THE OPTICAL ABSORPTION SPECTRA OF THE GARNETS ALMANDINE-PYROPE, PYROPE AND SPESSARTINE AND SOME STRUCTURAL INTERPRETATIONS OF MINERALOGICAL SIGNIFICANCE

P. G. MANNING*

ABSTRACT

The optical absorption spectra of the garnets almandine-pyrope, pyrope and spessartine are reported from the near infrared to the near ultraviolet (4,000 cm^{-1}–30,000 cm^{-1}). The spectra show a three-band system in the infrared (4,500 cm^{-1}, 6,000 cm^{-1} and 7,800 cm^{-1}) that has been attributed to 8-coordinate Fe(II). A number (6–7) of fairly sharp bands in the visible and ultraviolet regions have been attributed to spin-forbidden bands of either Fe(II) or octahedrally-bonded Fe(III). Some Mn(II) bands have also been observed and assigned.

No bands characteristic of tetrahedrally-bonded transition metal ions were observed. Absorption bands characteristic of octahedrally-bonded Fe(II) were not observed either. A few very weak absorption bands have not been assigned because absorptions due to other transition metal ions, e.g., Ti(III), Mn(III) or Cr(III) cannot be identified with any certainty.

INTRODUCTION

Useful information on the cation valence state and site symmetry can be obtained from an analysis of the *d-d* spectra of minerals that contain transition metals. The study of the *d-d* spectra of garnets is of interest because these silicates can contain Fe, Mn and Ti as a principal constituent or as an impurity, and also because these cations can be distributed between orthorhombic (8-coordinate), octahedral and tetrahedral sites. This paper, therefore, reports an analysis of the optical spectra of almandine-pyrope, pyrope and spessartine crystals.

The optical absorption spectra of the garnets almandine and pyrope have been reported by Clark (1957). A large number of bands were observed in the energy range 2,900–29,000 cm^{-1}, the energies of the principal of which are listed in Table 1. Clark (1957) attributed the 7,900 cm^{-1} band to 8-coordinated Fe(II) and the 20,000 cm^{-1} band to Fe(III).

In an orthorhombic field the degeneracy of the Fe 3*d* orbitals is removed and an absorption spectrum of three bands, corresponding to three spin-allowed transitions is expected. Bloomfield, Lawson & Rey (1961) used the energies of the 2,900 cm^{-1}, 6,000 cm^{-1} and 7,900 cm^{-1} bands (Table 1) to determine the charge on the oxygen atoms surrounding the Fe(II),

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*Research Scientist, Mineral Physics Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

TABLE 1. ENERGIES OF PRINCIPAL BANDS IN PYROPE AND ALMANDINE (Clarke, 1957)

Almandine	Pyrope
2,900 cm^{-1}	2,900 cm^{-1}
6,000	6,000
7,900	7,900
12,100	12,100
14,400	14,300
17,600	17,600
20,000	20,000
21,500 (weak)	
23,900	23,900
27,200	27,200

and this charge they then related to the degree of covalency of the Si—O bond. Their calculations were only approximate, however, and the accuracy of Clark's spectral observations was not confirmed.

Bloomfield, Lawson & Rey (1961) made no attempt at analysing the rich absorption spectrum of the garnets in the visible region, although they vaguely suggested that the 12,000 cm^{-1} and 14,000 cm^{-1} bands could be due to Fe(III) or Mn(II) impurities. Although it is highly probable that the absorption bands in the visible region are of the *d-d* type, no interpretations of garnet spectra have been made in terms of ligand field (*d-d* electronic transition) theory.

MATERIALS

Almandine, pyrope and spessartine represent three end-members of the isomorphous series of garnets, but a garnet corresponding in composition to any one end-member is rare. In this study, therefore, the name has been given according to the predominant species present. The garnets were obtained from H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada, Ottawa. The specimens of almandine-pyrope came originally from Gore Mountain, Essex County, New York, and from Madagascar. The pyrope was from Moravia, Czechoslovakia and the spessartine from Parry Sound, Ontario. The spessartine was brownish-red in colour, the almandine-pyropes deep-red and the pyrope blood-red.

The ideal formulae for the garnets are:

almandine	$Fe_3Al_2Si_3O_{12}$
pyrope	$Mg_3Al_2Si_3O_{12}$
spessartine	$Mn_3Al_2Si_3O_{12}$

EXPERIMENTAL DETAILS

Crystal slabs of dimensions 5 mm × 5 mm × 1 mm were cut from the parent garnet by a 0.003 in. tungsten wire saw. The polished slab was mounted in an aluminum crystal holder fitted with two variable-aperture windows. The holder was placed in the cell compartment of a Beckman DK-2A double-beam spectrophotometer. When necessary, the crystal was thinned down to permit resolution of the higher-energy bands. Crystal thicknesses were measured with a micrometer. Extinction coefficients were calculated from the expression

$$\epsilon = A/Cl,$$

where A is the absorbance at peak maximum, C is the cation concentration in moles/litre and l is the crystal thickness in cm.

The spectra were run at room temperature.

DISCUSSION

The absorption spectra of the almandine-pyropes, pyrope and spessartine are shown in Figures 1–4. The spectra exhibit many similar features, for example, each spectrum has a set of three similarly-shaped bands in the infra-red at the approximate energies of 4,500 cm^{-1}, 6,000 cm^{-1} and 7,800 cm^{-1}. The spectra in the visible region show a large number of fairly-sharp bands, and in all four spectra the three lowest-energy bands are at the approximate energies 14,500 cm^{-1}, 16,300 cm^{-1} and 17,600 cm^{-1}. It would seem, therefore, that the garnets contain at least one common transition metal ion. The energies of the absorption bands for the four garnets are tabulated in Table 2.

In garnets, the divalent metal ions are predominantly located in the distorted dodecahedral (orthorhombic) sites (Deer, Howie & Zussman, 1962). Because Fe is the principal divalent cation in the Gore Mountain almandine-pyrope and because Fe(II) *d-d* transitions are spin-allowed, absorption bands due to 8-coordinated Fe(II) should be readily observed. In pyrope and spessartine Fe(II) is not the principal divalent metal, but nevertheless considerable amounts of Fe(II) are often present (Deer, Howie & Zussman, 1962). Therefore, a logical point at which to begin the assignment of the spectral bands in Figures 1–4 is the identification of the Fe(II) bands from a comparison of the almandine-pyrope, pyrope and spessartine spectra. Because of the similar structures of the different species of garnet, it is reasonable to assume that the extinction coefficient of a band pertaining to a cation in a given O environment is approximately equal for all garnets.

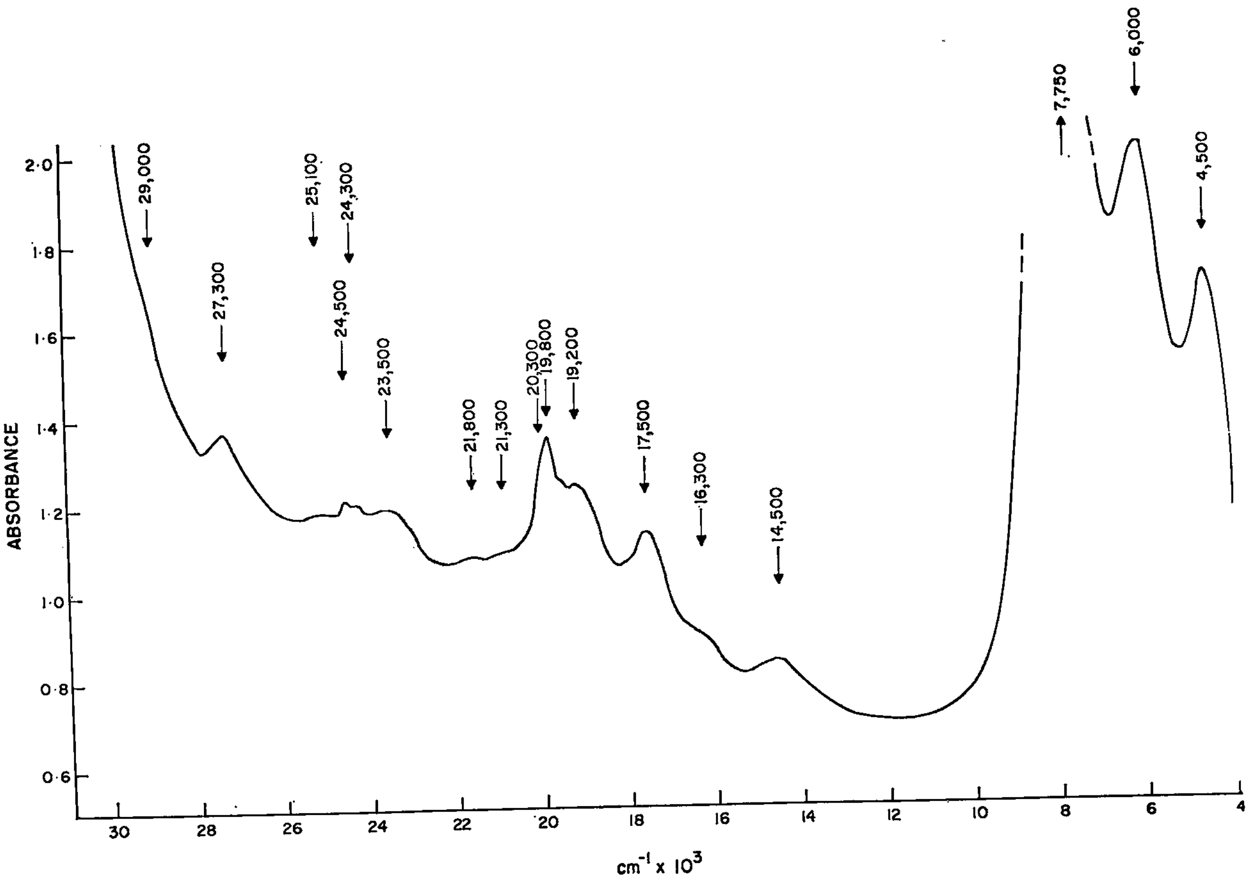

Fig. 1. Absorption spectrum of Madagascar almandine-pyrope. The 7,750 cm^{-1} band is not resolved in this particular spectrum. w designates a weak absorption. Crystal thickness = 1.2 mm.

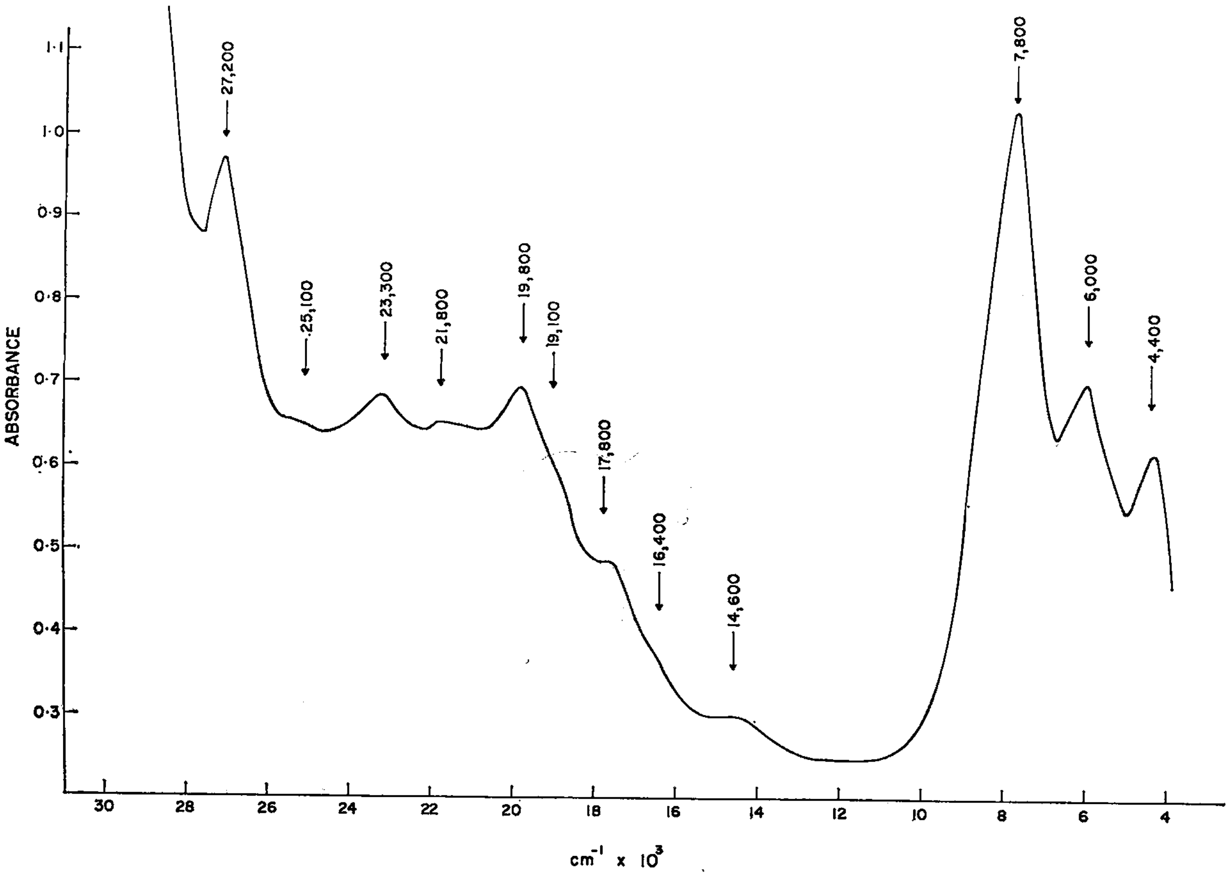

FIG. 2. Absorption spectrum of almandine-pyrope from Gore Mountain. Crystal thickness = 0.6 mm.

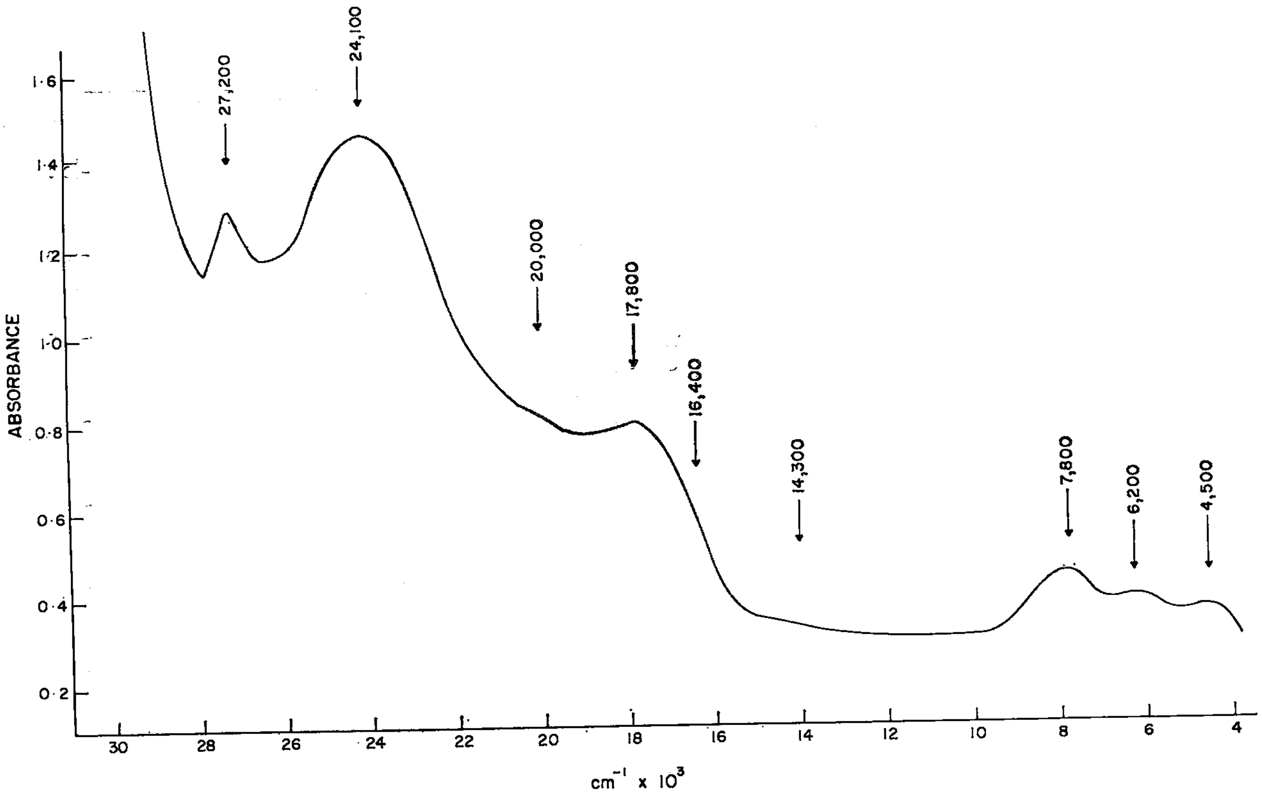

FIG. 3. Absorption spectrum of Moravian pyrope. Crystal thickness = 0.40 mm.

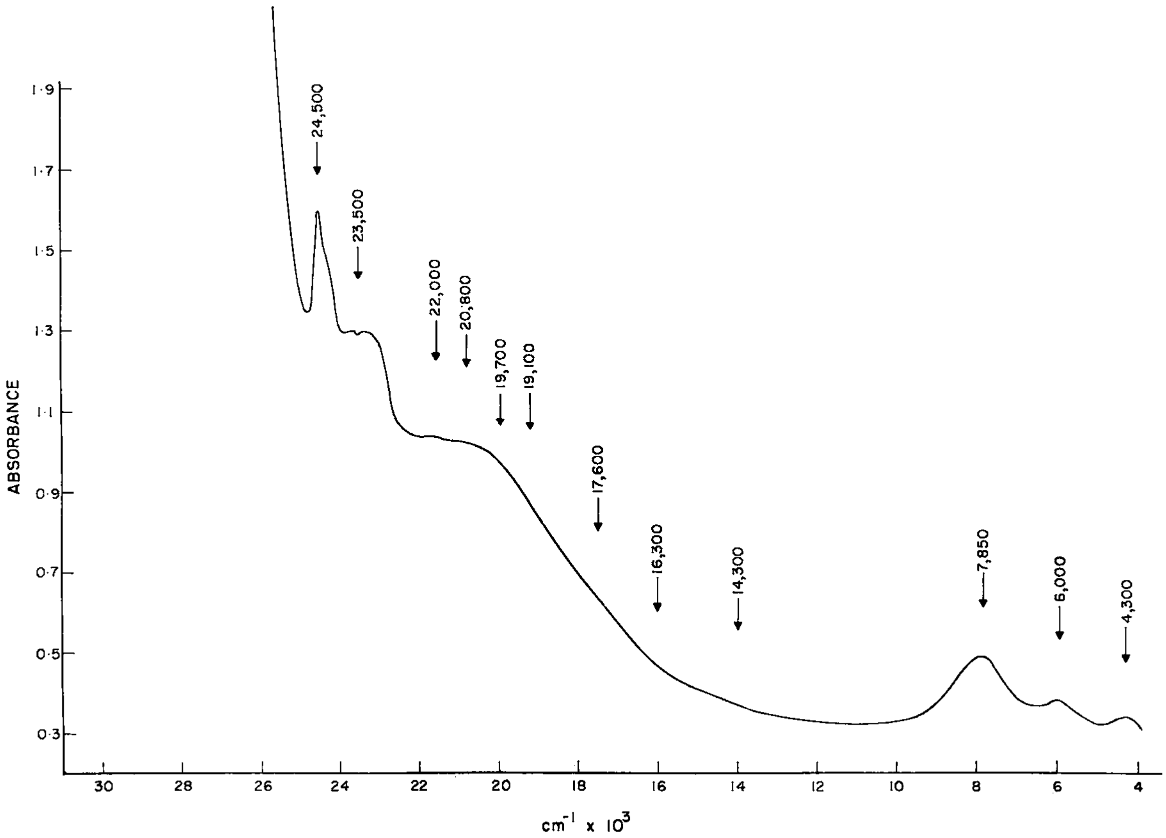

FIG. 4. Absorption spectrum of spessartine from Parry Sound, Ontario. Crystal thickness = 0.20 mm.

TABLE 2. ENERGIES OF ABSORPTION BANDS IN CURRENTLY-STUDIED GARNETS

	Gore Mtn.	Madagascar	Pyrope	Spessartine	
	4,400	4,500	4,500	4,300	
	6,000	6,000	6,200	6,000	
	7,800	7,750	7,800	7,850	
	14,600	14,500	14,300	14,300	
	16,400	16,300	16,400	16,300	
	17,800	17,500	17,800	17,600	
	19,100	19,200		19,100	Spessartine envelope contains strong Mn(II) and Fe(III) bands
			20,000		
	19,800	19,800		19,700	
				20,800	
	21,800	21,800	21,500(w)	22,000 (w)	
				23,500	
	23,300	23,500	24,100		
	24,300 (v.w.)	24,300		24,350	
	24,500 (v.w.)	24,500	24,500 (w)	24,500	
	25,100 (w)	25,100		25,100 (w)	
	27,200	27,300	27,200		
		29,000			
Very weak bands	19,500; 20,300; 21,300; 23,000.	19,500; 20,300; 21,300; 23,000.		$\sim$23,500	

Chemical analyses of two Gore Mountain garnets are shown in Table 3. The garnets correspond to a crystal with the following approximate mol. per cent end-members: almandine 41%, pyrope 42%, grossular 14% and andradite 2% (Deer, Howie & Zussman, 1962). Now, Fe(II) in octahedral sites exhibits a single absorption band corresponding to the transition $^5T_{2g} \rightarrow {}^5E_g$, although the band is sometimes split into two broad components with a peak separation of $\sim$2,000 cm^{-1} due to a dynamic Jahn–Teller (1937) mechanism. A broad absorption band has been observed at 10,000 cm^{-1} for Fe(OH$_2$)$_6^{2+}$ (Cotton & Meyers, 1960) and also for octahedrally-bonded Fe(II) in MgO (Low & Weger, 1960).

TABLE 3. CHEMICAL ANALYSES OF GORE MOUNTAIN GARNETS

	Crystal CT	Crystal XH
SiO_2	41.30%	39.29%
TiO_2	0.15	0.05
Al_2O_3	19.78	22.12
Fe_2O_3	1.80	0.73
FeO	17.80	19.63
MnO	0.49	0.38
MgO	10.60	11.48
CaO	6.98	6.16
H_2O	0.54	0.03

Analyses after Levin (1950).

We observe no band in the energy range 9,000–11,000 cm^{-1} in any of our spectra, which suggests that Fe(II) does not occur in octahedral sites in garnets to any noticeable degree. Assuming that an absorbance of 0.01 is significant, that $\epsilon = 1$ and $l = 0.05$ cm, then $C = 0.2$ moles/litre or [Fe(II)] in crystal = 0.3%. This corresponds to 0.4% FeO. This value of 0.3% is an upper limit for octahedrally-bonded Fe(II).

Tetrahedrally-bonded Fe(II), in an oxygen field, is characterised by a *d-d* band at ~4,500 cm^{-1}, e.g. in $Mg_{1-x}Fe_xAl_2O_4$ (Slack, 1964) and in Fe-containing ZnO (Bates, White & Roy, 1966). This absorption appears as a single band at room-temperature. It is possible that either the 6,000 cm^{-1} band or the 4,500 cm^{-1} band is due to tetrahedrally-bonded Fe(II). The relative intensities of the 4,500 cm^{-1}, 6,000 cm^{-1} and 7,800 cm^{-1} for five garnets are shown in Table 4, from which it is evident that the three bands pertain to a single absorbing species. It is very unlikely that two or three different absorbing species in different garnets would have such similar distributions between tetrahedral and other sites. We would further suggest that this three-band system characterises 8-coordinate Fe(II). Based on 18% FeO content (14% Fe) for the Gore Mountain almandine-pyrope, the value of $\epsilon_{7,800}$ is ~1.3 (Figure 2). The ϵ value is reasonable for a *d-d* band. Comparing the intensities of the 7,800 cm^{-1} band of pyrope and Gore Mountain almandine-pyrope, the FeO content in pyrope is ~5.2%. Deer, Howie & Zussman (1962) report 6.2% FeO for the Moravian pyrope. This calculation would seem to confirm that the three-band system in the infrared belongs to 8-coordinate Fe(II). The Moravian garnet is 70–75% pyrope (Deer, Howie & Zussman, 1962), and 14% almandine.

TABLE 4. RELATIVE INTENSITIES OF GARNET ABSORPTION BANDS

Garnet	4,500 cm^{-1}	6,000 cm^{-1}	7,800 cm^{-1}
Pyrope	1.0	1.4	1.7
Spessartine	1.0	1.4	2.1
Madagascar	1.0	1.2	2.0
Gore Mountain	1.0	1.25	1.85
Almandine*	1.0	1.2	1.8

*of unknown origin

We have examined the 2,900 cm^{-1} region of the spectrum with a Beckman IR-12 infrared spectrophotometer. The Gore Mountain and Madagascar almandine-pyrope crystals showed no evidence of a strong absorption band at this energy. Clark's (1957) observations of a 2,900 cm^{-1} band would seem to be in error. The present spectral investigation also suggests that Fe(II) does not substitute for Si in tetrahedral sites. Because *d-d* absorption bands for transition metal ions in tetrahedral sites are usually 10–100 times more intense than for the same ions in octahedral sites, we would put an upper limit for the Fe(II)-for-Si substitution at $\sim$0.03%.

In general, the intensities of the major bands common to the four spectra (Figures 1–4) in the visible region follow the intensities of the three Fe(II) bands in the near-infrared. This would suggest that these bands in the visible region (at 14,500 cm^{-1}, 16,300 cm^{-1} and 17,800 cm^{-1} for example) are spin-forbidden Fe(II) bands. If the spin-forbidden bands of Fe(II) and Fe(III) are of similar intensity, the analytical data in Table 3 suggest that the Fe(II) bands would predominate in the almandine-pyropes. The spectra in Figures 3 and 4 are dominated in the visible region by strong absorptions due, as we will propose later, to Cr(III) and Mn(II) respectively. Two possible assignment schemes are presented for the major bands in the visible region of the almandine-pyrope spectra (Figures 1 and 2).

Spin-forbidden bands of Mn(II) and Fe(III)

Figure 5 is an energy level diagram for d^5 ions in a cubic field. Because the electronic ground state is $^6A_1$ (derived from ^6S term) and all higher-energy states are quadruplets are doublets, Mn(II) and Fe(III) *d-d* bands are generally weak and are observed either in or flanking the visible region. It is apparent from Figure 5 that, if the free-ion terms retain their original energy values, electronic transitions from the ground state $^6A_1$ to the quadruplet states would be observed in the ultra-violet region. Many workers (e.g. Wickersheim & Lefever, 1962; Ginsberg & Robin, 1963) have suggested that the free-ion terms are reduced in a ligand field. Electronic transitions to field-independent states are often marked by sharp absorption bands, and the band at $\sim$24,000 cm^{-1} in the spectra of octahedrally-bonded Mn(II) is an excellent example of this (Cotton & Wilkinson, 1962; Mehra & Venkateswarlu, 1966). This characteristically sharp peak corresponds to the electronic transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$. Also, because the $^4A_1(G)$ and $^4E(G)$ states are not exactly degenerate, a shoulder is observed on either the low- or high-energy limbs of the main peak.

The absorption spectra of andradites in the visible region have been reported by Grum-Grzhimailo and co-workers (1963) and Manning (1967a). An impressively sharp band was observed at 22,700 cm^{-1}, and this was assigned to the transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in octahedrally-bonded Fe(III). The corresponding absorption for Fe(III) in vesuvianite has been observed at 21,600 cm^{-1} (Manning, 1967b).

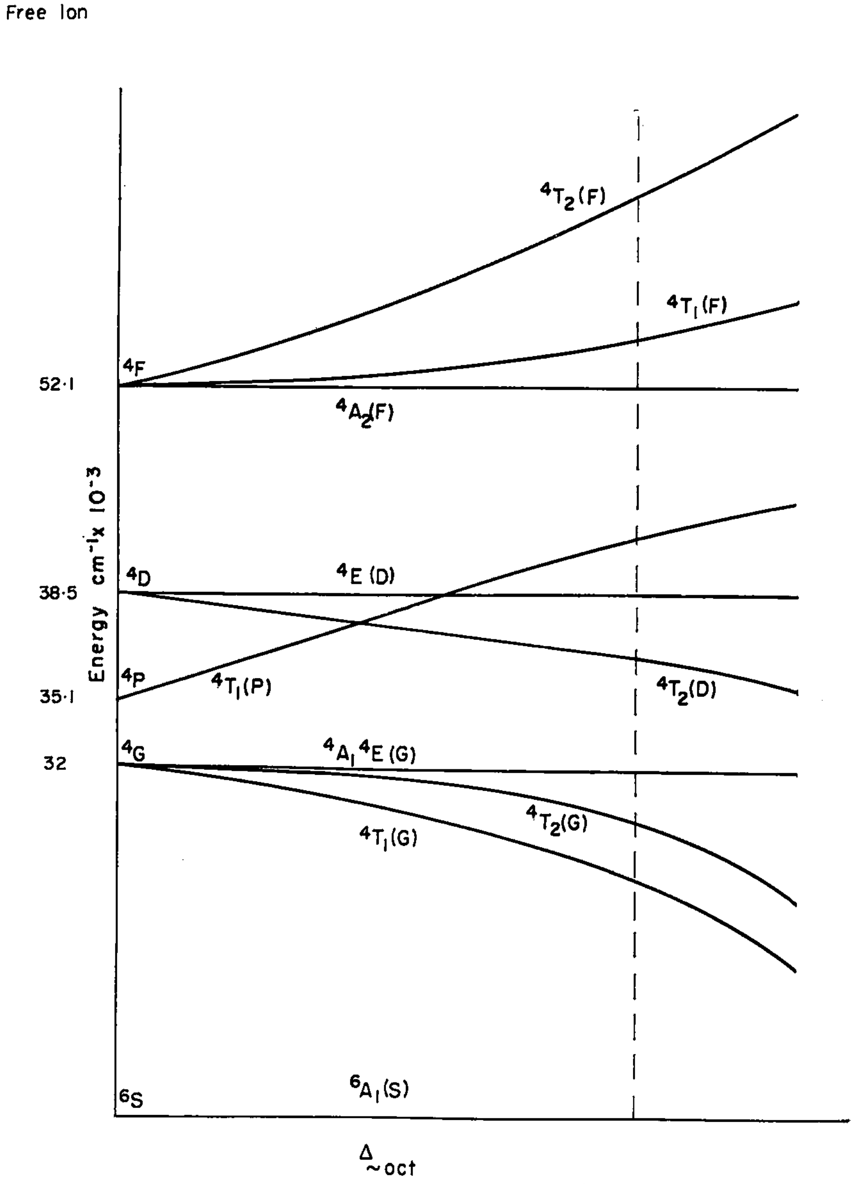

FIG. 5. Energy level diagram for $3d^5$.

The spectrum of spessartine (Figure 4) shows a very sharp *d-d* band at 24,500 cm^{-1} (with a shoulder at 24,300 cm^{-1}) that, according to the above description, characterizes Mn(II). The separation of peak and shoulder is ~200 cm^{-1}, in reasonable agreement with the separation (300 cm^{-1}) for $Mn(OH_2)_6^{2+}$ (Heidt, Koster & Johnson, 1958). Assuming that the ligand field for the dodecahedral site is similar to that of a cube, the Δ(dodecahedral) site $\simeq$8/9 Δ(octahedral site). The 24,500 cm^{-1} band could therefore be due to 8-coordinate Mn(II). In spessartine, Mn(II) occupies preferentially the 8-coordinate sites. Nevertheless, the $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition in octahedrally-bonded Mn(II) in bustamite, rhodonite, pyroxmangite and serandite is observed at 24,500 cm^{-1} (Manning, 1967c).

The strong absorptions in the spessartine spectrum (Figure 4) at 20,800 cm^{-1} and 23,500 cm^{-1} must also be Mn(II) bands, because these absorptions are not observed in the almandine-pyrope and pyrope spectra (Figures 1–3). The 20,800 cm^{-1} and 23,500 cm^{-1} bands are analogous to the 19,400 cm^{-1} and 22,700 cm^{-1} bands belonging to octahedrally-bonded Mn(II) in KCl (Mehra & Venkateswarlu, 1966), and could mark the transitions $^6A_1 \rightarrow {}^4T_1(G)$ and $^6A_1 \rightarrow {}^4T_2(G)$ respectively. The bands in spessartine are, therefore, raised generally to higher energies. Thinner sections of spessartine showed a strong band at 27,000 cm^{-1}, which compares with the band observed by Mehra & Venkateswarlu (1966) at 27,200 cm^{-1} ($^6A_1 \rightarrow {}^4T_2(D)$).

Let us now return to the spectrum of the Madagascar almandine-pyrope (Figure 1), which is the richer of the two almandine-pyrope spectra. The small peaks at 24,500 cm^{-1} and 24,300 cm^{-1} are clearly those of Mn(II), but these bands are not visible in the Gore Mountain spectrum (Figure 2). The concentration of Mn in the former garnet is 0.5%, giving a value of $\epsilon_{24,500}$ of 0.5.

The three absorption bands at the approximate energies 14,500 cm^{-1}, 16,300 cm^{-1} and 17,600 cm^{-1} appear in all four reported spectra (Figures 1–4), albeit rather weakly in the pyrope (Figure 3) and spessartine spectra (Figure 4). The relative intensities of the bands in the four spectra indicate that they belong to a single absorbing species. Their weakness in the spessartine spectrum (Figure 4) suggests that they would belong toFe (III) rather than Mn(II). The 19,100 cm^{-1}, 19,800 cm^{-1}, 23,500 cm^{-1} and 27,200 cm^{-1} bands are very prominent in the almandine-pyrope spectra (Figures 1 and 2) and these bands together with the three at 14,500 cm^{-1}, 16,300 cm^{-1} and 17,600 cm^{-1} can be considered a set. The two absorptions at 17,800 cm^{-1} and 24,100 cm^{-1} in the pyrope spectrum (Figure 3) clearly belong to another cation, and they "swamp" much of the detail in the visible region.

The very sharp absorption at 19,800 cm^{-1} in Figures 1 and 2 could mark the transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$, while the 27,200 cm^{-1} absorptions mark the second field-independent transition $^6A_1 \rightarrow {}^4E(D)$. The following assignment scheme seems reasonable for Fe(III) in octahedral sites in pyralspites:

14,500 cm^{-1} 16,300 cm^{-1}	$^6A_1 \rightarrow {}^4T_1(G)$
17,500 cm^{-1} 19,200 cm^{-1}	$^6A_1 \rightarrow {}^4T_2(G)$
19,800 cm^{-1}	$^6A_1 \rightarrow {}^4A_1{}^4E(G)$
23,500 cm^{-1}	$^6A_1 \rightarrow {}^4T_2(D)$
27,200 cm^{-1}	$^6A_1 \rightarrow {}^4E(D)$.

The $^4A_1{}^4E(G)$ level, therefore, would seem to be at 19,800 cm^{-1} in pyralspites, compared to 21,600 cm^{-1} for vesuvianite (Manning, 1967b) and 22,700 cm^{-1} for andradite (Manning, 1967a).

The splitting of the $T_1(G)$ and $T_2(G)$ levels (~1,700 cm^{-1}) is reasonable for a dynamic Jahn-Teller (1937) mechanism. The configurations of the Fe(III) excited states are $t_{2g}^4e_g^1$. Dynamic Jahn-Teller mechanisms of ~2,000 cm^{-1} have been proposed to account for band splittings in many Fe^{2+} complexes (Jones, 1967).

Spin-forbidden Fe(II) bands

Let us now consider the possibility that the 14,500 cm^{-1}, 16,300 cm^{-1}, 17,500 cm^{-1}, 19,200 cm^{-1}, 19,800 cm^{-1}, 23,500 cm^{-1} and 27,200 cm^{-1} bands are spin-forbidden bands of Fe(II). As mentioned earlier, this set of bands appears prominently in Figures 1 and 2 where the three spin-allowed Fe(II) bands are strong, and only very weakly in Figures 3 and 4 where the spin-allowed Fe(II) bands are weak. The extinction coefficient of the 14,500 cm^{-1} band in the Gore-Mountain spectrum is ~0.07 based on Fe(II) concentrations, and this is reasonable for a spin-forbidden band. Based on the Fe(III) concentration, the value of ϵ for the 14,500 cm^{-1} band is ~1, which is rather high for a spin-forbidden band.

In thicker sections, the 21,800 cm^{-1} band in the almandine-pyrope spectra (Figures 1 and 2 is also sharply pointed, but on thinning the crystals its sharpness becomes less evident. The 21,800 cm^{-1} band could mark the transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$. The 19,800 cm^{-1} band seems to be at rather a low energy for the $^4A_1{}^4E(G)$ level, since this level is observed at 21,600 cm^{-1} in vesuvianite (Manning, 1967b) and 22,700 cm^{-1} in andradite (Manning, 1967a). For epidote, Burns (1965) put the $^4A_1{}^4E(G)$ level at ~23,000 cm^{-1}. Based on an Fe(III) content of 1%, the extinction coefficient of the 21,800 cm^{-1} band in the Gore Mountain spectrum (Figure 2) is 0.4. The 25,200 cm^{-1} band could also be part of the Fe(III) spectrum, although this weak band has no prominent features (e.g. sharpness) that would lead to a rigorous assignment.

A few minor bands remain unassigned, e.g. at 20,300 cm^{-1} (a weak shoulder in Figure 1), but they are not sufficiently important to warrant a detailed study.

GENERAL DISCUSSION

It is difficult to decide unequivocally which of the two assignment schemes is correct. Attributing the 14,500 cm^{-1}, 16,300 cm^{-1}, 17,800 cm^{-1}, 19,200 cm^{-1}, 19,800 cm^{-1}, 23,500 cm^{-1} and 27,200 cm^{-1} bands to octahedrally-bonded Fe(III) leads to a reasonable assignment scheme in which the $T_1(G)$ and $T_2(G)$ states are split by a Jahn-Teller (1937) mechanism. The 19,800 cm^{-1} and 27,200 cm^{-1} absorptions are sharp and could have been due to transitions to the field-independent states $^4A_1{}^4E(G)$ and $^4E(D)$. Unfortunately, the extinction coefficients seem rather large when calculated on the basis of 1% Fe(III), e.g. $\epsilon_{19,800}$ ~5. Also, the $^4A_1{}^4E(G)$ level at 19,800 cm^{-1} would seem to be at a rather low energy compared to vesuvianite (21,600 cm^{-1}), andradite (22,700 cm^{-1}) and epidote (~23,000 cm^{-1}). The 21,800 cm^{-1} band would seem to be of reasonable intensity for an Fe(III) band. Dunn (1960) has pointed out that some excited triplet states of Fe(II) are field-independent in cubic fields, and because spin-forbidden Fe(II) are generally observed in the visible, the sharp bands in the almandine-pyrope spectra may be due to Fe(II). We favour the assigning of the major bands in the almandine-pyrope spectra (Figures 1 and 2) to Fe(II), the dominant ion.

Absorption bands of Cr(III)

The 24,100 cm^{-1} and 17,800 cm^{-1} bands in pyrope (Figure 3) are clearly not of the same origin as the bands in the almandine-pyrope spectra (Figure 5). The pyrope contains 0.5% Cr and it is possible that the two absorptions pertain to octahedrally-bonded Cr(III). The ϵ values are ~25, which compare well with the values of $\epsilon(=15)$ for the 17,400 cm^{-1} and 24,500 cm^{-1} bands for $Cr(OH_2)_6^{3+}$ (Ballhausen, 1962). The blood-red colour of pyrope has earlier been attributed to Cr (Bragg, 1958). It is likely, therefore, that the 17,800 cm^{-1} and 24,100 cm^{-1} bands belong to octahedrally-bonded Cr(III).

CONCLUSION

A three-band system in the near infrared in the optical absorption spectra of pyralspite garnets has been assigned to 8-coordinate Fe(II). The more prominent bands in the visible region have been assigned to spin-forbidden bands of Fe(II) and Fe(III). Absorption bands peculiar to Mn(II) and Cr(III) have also been recorded.

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