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Thermally Modulated Absorption of Fe^{2+}, Fe^{3+}, and Mn^{2+} in Spessartine and Almandine Garnets

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Abstract

The thermally modulated absorption (TMA) of two spessartine and two almandine garnets show absorption peaks with positive temperature coefficient in the region between 10,000 cm^{-1} and 25,000 cm^{-1} at room temperature. The TMA peaks in the 16,000-25,000 cm^{-1} region are $3d \rightarrow 3d$ forbidden transitions of Fe^{2+}, Fe^{3+} and Mn^{2+} ions and agree generally with the presently accepted assignment.

In the 10,000-16,000 cm^{-1} region, The TMA spectra show an unexpected strong band near 12,000 cm^{-1}. This new 12,000 cm^{-1} band and the known 14,000 cm^{-1} band are interpreted as intervalence charge transfer (IVCT) from 8-coordinate Fe^{2+} (VIII) to Fe^{3+} at octahedral (VI) and tetrahedral (IV) site, respectively. We speculate that the temperature coefficient of IVCT absorption, $d\alpha/dT$, can be positive or negative depending on whether the initial and final site of IVCT being different, (*e.g.*, garnets) or equivalent (*e.g.*, micas and vivianite) type(s), respectively.

We propose a minor modification on the $3d \rightarrow 3d$ forbidden assignment of Fe^{2+} (VIII). We also introduce a field-independent level ${}^4A_1(G)$ ${}^4E(G)$ of Fe^{3+}(IV) in spessartine and almandine at 22,300 cm^{-1}, which coincides with that in the closely related ugrandite garnets.

Introduction

The complicated absorption spectra of silicate garnets in the visible region have been extensively measured and are attributed to the absorption of $3d \rightarrow 3d$ forbidden transitions of Fe^{2+}, Fe^{3+}, Mn^{2+} *etc* (*e.g.*, Manning, 1967, 1972). The most recent assignment is based on the linear dependence of the band intensity on the ion-concentration and the overall fit of the spectra by computer-generated energy level diagrams (Moore and White, 1972).

The measurement of thermally modulated absorption spectra (TMA), which records directly the spectra of the temperature-derivative of the absorption coefficient, $d\alpha/dT$, has been demonstrated (Loh, 1972) to be a useful technique in supplementing the conventional absorption spectra.

This paper reports the TMA spectra of two spessartine and two almandine natural garnets between 10,000 cm^{-1} and 25,000 cm^{-1} at room temperature.

Results and Discussion

The experimental setup and the sample requirements of TMA have been reportedly previously (Loh, 1972). P. G. Manning of Ottawa has generously contributed all samples and W. Richmond of Great Malvern has kindly performed the TMA measurements.

In Figure 1 the TMA spectra are given for spessartine from Ceara, Brazil (curve **A**) and from Broken Hill, New South Wales (curve **B**), as well as for almandine from Gore Mountain, New York (curve **C**) and from Zillerthal, Austria (curve **D**). The peaks for the Ceara spessartine and the Zillerthal almandine (see Table 1 for assignments) are designated by the same lower-case letters and numbers used by Moore and White (1972) for pyralspite and ugrandite garnets. These spectra may be interpreted to represent:

(a) intervalence charge transfer $Fe^{2+} \rightarrow Fe^{3+}$ in the low-energy region, from 10,000 cm^{-1} to ~ 15,000 cm^{-1}.

(b) $3d \rightarrow 3d$ forbidden transitions of 8-coordinate Fe^{2+} between 16,000 cm^{-1} and 25,000 cm^{-1}.

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(c) $3d \rightarrow 3d$ forbidden transition of octahedral Fe^{3+} at 23,300 cm^{-1}.

(d) $3d \rightarrow 3d$ forbidden transitions of 8-coordinate Mn^{2+} at 21,000 cm^{-1}, 23,700 cm^{-1} and 24,500 cm^{-1} in spessartine.

(e) a possible $3d \rightarrow 3d$ transition of tetrahedral Fe^{3+} at ~ 22,300 cm^{-1}.

a. Intervalence Charge Transfer from Fe^{2+} to Fe^{3+} at ~12,000 cm^{-1} and ~14,000 cm^{-1}

The most surprising result of the TMA spectra of Figure 1 is the presence of a strong peak at ~12,500 cm^{-1} for spessartines and at ~12,200 cm^{-1} for almandines. In Manning's spectra (Manning, 1967, Figs. 1–4), this peak seems hidden in the background absorption which is contributed, on the low-energy side, by the high-energy tail of the strong Fe^{2+} absorption at ~8,000 cm^{-1} and, on the high-energy side, by the onset of visible absorptions from ~14,000 cm^{-1} on. We emphasize that TMA spectra, like other types of derivative spectra, will "pull" out the broad and weak absorption band from absorption tails of neighboring bands. The strength of a TMA band is not necessarily proportional to the absorption strength of the band but is proportional to the derivative of the absorption with respect to temperature.

To demonstrate that the TMA spectra in Figure 1 are real and not due to instrumental artifacts, we intentionally included in curve **D** the false signal at its left end, ≤9,500 cm^{-1}. This portion of curve **D**—which starts from the low value of the $d\alpha/dT \approx 0$ at frequency ~9,000 cm^{-1}, reaches a maximum negative $d\alpha/dT$ at ~9,500 cm^{-1}, and thence starts to yield "real" signal at higher photon energies—illustrates that the AC output of the photomultiplier is not a true signal if $d\alpha/dT$ starts from a small (positive or negative) value since the signal-to-noise ratio there is low. On the other hand, the left ends of curves **A**, **B**, and **C** (Fig. 1) represent true signals since the curves start from large (negative) values of $d\alpha/dT$, instead of small (negative) values of $d\alpha/dT$. It is understandable that samples **A**, **B**, and **C** have larger AC signal-to-noise ratios than that of sample **D**, because the former are thinner and hence more transparent than the latter, as indicated in the caption of Figure 1. Previous TMA spectra below ~10,000 cm^{-1} compare satisfactorily with known DC spectra (Loh, 1972).

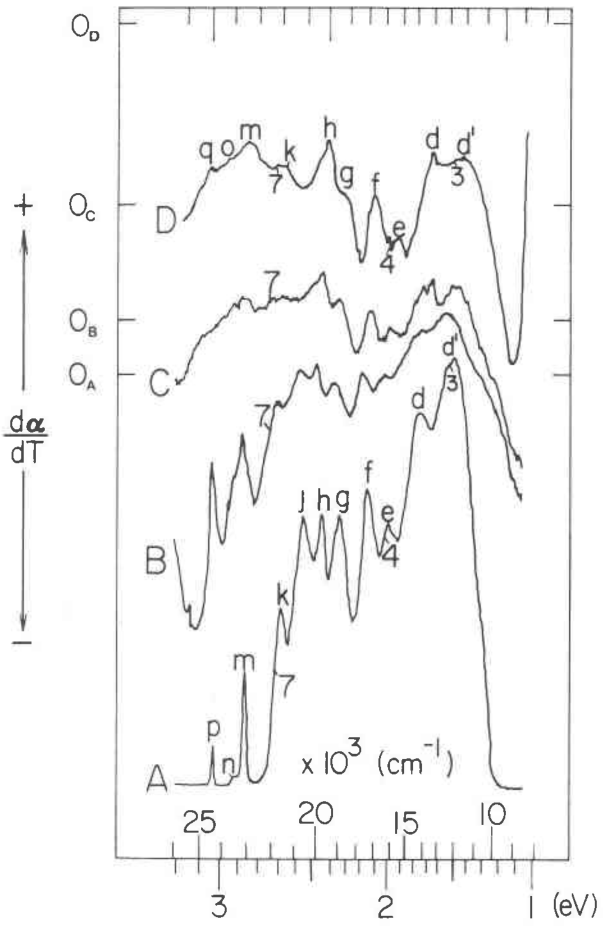

FIG. 1. Thermally modulated absorption spectra, the temperature derivative of the absorption coefficient $d\alpha/dT$ versus the photon energy, of spessartine and almandine garnets at room temperature. **A**—spessartine 0.25 mm × 9 mm × 7 mm from Ceara, Brasil; **B**—spessartine 0.32 mm × 7 mm × 5 mm from Broken Hill, New South Wales; **C**—almandine 0.34 mm × 7 mm × 2 mm from Gore Mountain, New York; **D**—almandine 0.45 mm × 9 mm × 6 mm from Zillerthal, Austria. (The big dip at ~10,000 cm^{-1} on curve **D** is an instrumental artifact. In this near infrared region the photomultiplier is not sensitive enough to deliver the true signal).

We assign the closely related bands, **d′**(~12,500 cm^{-1}) and **d**(~14,000 cm^{-1}), as intervalence charge-transfer bands which correspond to the transfer of an electron from Fe^{2+} on the dodecahedral site to Fe^{3+} on the octahedral site, and to Fe^{3+} on the tetrahedral site, respectively. Reasons for these assignments are:

1. The strength, the bandwidth of ~3,000 cm^{-1} at half-height, and the location at ~12,000 cm^{-1} to ~15,000 cm^{-1} of both **d′** and **d** bands are all comparable to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band in micas and vivianite (Loh, 1972).

TABLE 1. Absorption Peaks and Level Assignments of Fe^{2+}, Fe^{3+}, and Mn^{2+} in Spessartine and Almandine Garnets

Label	Almandine from Zillerthal	Spessartine from Ceara	Assignment		
d'	12,200	12,500	Fe^{2+}(VIII) + Fe^{3+}(VI) --- Fe^{3+}(VIII)+ Fe^{2+}(VI)		
d	14,000	14,700	Fe^{2+}(VIII) + Fe^{3+}(IV) --- Fe^{3+}(VIII)+ Fe^{2+}(IV)		
e	16,200	16,600	Fe^{2+}(VIII)	$^3T_1$	
f	17,600	17,900			
g	19,200	19,300	Fe^{2+}(VIII)	^3E	
h	20,000	20,200			
j		21,000	Mn^{2+}(VIII)	$^4T_1$	
k	21,800	21,800	Fe^{2+}(VIII)	$^3T_1$	$^3T_2$
m	23,300	23,300	Fe^{3+}(VI)	$^4A_1$(G)	^4E(G)
n		23,700	Mn^{2+}(VIII)	$^4T_2$(G)	
o	24,000				
p		24,600	Mn^2(VIII)	$^4A_1$(G)	^4E(G)
q	25,000				
7	22,300	22,300	Fe^{3+}(IV)	$^4A_1$(G)	^4E(G)
4	16,300	16,800	Fe^{3+}(VI)	$^4T_2$(G)	
3	12,800	12,800	Fe^{3+}(VI)	$^4T_1$(G)	

2. The **d′** and **d** bands are stronger and broader than the rest of high-energy peaks, which are known to be $3d \rightarrow 3d$ forbidden transitions of Fe^{2+}, Fe^{3+}, and Mn^{2+} (*e.g.*, Moore and White, 1972; Manning, 1972). This is best illustrated by curve **A** in Figure 1.

3. The energy levels of Fe^{2+}(VIII) in the Tanabe-Sugano diagram of Moore and White (1972) can not include this ~12,000 cm^{-1} new band **d′** as a split component of $^3T_1$ level, since peaks **d**, **e**, and **f** have already been used as the three components of $^3T_1$ level in D_2 site symmetry. Furthermore, the energy of band **d′** at ~12,000 cm^{-1} is either too low for $^3T_1$ level or too high for the allowed transition to ^5E level, as can be seen from the Tanabe-Sugano diagram of Moore and White (1972, Fig. 7).

4. We assign the **d′** band at ~12,500 cm^{-1} as Fe^{2+}(VIII) + Fe^{3+}(VI) → Fe^{3+}(VIII) + Fe^{2+}(VI) and **d** band at ~14,000 cm^{-1} as Fe^{2+}(VIII) + Fe^{3+}(IV) → Fe^{3+}(VIII) + Fe^{2+}(IV) because:

a. The octahedral site (VI) with Al – 0 = 1.89 Å is larger than the tetrahedral site (IV) with Si–O = 1.63 Å (Gibbs and Smith, 1965). The large Fe^{2+}ion will, therefore, have lower energy at the VI-site than at the IV site.

b. The octahedron around Fe^{3+}(VI) shares an edge with a neighboring dodecahedron around Fe^{2+}(VIII), while the tetrahedron around Fe^{3+}(IV) has only a corner common with a neighboring dodecahedron (Gilleo and Geller, 1958). This may again suggest that the charge transfer between the VI and VIII sites occurs at lower energy than that between the IV and VIII sites.

c. The **d′** band is stronger than the **d** band in spessartines (curves **A** and **B**, Fig. 1), while the **d** band is equally strong, if not stronger, as the **d′** band in almandines (curves **C** and **D**, Fig. 1). This observation is consistent with the finding by Manning (1972) that the ratio of the Fe^{3+} concentration on the octahedral site to that on the tetrahedral site is larger in spessartine than in almandine.

For the **d′** and **d** bands in Figure 1, $d\alpha/dT$ is positive whereas it is negative for $Fe^{2+} \rightarrow Fe^{3+}$ absorption in micas and vivianite (Loh, 1972). We attribute this change in sign to the change of site-type involved in the charge transfer of $Fe^{2+} \rightarrow Fe^{3+}$. The electron-transfer from Fe^{2+} on one type of site, *e.g.*, 8-coordinated, to Fe^{3+} on a site of different type, *e.g.*, octahedral or tetrahedral, will be enhanced at higher temperatures, while the charge-transfer between Fe^{2+} and Fe^{3+} on equivalent sites, *e.g.*, octahedral sites (VI) in micas and vivianite, will rise at lower temperatures. In the former case, the structure is distorted in the final state. At higher temperatures the lattice is more tolerant of such distortion and hence may allow more charge-transfer. In the case of equivalent sites, there is no additional lattice distortion which needs to be relieved at higher temperatures. The charge transfer, however, will be enhanced at lower temperatures because of the increasing orbital overlap at constricted interatomic distances. It would be interesting to test this speculation on the two types of intervalence charge-transfer by taking the TMA spectra of corderite and tourmaline, which have transitions of Fe^{2+}(VI) + Fe^{3+}(IV) → Fe^{3+}(VI) + Fe^{2+}(IV) at ~17,500 cm^{-1} and Fe^{2+}(VI) + Fe^{3+}(VI) → Fe^{3+}(VI) + Fe^{2+}(VI) at ~14,000 cm^{-1}, respectively (Faye *et al*, 1968). The sign of $d\alpha/dT$ should be positive for the former and negative for the latter. This experiment is being prepared.

b. 3d → 3d Forbidden Transitions of 8-Coordinated Fe^{2+}

Following Moore and White (1972) the peaks **e**, **f**, **g**, **h**, **k**, and **c** in Figure 1 are $3d \rightarrow 3d$ forbidden transitions of Fe^{2+}(VIII). Since we assign peak **d**, which has been interpreted by Moore and White as $3d \rightarrow 3d$ forbidden absorption of Fe^{2+}(VIII), with **d′** as charge transfer bands, we suggest also a minor modification on the energy level of Fe^{2+}(VIII) assigned by Moore and White. We assign the absorption in the regions of peaks **ef**, **gh**, and **k** as the levels of $^3T_1$, ^3E and $^3T_2$ respectively, of Fe^{2+}(VIII) in spessartine and almandine. The effect of D_2 splitting of these levels is likely hidden in the complicated structure, which may be resolved in a low temperature TMA spectra.

c. 3d → 3d Forbidden Transitions of Octahedral Fe³⁺

The sharpness of the peak **m** at 23,300 cm^{-1} in curve **A** (Fig. 1) supports its assignment by Manning (1972) and by Moore and White (1972) as the field-independent level $^4A_1{}^4E(G)$ of Fe^{3+}(VI). Lower levels of Fe^{3+}(VI) probably appear as minor structures in curve **A**, *e.g.*, $^4T_2(G)$ as a rest, No. 4, at ~16,800 cm^{-1} and $^4T_1(G)$ as a shoulder, No. 3, at ~12,800 cm^{-1}.

d. 3d → 3d Forbidden Transitions of 8-Coordinated Mn²⁺ in Spessartine

Following Manning and Moore and White, the sharp peak **p** at 24,600 cm^{-1} should be the field-independent level $^4A_1(G)$ $^4E(G)$. The shoulder **n** at 23,700 cm^{-1} and peak **j** at 21,000 cm^{-1} are $^4T_2(G)$ and $^4T_1(G)$, respectively, of Mn^{2+}(VIII) in spessartine, curves **A** and **B**.

e. A Possible 3d → 3d Forbidden Transition of Tetrahedral Fe³⁺

There is some controversy over the observation of Fe^{3+}(IV) absorption in almandine and spessartine. Manning (1972) assigned some $3d \rightarrow 3d$ forbidden peaks of Fe^{3+}(IV) in almandine ($^4A_1{}^4E(G)$ at 24,200 cm^{-1} and 24,800 cm^{-1}) and in spessartine. He determined the peaks of Fe^{3+}(IV) by curve-resolution of the optical spectra combined with a comparison with the Fe^{3+}(IV) spectra of yttrium garnets. Moore and White (1972) reported the Fe^{3+}(IV) absorption in ugrandite garnets, which have Ca^{2+} on the dodecahedral site and are otherwise very closely related to almandine and spessartine and assigned the field independent level $^4A_1{}^4E(G)$ of Fe^{3+}(IV) at ~22,300 cm^{-1}. But they did not observe the Fe^{3+}(IV) absorption in almandine and spessartine.

We suggest that the field-independent level $^4A_1{}^4E(G)$ of Fe^{3+}(IV) in spessartine and almandine appears as a minor peak (No. 7, Fig. 1) at ~22,300 cm^{-1}, the same location as that in ugrandite garnets assigned by Moore and White. A field independent peak should be sharp, but our best TMA spectrum (curve **A**, Fig. 1) shows only two sharp peaks **m** and **p**, which have been previously assigned as field-independent levels of Fe^{3+}(VI) and Mn^{2+}(VIII). Curve **A** does not show a third sharp peak which could be assigned to Fe^{3+}(IV). However, such a third sharp peak could appear as a minor structure, No. 7, hidden in the long steep slope at ~22,300 cm^{-1} on the high-energy side of the peak **k** in both curves **A** and **B** for spessartines. Furthermore, the TMA spectra of almandine in curves **C** and **D**, which exhibit a broad, peak **m** even for the well-accepted field-independent level of octahedral Fe^{3+} (Manning, 1972; Moore and White, 1972), shows a moderate peak No. 7 at ~22,300 cm^{-1}. Our observation that the No. 7 peak is relatively more distinct in the TMA spectra of almandine than that of spessartine is consistent with the finding of Manning (1972) that the concentration ratio Fe^{3+}(IV)/Fe^{3+}(VI) in almandine is greater than that in spessartine.

Conclusion

The thermally modulated absorption spectra of spessartine and almandine reveal a new band at ~12,000 cm^{-1} which has been hidden in the background absorption in the conventional optical spectra. This new band and the known band at ~14,000 cm^{-1} may be interpreted as intervalence charge transfer from Fe^{2+}(VIII) to Fe^{3+}(VI) and Fe^{3+}(IV), respectively.

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