

## OPTICAL ABSORPTION SPECTRA OF $\text{Fe}^{3+}$ IN OCTAHEDRAL AND TETRAHEDRAL SITES IN NATURAL GARNETS

P. G. MANNING

*Hydrologic Sciences Division, Inland Waters Branch, Environment Canada,  
No. 8 Temporary Building, Carling Avenue, Ottawa, Ontario*

### ABSTRACT

Curve-resolution of the optical absorption spectra of several almandines and a schorlomite have revealed two weak absorptions, at  $20300\text{ cm}^{-1}$  and  $21800\text{ cm}^{-1}$  in the former crystals and  $20200\text{ cm}^{-1}$  and  $21400\text{ cm}^{-1}$  in the latter, that have been assigned to tetrahedral- $\text{Fe}^{3+}$ . Two very sharp bands in spessartine spectra at  $23300\text{ cm}^{-1}$  and  $23700\text{ cm}^{-1}$ , and two other absorptions at  $20700\text{ cm}^{-1}$  and  $21800\text{ cm}^{-1}$ , have been assigned to octahedral- and tetrahedral- $\text{Fe}^{3+}$ , respectively. A major new absorption is evident in spectra of almandines at  $\sim 21000\text{ cm}^{-1}$  ( $475\text{ nm}$ ) that is probably part of the  $\text{Fe}^{2+}$  spectrum. An absorption at  $24400\text{ cm}^{-1}$  in spectra of low-Ti andradites has been attributed to tetrahedral- $\text{Fe}^{3+}$ .

In almandines,  $\text{Fe}^{3+}$  prefers the tetrahedral site, whereas the octahedral: tetrahedral  $\text{Fe}^{3+}$  ratio in spessartines is close to unity. Geochemical relationships are evident in pyralspites between cube- $\text{Fe}^{2+}$ , octahedral- $\text{Fe}^{3+}$  and tetrahedral- $\text{Fe}^{3+}$ .

### INTRODUCTION

The optical absorption spectra of natural garnets are often difficult to interpret because a number of transition-metal ions in different valence states can occupy one of more of the octahedral, cube and tetrahedral sites. In instances where the spectra are dominated by absorption bands of one cation, the assignments are reasonably well established (Table 1), notably the three near-infrared bands of  $\text{Fe}^{2+}$  in cube sites, the strong absorptions of  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$  in octahedral sites, and the characteristically-sharp bands of  $\text{Fe}^{3+}$  in octahedral sites in andradites. In other garnets, the optical spectra can be very complicated, in spectra of almandines, for example, at least 10 bands can be discerned in the optical region ( $700\text{-}400\text{ nm}$ ) by eye alone. Curve-resolution of almandine spectra, as illustrated in Fig. 5 of the current work, yields up to 13 absorption bands. Almandines, of ideal formula  $\text{Fe}_3^{2+}\text{Al}_2^{3+}\text{Si}_3\text{O}_{12}$ , contain predominantly  $\text{Fe}^{2+}$  in cube sites, with smaller amounts of  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ . All  $d-d$  bands of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the optical region are spin-forbidden and often relatively sharp. In the case of  $\text{Fe}^{3+}$ , in particular, distribution is possible, and indeed likely, between octahedral and tetrahedral sites, since

synthetic garnets based on octahedral and tetrahedral Fe<sup>3+</sup> ions are well characterized (Geller & Gilleo 1957). Ferric iron also occurs in both types of sites in the garnet kimzeyite (Ito & Frondel 1967). I have earlier suggested that two sharp bands at 23300 cm<sup>-1</sup> and 23700 cm<sup>-1</sup> in spessartine spectra mark transitions to the <sup>4</sup>A<sub>1</sub>E(G) levels in octahedral Fe<sup>3+</sup> (Manning 1970).

In the current work, the optical spectra of some natural garnets are discussed and compared to spectra of synthetic garnets of controlled composition. New absorption bands not previously observed in almandine spectra are reported. Emphasis is placed on the identification of bands due to Fe<sup>3+</sup> in octahedral (Al) and tetrahedral (Si) sites.

TABLE 1. SURVEY OF IDENTIFIED AND ASSIGNED ABSORPTIONS IN GARNETS

Ion	Garnet Site		Band Energies in cm <sup>-1</sup>		Reference	
Fe <sup>2+</sup>	Alm		2900	6000	7900	Clark (1957)
	Alm	Cube		7200		Balchan <i>et al.</i> (1959)
	Alm		4500	6000	7800	Manning (1967a)
	Gross		5700	8200		Manning (1969)
Cr <sup>3+</sup>	Alm-Pyr		17700	25000		Wiegel & Ufer (1928)
	Pyr		17760	24270		Neuhaus (1960)
	Pyr	Oct	17800	24100		Manning (1967a)
	Uva			16700		Kolbe (1934)
	And			22570		Anderson (1959)
	Uva		16520	24800		Neuhaus (1960)
	Uva		16600	23100		Manning (1969)
Fe <sup>3+</sup>	And	Oct	11900	16600	22700	Grum-Grzhimailo <i>et al.</i> (1963)
	25930					
	And	Oct	12000	16700	22700	Manning (1967b)
	26000			27000		
Gross		12000	23100	26000	Manning (1969)	
			27000			
Mn <sup>2+</sup>	Spess	Cube		24500		Manning (1967a)
Ti <sup>3+</sup>	And	Oct		19000		Manning (1967b)

## EXPERIMENTAL

Spectra were recorded on Cary-14 and Beckman DK-2A spectrophotometers; experimental details have been described earlier (Manning 1967a).

Almandine crystals from the following localities were studied in detail: Madagascar; Gore Mountain, N.Y.; Shatford Lake, Ontario; Zillertal, Austria; River Valley, Ont. Spectra of several other almandines were also recorded, but all almandines showed very similar spectral features. Spessartines from the following localities were studied: Ceara, Brazil; Broken Hill, New South Wales; Lieper's Quarry, Delaware Cty; Parry Sound, Ontario; and a spessartine from an unknown locality. The andradite crystals came from Stanley Peak, Arizona, and the schorlomite and

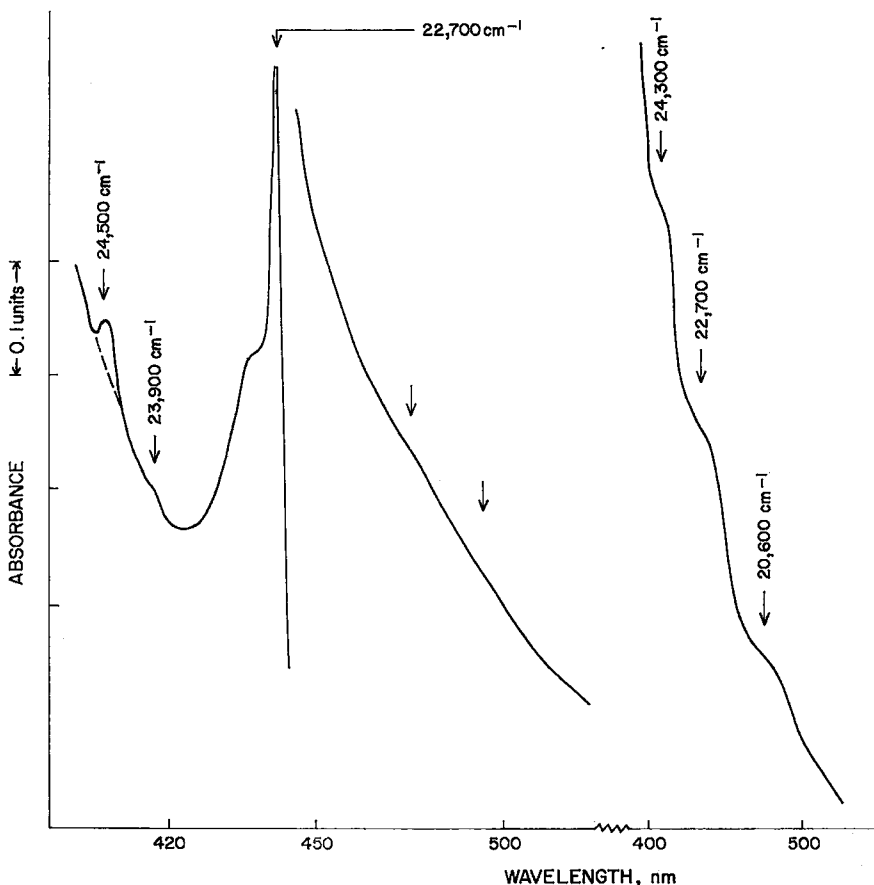


FIG. 1. Portions of optical spectra of Stanley Peak andradite (L.H.S.) and Magnet Cove kimzeyite. Thickness of andradite = 0.35 cm.

kimzeyite from Magnet Cove, Arkansas. I thank Messrs L. Moyd and H. R. Steacy, Curators of the National Mineral Collection, for the donation of crystals.

Extinction coefficients,  $\epsilon$  are defined in the usual manner

$$\epsilon = A/C.l, \text{ litres/mole-cm,}$$

where  $A$  is net absorbance,  $C$  is cation concentration in moles/litre, and  $l$  is crystal thickness in cm.

Spectra were resolved using a Dupont Model 310 Curve Resolver.

## RESULTS AND DISCUSSION

### *Spectra of andradite, kimzeyite and schorlomite*

Portions of the optical spectra of andradite and kimzeyite are presented in Figure 1, while the spectrum of schorlomite is shown in Figure 2.

TABLE 2. OBSERVED BANDS IN GARNETS AND PROPOSED ASSIGNMENTS (energies in cm<sup>-1</sup>)

Andradite	Kimzeyite	Schorlomite	YIG + YGG	Almandine	Spessartine	Fe <sup>3+</sup> bands
12000			11100			OCT, <sup>4</sup> T <sub>2</sub> (G)
				14350	14350	
				16300	16300	
16700	16700	16700	16400			OCT, <sup>4</sup> T <sub>1</sub> (G)
				17500	17500	
				19100	19100	
				19800	19800	
{ 21400	20600	20200	20410	20300	20700	TET, <sup>4</sup> T <sub>1</sub> (G)
		21400	21050	21800	21800	
				21000		
22700	22700	22700	~23000		23300	OCT, <sup>4</sup> A <sub>1</sub> <sup>4</sup> E(G)
					23700	
				23300		
{ 23900	24300		23870	24200		TET, <sup>4</sup> A <sub>1</sub> <sup>4</sup> E(G)
			24270	24800		
26000 *			26300	26000		OCT, <sup>4</sup> E(D) **
26950 *			26670	27100	27000	

Prominent Mn<sup>2+</sup> bands at ~20000 cm<sup>-1</sup>, ~23000<sup>-1</sup> and 24500<sup>-1</sup> in spessartines not included (Manning 1967a).

\* Bands observed in var. colophonite (Manning 1969).

\*\* Manning (1970).

Absorptions of octahedral-Fe<sup>3+</sup> have been assigned earlier (See Table 1).

The absorption bands at  $16700\text{ cm}^{-1}$  (that of kimzeyite is not shown here) and  $22700\text{ cm}^{-1}$  mark the well-known transitions  ${}^6A_1 \rightarrow {}^4T_2(G)$  and  ${}^6A_1 \rightarrow {}^4A_1E(G)$  in octahedral  $\text{Fe}^{3+}$ . The same transitions are observed at similar energies in other  $\text{Fe}^{3+}$ -bearing minerals, e.g. epidote (Burns & Strens 1967) and corundum (Lehmann & Harder 1970). Absorption bands due to Fe in optical spectra of garnets are listed in Table 2.

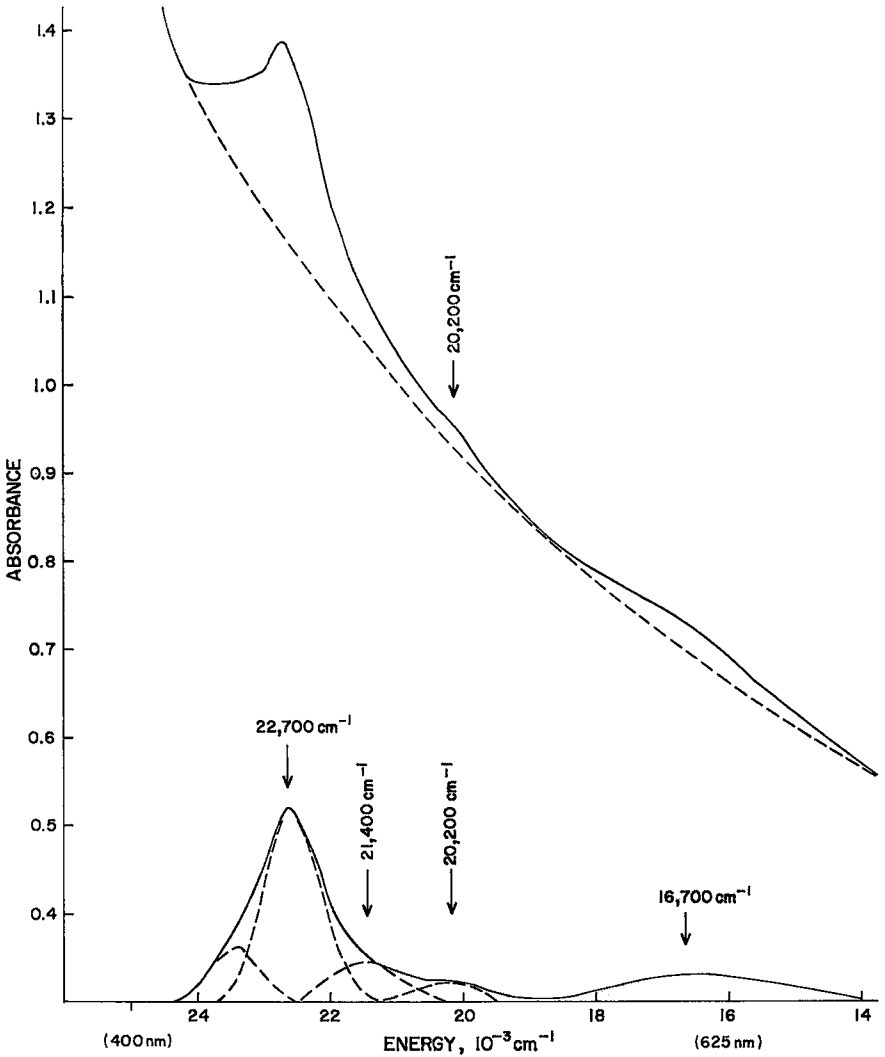


FIG. 2. Portion of optical spectrum of Magnet Cove schorlomite, thickness  $0.0015\text{ cm}$ . Note resolved absorptions at  $20200\text{ cm}^{-1}$  ( $495\text{ nm}$ ) and  $21400\text{ cm}^{-1}$  ( $467\text{ nm}$ ).

The spectra of six low-Ti andradites studied earlier (Manning 1967b) showed a broad absorption at  $\sim 21400\text{cm}^{-1}$  that I assigned to part of the octahedral- $\text{Fe}^{3+}$  spectrum, in particular to the upper component of transitions to a split  ${}^4T_2(G)$  level. However, because of the magnitude of the splitting ( $\sim 5000\text{cm}^{-1}$ ), the regularity of octahedral sites in natural garnets (Gibbs & Smith 1965) and the negligible or much smaller splitting of the  ${}^4T_2(G)$  level in  $\text{Fe}^{3+}$  in other silicates, this assignment is probably incorrect. Absorption bands are evident at  $\sim 20500\text{cm}^{-1}$  in spectra of kimzeyite (Figure 1) and schorlomite (Figure 2). Curve-resolution of the schorlomite spectrum shows a second weak band at  $\sim 21400\text{cm}^{-1}$ . Measuring garnet spectra at 77K does not sharpen bands very appreciably, but there is a suggestion that the  $\sim 21400\text{cm}^{-1}$  envelope in low-Ti andradites has at least two components, at  $\sim 21400\text{cm}^{-1}$  and  $\sim 20700\text{cm}^{-1}$ . These two bands would seem to have their counterparts in spectra of natural almandines and spessartines and synthetic garnets (Table 2 and Figures 1-6).

The band at  $24400\text{cm}^{-1}$  in spectra of andradites I assigned, with reservations, to the field-independent transition  ${}^6A_1 \rightarrow {}^4A_1E(G)$  in  $\text{Mn}^{2+}$  (Manning 1967b) on account of its sharpness and the fact that  $\text{Mn}^{2+}$  in cubic fields in other silicates absorbs at  $\sim 24500\text{cm}^{-1}$ . However, the  $\epsilon$ -value of the band (10) is very large compared to the  $\epsilon$ -values of  $\text{Mn}^{2+}$  bands in other silicates (1, Manning 1968). The sharpness of the

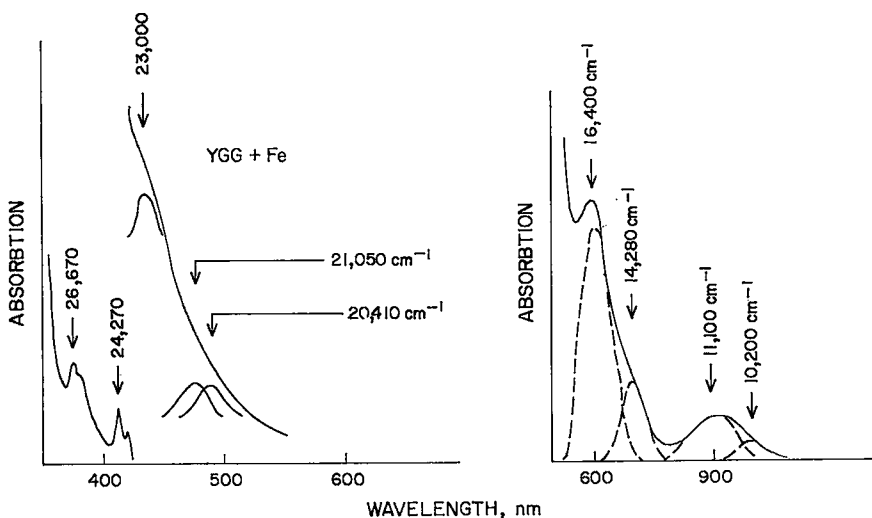


FIG. 3. Optical spectra of yttrium iron garnet and yttrium gallium garnet (Wood & Remeika 1967).

band does suggest a transition to a field-independent state, hence there would seem to be justification in assigning the band to transitions to one of the levels  ${}^4A_1{}^4E(G)$  or  ${}^4E(D)$  in tetrahedral- $\text{Fe}^{3+}$ . Based on an  $\epsilon$ -value of 5, the calculated concentration of tetrahedral- $\text{Fe}^{3+}$  responsible for the  $24400\text{ cm}^{-1}$  band is 0.5%, which is not unreasonable bearing in mind that the total-Fe concentration is 20%. A weak absorption is also present at  $23900\text{ cm}^{-1}$  (418 nm), which could be the second component-band-marking transitions to the  ${}^4A_1{}^4E(G)$  levels. The splitting of the  ${}^4A_1$  and  ${}^4E$  levels,  $600\text{ cm}^{-1}$ , is not unreasonable.

In yttrium iron garnet (YIG) and Fe-doped yttrium gallium garnet (YGG + Fe),  $\text{Fe}^{3+}$  occupies both octahedral and tetrahedral sites. The Fe-O octahedral distance in andradite is  $2.02\text{ \AA}$  (G. V. Gibbs, private communication), similar to the reported values of  $2.00\text{-}2.01\text{ \AA}$  for a number of synthetic iron garnets (Lind & Geller 1969). Hence, it seems reasonable to suggest that the  $11100\text{ cm}^{-1}$ ,  $16400\text{ cm}^{-1}$ , and  $23000\text{ cm}^{-1}$  bands in spectra of YIG and YGG + Fe mark the transitions  ${}^6A_1 \rightarrow$

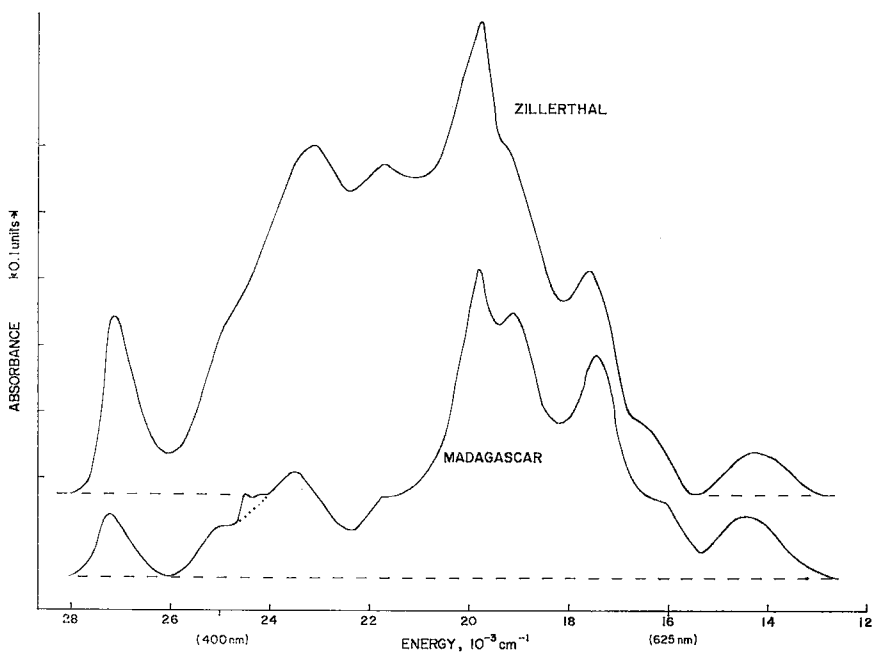


Fig. 4. Absorption spectra of natural almandines, above background. Crystal thickness =  $0.11\text{ cm}$  for Zillertal and  $0.15$  for Madagascar. Dotted line signifies effective baseline for minor  $\text{Mn}^{2+}$  peaks (Manning 1967a) not further considered.

${}^4T_1(G)$ ,  ${}^4T_2(G)$  and  ${}^6A_1{}^4E(G)$  in octahedral- $\text{Fe}^{3+}$ , respectively. The shoulders at  $10200\text{ cm}^{-1}$  and  $14280\text{ cm}^{-1}$  in the YIG spectrum reflect distortions in the octahedron. I assign the bands in spectra of YGG + Fe at  $20410\text{ cm}^{-1}$ ,  $21050\text{ cm}^{-1}$  and the sharp pair at  $23870\text{ cm}^{-1}$  and  $24270\text{ cm}^{-1}$  to tetrahedral- $\text{Fe}^{3+}$ , the two latter bands being reminiscent of transitions to the  ${}^4A_1{}^4E(G)$  levels. The bands at  $20410\text{ cm}^{-1}$  and  $21050\text{ cm}^{-1}$ , which would mark the transitions  ${}^6A_1 \rightarrow {}^4T_1(G)$  and  ${}^4T_2(G)$ , seem to have their counterparts at  $20200\text{ cm}^{-1}$  and  $21400\text{ cm}^{-1}$  in schorlomite spectra (Figure 2) and at very similar energies in spectra of andradite (Figure 1, moulded in the  $21400\text{ cm}^{-1}$  band), kimzeyite (Figure 1, one component at  $20600\text{ cm}^{-1}$ ) and almandines and spessartines (Figures 4-6, Table 2).

### Spectra of almandines

In Figure 4 are presented net absorption spectra above background of two almandines, the spectrum of the Madagascar crystal having been shown in conventional fashion earlier (Manning 1967a). Figure 5 dis-

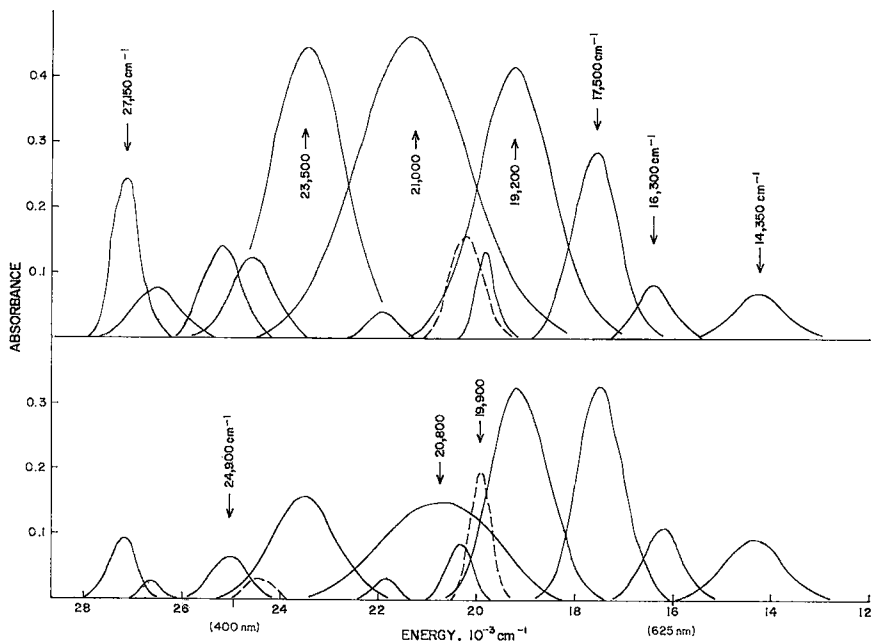


FIG. 5. Resolved spectra of Zillertal and Madagascar almandines. Note resolved absorptions at  $20300\text{ cm}^{-1}$  (493 nm) and  $21800\text{ cm}^{-1}$  (459 nm). See note p. 839.



plays the results of curve-resolution, which shows the presence of 13 absorption bands, most of which are apparent by the eye in the original spectrum. Features of particular interest are, (i) the resolution of a major absorption band at  $\sim 21000\text{ cm}^{-1}$  (476 nm) which has not been reported previously, (ii) the resolution of a relatively-sharp band at  $20300\text{ cm}^{-1}$  on the higher-energy flank of the prominent  $19900\text{ cm}^{-1}$  band, and which would seem to pair up with the  $21800\text{ cm}^{-1}$  band to characterise tetrahedral- $\text{Fe}^{3+}$ , and (iii) the resolution of two relatively-sharp (half-width  $800\text{ cm}^{-1}$ ) bands at  $24200\text{ cm}^{-1}$  and  $24800\text{ cm}^{-1}$ . These latter two bands would seem to have their counterparts at  $23870\text{ cm}^{-1}$  and  $24270\text{ cm}^{-1}$  in spectra of YGG + Fe,  $24400\text{ cm}^{-1}$  (and possibly  $23900\text{ cm}^{-1}$ ) in andradites and  $24300\text{ cm}^{-1}$  in kimzeyite, and which it is proposed characterise tetrahedral- $\text{Fe}^{3+}$ . The other more prominent absorp-

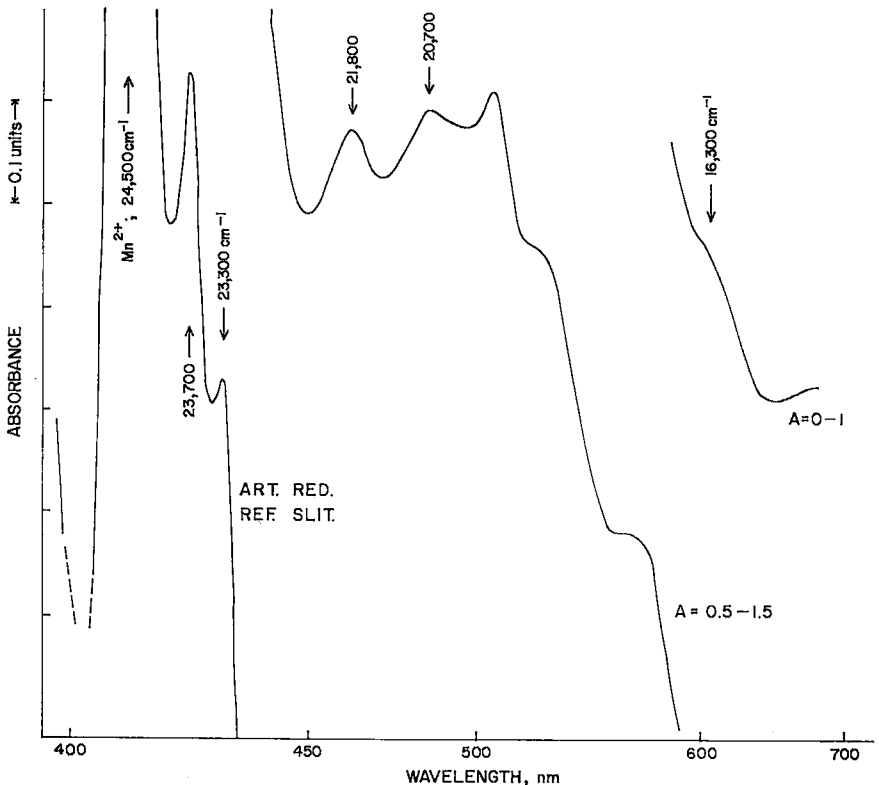


FIG. 6. Optical spectrum of Ceara spessartine,  $l = 0.16\text{ cm}$ . Note prominent absorptions at  $20700\text{ cm}^{-1}$  (483 nm) and  $21800\text{ cm}^{-1}$  (459 nm).

tions at 23300 cm<sup>-1</sup>, 21000 cm<sup>-1</sup> and 19900 cm<sup>-1</sup>-14350 cm<sup>-1</sup> are likely spin-forbidden bands of Fe<sup>2+</sup> (Manning 1967a). Intensities and average half-widths of bands in almandine spectra are listed in Table 3.

The 21000 cm<sup>-1</sup> band of half-width 2700 cm<sup>-1</sup> in almandine spectra is too narrow and at too high an energy to be due to either octahedrally-bonded Mn<sup>3+</sup> or Ti<sup>3+</sup>. The half-width of the 19000 cm<sup>-1</sup> Ti<sup>3+</sup> band in Ti-andradites is 5000-6000 cm<sup>-1</sup> (Manning & Harris 1970). I have observed the transition <sup>5</sup>E → <sup>5</sup>T<sub>2</sub>(D) in Mn<sup>3+</sup> in rose garnet (grossular, *a* = 11.848Å, Mn = 0.2%) at 19200 cm<sup>-1</sup>, with band half-width 3500 cm<sup>-1</sup>. The 21000 cm<sup>-1</sup> band is much too broad to characterize tetrahedral-Fe<sup>3+</sup> (Faye & Hogarth 1969, Faye 1969).

### *Spectra of spessartines*

The spectrum of a representative spessartine, one of six examined, is shown in Figure 6. Because Mn<sup>2+</sup> has replaced much of the Fe<sup>2+</sup> in cube sites, the two absorptions at 20700 cm<sup>-1</sup> and 21800 cm<sup>-1</sup> are clearly visible. The strong 24500 cm<sup>-1</sup> band in spessartine spectra, which marks the transition <sup>6</sup>A<sub>1</sub> → <sup>4</sup>A<sub>1</sub><sup>4</sup>E(G) in Mn<sup>2+</sup> (Manning 1967a), obliterates the weaker Fe<sup>3+</sup> (IV) absorptions at ~24200 cm<sup>-1</sup> and 24800 cm<sup>-1</sup> which are expected from comparison with spectra of almandines. Therefore, the earlier assigning of the very sharp bands at 23300 cm<sup>-1</sup> and 23700 cm<sup>-1</sup> to octahedral-Fe<sup>3+</sup> is not inconsistent with current assignments. The

TABLE 3. AVERAGE HALF-WIDTH AND ABSORBANCE VALUES OF ALMANDINE BANDS

Band cm <sup>-1</sup>	Half-width cm <sup>-1</sup>	Madag.	Gore Mtn. Absorbance	Shat. Lake units	Zillerthal	River Valley
14350	1200	0.09	0.04	0.04	0.07	0.04
16300	1000	0.11	0.06	0.07	0.08	0.06
17500	1100	0.33	0.21	0.16	0.28	0.19
19100	1700	0.33	0.33	0.27	0.41	0.24
19900	550	0.20	0.13	0.07	0.13	0.15
20300	600	0.08	0.08	0.05	0.15	0.05
21800	700	0.03	0.05	0.02	0.05	0.02
21000	2700	0.16	0.37	0.24	0.46	0.10
23300	1700	0.15	0.25	0.16	0.44	0.06
24200	900	0.03	0.07	0.06	0.12	
24800	900	0.06	0.05	0.04	0.14	
27100	700	0.10	0.80	0.25	0.24	

$\sim 27000\text{ cm}^{-1}$  bands in garnet spectra have been assigned earlier to  ${}^6A_1 \rightarrow {}^4E(G)$  transitions in octahedral- $\text{Fe}^{3+}$  (Manning 1970). In line with this, the  $\sim 26000\text{ cm}^{-1}$  absorption (Figures 4 and 5) could mark transition  ${}^6A_1 \rightarrow {}^4T_2(D)$  in octahedral- $\text{Fe}^{3+}$ . Energy-level diagrams for  $3d^5$  ions in cubic fields, based on Racah-values of  $B = 614\text{ cm}^{-1}$  and  $C = 3332\text{ cm}^{-1}$  that are reasonable for  $\text{Fe}^{3+}$ , have been calculated by Berkes (1968).

### General discussion

The spectrum of reversely-pleochroic phlogopite, in which  $\text{Fe}^{3+}$  is known to substitute into tetrahedral sites, exhibits two bands at  $19200\text{ cm}^{-1}$  and  $20300\text{ cm}^{-1}$  (Faye & Hogarth 1969), of similar half-widths to the  $\sim 20500\text{ cm}^{-1}$  and  $\sim 21800\text{ cm}^{-1}$  bands in garnets. Tetrahedral- $\text{Fe}^{3+}$  in orthoclase absorbs at  $20700\text{ cm}^{-1}$  (Faye 1969) with band half-width  $1000\text{ cm}^{-1}$ . Mossbauer studies of titanian garnets and kimzeyite by Dowty & Mark (1968) have demonstrated the presence of tetrahedral- $\text{Fe}^{3+}$ . There is strong support, therefore, for assigning the  $\sim 20500\text{ cm}^{-1}$  and  $\sim 21800\text{ cm}^{-1}$  bands in garnets to tetrahedral- $\text{Fe}^{3+}$ .

The net absorbance of the  $22700\text{ cm}^{-1}$  octahedral- $\text{Fe}^{3+}$  band in the Stanley Peak andradite (Figure 1) is 10 times that of the  $24400\text{ cm}^{-1}$ . However, the  $\epsilon$ -value for the tetrahedral- $\text{Fe}^{3+}$  band cannot be estimated accurately, but because of the lower symmetry of a tetrahedron compared to an octahedron,  $\epsilon(\text{tetrahedral}) > \epsilon(\text{octahedral})$ . Hence, it is reasonable to suggest that a maximum of 10% of total  $\text{Fe}^{3+}$  is tetrahedral- $\text{Fe}^{3+}$ . Mossbauer studies by Dowty & Mark (1968) indicate the presence of octahedral- $\text{Fe}^{3+}$  only in low-Ti andradites.

It is interesting to note that whereas the bands at  $20300\text{ cm}^{-1}$  and  $21800\text{ cm}^{-1}$  in spectra of almandines are of comparable intensity to the  $20700\text{ cm}^{-1}$  and  $21800\text{ cm}^{-1}$  bands of spessartines, the two very sharp (Figures 4-6) absorptions at  $23300\text{ cm}^{-1}$  and  $23700\text{ cm}^{-1}$  in spessartine spectra are not observed in almandine spectra. This would seem to confirm the earlier assignment (Manning 1970) of the latter two bands to the  ${}^6A_1 \rightarrow {}^4A_1$   ${}^4E(G)$  transition in octahedral- $\text{Fe}^{3+}$ . The two absorptions at  $24200\text{ cm}^{-1}$  and  $24800\text{ cm}^{-1}$  in almandine spectra (Figures 4 and 5) could mark the same transitions in tetrahedral- $\text{Fe}^{3+}$ . Clearly, the octahedral- $\text{Fe}^{3+}$  : tetrahedral- $\text{Fe}^{3+}$  ratio is greater in spessartines.

Consistent with the small dimensions of the octahedral ( $\text{Al-O} = 1.89\text{ \AA}$ ) and tetrahedral ( $\text{Si-O} = 1.63\text{ \AA}$ ) sites in pyralspites (Gibbs & Smith 1965), the solubility of  $\text{Fe}^{3+}$  in these sites is very low. Assuming  $\epsilon$ -values of one for the  $20700\text{ cm}^{-1}$  and  $23700\text{ cm}^{-1}$  bands in the Ceara spessartine, the calculated concentrations of tetrahedral- $\text{Fe}^{3+}$  and octahe-

dral- $\text{Fe}^{3+}$  are  $\sim 0.5\%$  and  $\sim 1\%$  by weight, respectively, the total Fe concentration being  $\sim 10\%$ . The  $A/l$  ratios ( $= \epsilon.C$ ) for the  $20300 \text{ cm}^{-1}$  band in five almandines are in the range 0.5-1.8, while the  $\epsilon.C$  values for the  $20700 \text{ cm}^{-1}$  band in spessartines are 0.2-0.5. Unfortunately,  $\epsilon$ -values for the  $\text{Fe}^{3+}$  bands may not be equal in almandines and spessartines, since, for example, the  $20300 \text{ cm}^{-1}$  band is stronger than the  $21800 \text{ cm}^{-1}$  in almandine spectra, whereas the  $20700 \text{ cm}^{-1}$  and  $21800 \text{ cm}^{-1}$  bands are of approximately equal intensity in spessartine spectra (Figures 4-6). The  $\epsilon$ -values of  $\text{Fe}^{3+}$  bands, especially in the green and blue regions, are critically dependent upon charge-transfer effects (Faye & Hogarth 1969; Manning & Townsend 1970). Nevertheless,  $\epsilon$ -values of  $\text{Fe}^{3+}$  bands in the  $20000 \text{ cm}^{-1}$  region in spectra of almandines and spessartines should be approximately equal within a factor of, say, 2-3, indicating that the tetrahedral- $\text{Fe}^{3+}$  concentration in almandines is not less than that in spessartines. Total-Fe concentrations in almandines are of course considerably greater than in spessartines (Deer, Howie & Zussman 1962).

Bearing in mind the absence of octahedral- $\text{Fe}^{3+}$  bands at  $\sim 23300 \text{ cm}^{-1}$  and  $\sim 23700 \text{ cm}^{-1}$  in almandine spectra, it would appear that  $\text{Fe}^{3+}$  has a preference for the tetrahedral site ( $\text{Si-O} = 1.63\text{\AA}$ ) over the octahedral ( $\text{Al-O} = 1.89\text{\AA}$ ). This is surprising in view of the fact that  $\text{Al}^{3+}$  is smaller than  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  being a major component of almandines it might be expected that most of the  $\text{Fe}^{3+}$  would be swept into octahedral sites. Hertman (1969) has suggested that the order of substitution into tetrahedral sites in garnets is  $\text{Al} > \text{Fe}^{3+} > \text{Ti}^{4+}$ . Ratios of the absorbances of the  $19100 \text{ cm}^{-1}$   $\text{Fe}^{2+}$  band and  $20300 \text{ cm}^{-1}$  tetrahedral- $\text{Fe}^{3+}$  band in almandines are approximately constant ( $\sim 4$ , Table 2), as are also the ratios of the absorbances of the  $23700 \text{ cm}^{-1}$  octahedral- $\text{Fe}^{3+}$  and  $20700 \text{ cm}^{-1}$  tetrahedral- $\text{Fe}^{3+}$  bands in five spessartines studied. Moreover,  $\epsilon.C$ -values are fairly constant for the  $20300 \text{ cm}^{-1}$  and  $20700 \text{ cm}^{-1}$  bands in spectra of almandines and spessartines, respectively (see above). It would appear, therefore, that significant geochemical relationships exist in pyralspite garnets between cube- $\text{Fe}^{2+}$ , octahedral- $\text{Fe}^{3+}$  and tetrahedral- $\text{Fe}^{3+}$ .

### CONCLUSION

Absorption bands marking electronic transitions in octahedral- $\text{Fe}^{3+}$  and tetrahedral- $\text{Fe}^{3+}$  in pyralspites, and tetrahedral- $\text{Fe}^{3+}$  in ugrandites, have been identified. A new major absorption at  $\sim 21000 \text{ cm}^{-1}$  in spectra of almandines has been resolved and attributed to  $\text{Fe}^{2+}$ . The spectra indicate that geochemical relationships exist between cube- $\text{Fe}^{2+}$ , octahedral- $\text{Fe}^{3+}$  and tetrahedral- $\text{Fe}^{3+}$ .

## REFERENCES

- ANDERSON, B.W. (1959) : Properties and classification of individual garnets. *J. Gemmology*, **7**, 1.
- BALCHAN, A.S. & DRUCKAMER, H.G. (1959) : Effect of pressure on the spectra of olivine and garnet. *J. Appl. Phys.*, **30**, 1446.
- BERKES, J.S. (1968) : Energy-level diagrams for transition-metal ions in cubic crystal fields. *MRL Monograph No. 2, Materials Research Bulletin*, Pennsylvania State University, Pa.
- BURNS, R.G. & STRENS, R.G.J. (1967) : Structural interpretations of polarized absorption spectra of the Al-Fe-Mn-Cr epidotes. *Mineral. Mag.*, **36**, 204.
- CLARK, S.P. (1957) : Absorption spectra of some silicates in the visible and near infrared. *Amer. Mineral.*, **42**, 732.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962) : *Rock-forming minerals*, **1**, Longmans, London.
- DOWTY, E. & MARK, R. (1968) : Titanian garnets: mossbauer and infrared spectroscopy. *Geol. Soc. Amer. Spec. Pap.* **121**, 80.
- FAYE, G.H. (1969) : The optical absorption spectrum of tetrahedrally-bonded  $\text{Fe}^{3+}$  in orthoclase. *Canad. Mineral.*, **10**, 112.
- & HOGARTH, D.D. (1969) : On the origin of "reverse pleochroism" of a phlogopite. *Canad. Mineral.*, **10**, 25.
- GELLER, S. & GILLO, M. (1957) : The crystal structure & ferri-magnetism of yttrium iron garnet. *J. Phys. Chem. Solids*, **3**, 30.
- GIBBS, G.V. & SMITH, J.V. (1965) : Refinement of the crystal structure of synthetic pyrope. *Amer. Mineral.*, **50**, 2023.
- GRUM-GRZHMAILO, S.V., BRILLANTOV, N.A., SVIRIDOV, D.T., SVIRIDOVA, R.K. & SUKHANOVA, O.N. (1963) : Absorption spectra of crystals containing  $\text{Fe}^{3+}$ . *Opt. Spectr. (USSR)* (English Translation), **14**, 118.
- HARTMAN, P. (1969) : Can  $\text{Ti}^{4+}$  replace  $\text{Si}^{4+}$  in silicates. *Mineral. Mag.*, **37**, 366.
- ITO, J. & FRONDEL, C. (1967) : Synthetic zirconium and titanium garnets. *Amer. Mineral.*, **52**, 773.
- KOLBE, E. (1934) : The colouring of minerals by manganese, chromium and iron. *Neues Jahrbuch Mineral.*, **69A**, 183.
- LEHMAN, G. & HARDER, H. (1970) : Optical spectra of di- and trivalent iron in corundum. *Amer. Mineral.* **55**, 98.
- LIND, M.D. & GELLER, S. (1969) : Crystal structure of the garnet  $\text{Mn}_3 \text{Fe}_2 \text{Ge}_3 \text{O}_{12}$ . *Zeit. Krist.* **129**, 427.
- MANNING, P.G. (1967a) : The optical absorption spectra of the garnets almandine-pyrope, pyrope and spessartine. *Canad. Mineral.* **9**, 237.
- (1967b) : The optical absorption spectra of some andradites and the identification of the  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 {}^4\text{E}(\text{G})$  transition in octahedrally-bonded  $\text{Fe}^{3+}$ . *Canad. J. Earth Sci.* **4**, 1039.
- (1968) : Optical absorption spectra of the Mn-bearing chain silicates. *Canad. Mineral.* **9**, 348.
- (1969) : Optical absorption studies of grossular, andradite and uvarovite. *Canad. Mineral.* **9**, 723.
- (1970) : Racah parameters and their relationship to lengths and covalencies of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  oxygen bonds in silicates. *Canad. Mineral.* **10**, 677.
- & HARRIS, D.C. (1970) : Optical-absorption and electron-microprobe studies of some high-Ti andradites. *Canad. Mineral.* **10**, 260.
- & TOWNSEND, M.G. (1970) : Effect of next-nearest neighbour interaction on oscillator strengths in garnets. *J. Phys. C*, **3**, L14.

- NEUHAUS, A. (1960) : Über die Ionenfarben der Kristalle und Minerale am Beispiel der Chromfärbungen. *Zeit. Krist.* **113**, 195.
- WIEGEL, O. & UFER, H. (1928) : Die Absorption einiger Rotgefärbter Mineralien. *Neues Jahrbuch Mineral.* **57A**, 397.
- WOOD, D.L. & REMEIK, J.P. (1967) : Effect of impurities on the optical properties of yttrium iron garnet. *J. Appl. Phys.*, **38**, 1038.

*Manuscript received September 1971, emended October 1971.*

Note added in press : on Figures 2, 4, 5 read for abscissa, Energy  $10^3\text{cm}^{-1}$ .