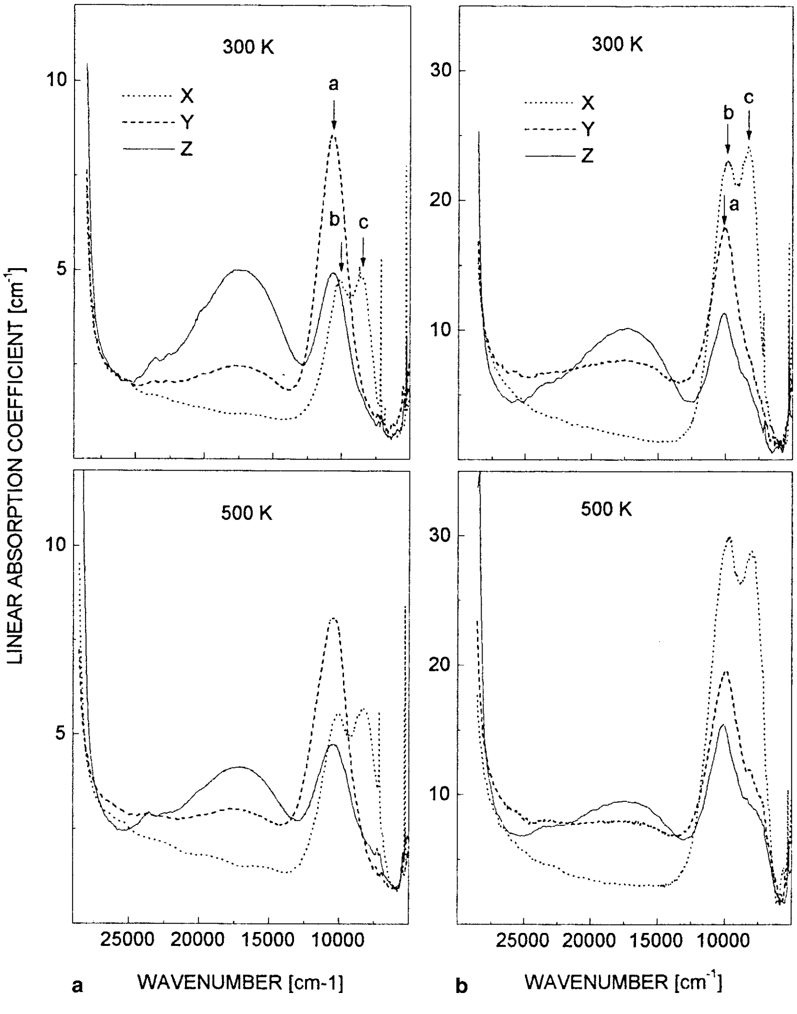

Fig. 8a, b Polarized single-crystal spectra of low- and high-iron cordierites, **a** and **b**, respectively (Table 1) at different temperatures

In both samples, all three bands assigned to spin-allowed *dd* transitions in Fe^{2+} broaden and shift to lower energies upon heating. The shift is different for different bands: in cordierite, $\mathrm{d}\nu/\mathrm{d}T = -1.15, -0.15$ and $-1.80\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$ for bands a, b and c, respectively. Besides, there is a distinct difference in the temperature behaviour of intensities of the bands. Bands b and c significantly increase in both linear and integral intensities, while the ratio of the intensity of these two components changes only slightly. The integral intensity of the a band remains almost unchanged. Besides, in the sekaninaite spectra, splitting between the a band and the low-energy shoulder becomes larger, which makes the latter more distinct at elevated temperatures (Fig. 8). Taking into account a comparatively strong temperature-induced shift of the c band (X) to lower energies (see above), this may be regarded as an additional confirmation of Goldman et al.'s (1977) assignment of the shoulder as a weak Y- and Z-polarized components of the c band.

The temperature-induced intensification of bands b and c is in agreement with their interpretation as spin-allowed *dd* transition derived from $^5T_{2g} \rightarrow {}^5E_g$ in Fe^{2+} in octahedral sites of the cordierite structure (Goldman et al. 1977). The distance distortion of the position is small enough to be regarded as a regular octahedron, wherein the intensity of *dd* transitions should increase with *T*. In fact, this octahedron has smaller distance distortion, $\Delta = 0.00001$, than, for example, the M1 octahedra in ortho- and clinopyroxene, $\Delta = 0.00041$ and $\sim$0.0003, respectively, which are frequently regarded as almost regular ones.

The temperature behaviour of the intensity of band a most likely indicates some strongly distorted noncentrosymmetric position of Fe^{2+} ions. We cannot yet clearly decide between the two alternatives proposed thus far, either a tetrahedral site proposed by Vance and Price (1984) or, as Goldman et al. (1977) assume, a position in the structural channels.

Almandine $\mathrm{Ca_3Fe_2Si_3O_{12}}$

In the structure of silicate garnet, Fe^{2+} ions have an eightfold coordination entering the dodecahedral X-position of the point symmetry 222 (Novak and Gibbs 1971), which may be regarded as a distorted cube ($\Delta = 0.001$). Electronic spectra of the garnet of a composition close to the end-member almandine (Table 1) are shown in Fig. 9. Three broad intense bands, a, b and c, at 7650, 5850 and 4340 cm^{-1}, respectively, are attributed to spin-allowed $^5E \rightarrow {}^5T_2$ transition in Fe^{2+} split by the low-symmetry crystal field (White and Moore 1972; Runciman and Sengupta 1974; Huggins 1975). A series of much weaker characteristic bands in the visible superimposed by the absorption edge, are undoubtedly caused by the spin-forbidden *dd* transitions of Fe^{2+}_{VIII} (Moore and White 1972; Frentrup and Langer 1982).

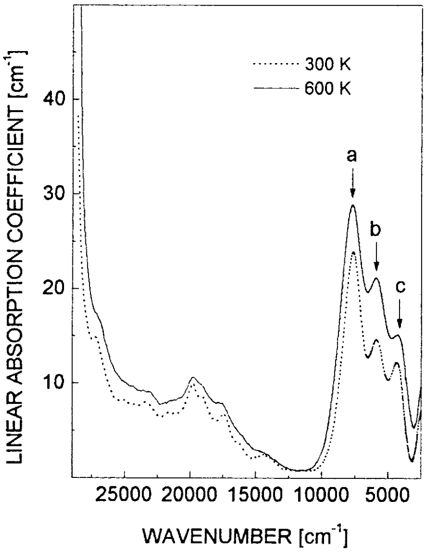

Fig. 9 Temperature-dependent almandine spectra

A deviation of the X position from centrosymmetry implies that the intensity of spin-allowed bands a, b and c of Fe^{2+}_{VIII} in the garnet spectra should not be strongly temperature-dependent. Nevertheless, a certain increase in intensity occurs upon heating, $1/A_0 \cdot \mathrm{d}A/\mathrm{d}T \cong 0.83 \times 10^{-3}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$, $0.68 \times 10^{-3}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$ and $0.73 \times 10^{-3}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$, respectively. Note that these values are somewhat lower than those of bands a and d of Fe^{2+} in centrosymmetric M_1 site of olivine (Table 2). It was established recently that the intensity of both spin-allowed bands of Cr^{3+} and spin-forbidden bands of Fe^{3+} in octahedral Y site of the garnet structure increases with heating (Taran et al. 1994; Taran and Langer 2000), and that this is consistent with the centrosymmetry of the Y sites. In the case of a, b and c bands of Fe^{2+}_{VIII} in the X site of symmetry 222, the observed increase upon heating is not in accordance with the lack of 1 in the site. We speculate that the reason may be a relatively small deviation of the triangular dodecahedron from centrosymmetry in terms of distances and angles.

The first two bands of Fe^{2+}_{VIII}, a and b, shift slightly to higher energies, $\Delta\nu \approx 100\ \mathrm{cm}^{-1}$ in the temperature range 300–600 K, whereas band c remains nearly at the same energy (Fig. 9). A similar effect was established in almandine spectra by White and Moore (1972) and Parkin and Burns (1980). We cannot imply that the $\mathrm{FeO_8}$ dodecahedra in the garnet structure are compressed upon heating. That would contradict results of X-ray structure refinements of almandine at different temperatures, which prove that the $\mathrm{FeO_8}$ dodecahedra became larger and more distorted upon increasing *T* in the range 100 to 293 K (Armbruster et al. 1992). The high-energy shifts of bands a and b may, therefore, be caused by temperature-induced increases in the distortion of the polyhedron, that causes the splitting of the ^5E state to increase.

Spinel (Mg, Fe)Al_3O_4

In the (Mg-Al)-spinel structure, Fe^{2+} ions enter the regular tetrahedral sites with point symmetry $\bar{4}3m$ (Yamanaka and Takéuchi 1983), substituting for Mg^{2+}. It is to be expected that the lack of a centre of symmetry in this case causes a very high intensity of the spin-allowed *dd* band $^5E \rightarrow {}^5T_2$ of Fe^{2+}, when compared with those in octahedral coordinations under strong distortion (Burns 1993). In our pale pink spinel, the iron content is lower than the detection limit of microprobe analysis (Table 1). Despite this, at 300 K its spectrum displays a very strong and broad split band with peaks at ~4840 cm^{-1} (band a) and 3620 cm^{-1} (band b) (Fig. 10), which are undoubtedly caused by the spin-allowed *dd* transition $^5E \rightarrow {}^5T_2$ in Fe^{2+}_{IV}. This result is in accordance with the above-mentioned expectation. The narrow lines around 3610 cm^{-1} are most likely caused by traces of OH. The splitting, unexpected for the point symmetry $\bar{4}3m$ of the spinel tetrahedral site, is possibly caused by a dynamic Jan-Teller effect, intrinsic for ions with degenerate ground states, especially for the *E* level (e.g. Bersuker 1996). In the visible and near-UV range of the spectrum, there are also two broad, weak absorption bands undoubtedly caused by the spin-allowed transitions in Cr^{3+}_{VI} traces (cf. Table 1), because their characteristics are close to the Cr^{3+} bands in spinels (e.g. Wood et al. 1968; Taran et al. 1994).

With increasing temperature, the configuration of bands a and b significantly changes (Fig. 10). The splitting between a and b components increases, accompanied by a significant redistribution of the intensity between them, which may be caused by the superposition of the Jan-Teller and vibronic interactions, as well as a strong decrease in the OH vibrations. Besides, a new component (~6300 cm^{-1}), seen as a vague distortion of the a-band shape at RT, becomes more distinct because of an enlarged splitting. Therefore, at a temperature of ca. 600 K, the degeneracy of excited $^5T_2$ level of Fe^{2+} is completely lifted. In addition, the barycenter of the $^5T_2$ state shifts to higher energies. Therefore, one may suggest that at elevated temperatures, *Dq* and CFSE of Fe^{2+}_{IV} in spinel increase, which could hardly be caused by the compression of the FeO_4 tetrahedra. The increased split between sublevels of the $^5T_2$ state evidences that FeO_4 tetrahedra become more distorted upon increasing temperature. As in the case of almandine (see above), the shift of the barycenter of the $^5T_2$ state to higher energies may be caused by an additional temperature-induced splitting of the ground state ^5E.

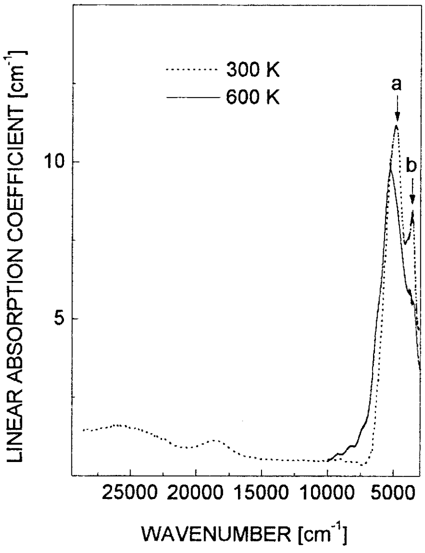

Fig. 10 Temperature-dependent spectra of a near to end-member (Mg-Al)-spinel with trace amount of Fe^{2+} and Cr^{3+}

It was expected that the integral intensity of the band of Fe^{2+}_{IV} should not depend on *T* because of the lack of centrosymmetry in the tetrahedral site that mixes states of odd parity into the ^5E and $^5T_2$ state of the Fe^{2+} ion, thereby making the $^5E \rightarrow {}^5T_2$ transition electric-dipole allowed (Slack et al. 1966). Indeed, as one can see in Fig. 10, at increasing *T*, the decrease in linear intensity is accompanied by broadening of the bands, so that their integral intensity does not strongly change. Note that this observation differs from results of Parkin and Burns (1980) for Fe^{2+} in staurolite tetrahedra, in which the spin-allowed bands of Fe^{2+}_{IV} are found to increase strongly with heating.

Conclusions

Spin-allowed *dd* bands of Fe^{2+} ions in various crystal structures display temperature dependencies of energies and intensities more variable than, for instance, spin-allowed *dd* bands of Cr^{3+}, whose temperature behaviour is nearly in accordance with expectations. The main reason is the different electronic configurations of the two ions, d^3 in case of Cr^{3+}, and d^6 in case of Fe^{2+}. In octahedral, dodecahedral and tetrahedral crystal fields, the Fe^{2+} ion has a degenerated ground state, which splits depending on the symmetry of the site. Temperature, which usually increases the distortion, increases the splitting of the ground state. In some of the minerals studied that have Fe^{2+} ions in non-octahedral coordinations (almandine and spinel), the bands shift to higher energies, which can be explained by an increase in distortions of the Fe^{2+}-bearing polyhedra. This causes temperature-induced shifts of spin-allowed bands of Fe^{2+} to higher energies, which were never observed in the spectra of the Cr^{3+} ion, that has a non-degenerate A_{2g} ground state. Besides, the Fe^{2+} ion d^6-electronic configuration undergoes a relatively high electronic delocalization, which facilitates both an IVCT process and formation of ECP with Fe^{3+} ions in adjacent structural positions. In some minerals studied, this causes intense Fe^{2+}/Fe^{3+} IVCT bands, which partly overlap spin-allowed *dd* bands of Fe^{2+}, somewhat obscuring their temperature behaviour. Besides, in the clinopyroxene spectra, temperature dependence of spin-allowed bands of Fe^{2+} is subjected to the $Fe^{2+}Fe^{3+}$ ECP effect.

In contrast to Cr^{3+}, which enters octahedral sites only, Fe^{2+} ions may admit various coordination numbers, from four- to eightfold in the samples studied here. This implies a certain lability of the ligand surrounding the Fe^{2+} ion in mineral structures. At changing temperature, Fe^{2+}-bearing coordination polyhedra can significantly change their symmetry, which supposedly takes place in the Fe^{2+}(M1) octahedra of orthopyroxene structure. In clinopyroxene, Fe^{2+}(M2) ions probably continually change their coordination number at heating. Such temperature-induced structural changes significantly influence the temperature dependence of the optical absorption bands in question.

The experimental results show that the response of the characteristics of absorption bands, such as width, intensity and energy caused by *dd* transition of Fe^{2+} in oxygen-based minerals to increasing temperature, is not always uniform and is at variance with expectation. Therefore, this temperature dependence cannot be used directly to solve band-assignment problems, as earlier proposed in the literature.

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