ABSORPTION SPECTRA OF THE MANGANESE-BEARING CHAIN SILICATES PYROXMANGITE, RHODONITE, BUSTAMITE AND SERANDITE

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ABSTRACT

The optical absorption spectra of the chain silicates pyroxmangite, rhodonite, bustamite and serandite are reported in the energy range 3,500 cm^{-1} to 30,000 cm^{-1} (2.85 − 0.34 μ). A set of 5 absorption bands in the visible and near ultraviolet regions, at the approximate energies 19,000 cm^{-1}, 23,000 cm^{-1}, 24,500 cm^{-1}, 27,700 cm^{-1} and 29,000 cm^{-1}, has been assigned to octahedrally-bonded Mn(II). The spectrum of pyroxmangite also shows prominent absorptions due to octahedrally-bonded Fe(II). The pink colours of pyroxmangite, rhodonite and serandite are due primarily to octahedrally-bonded Mn(II). The brown colour of bustamite is due to the super-imposition of the Mn(II) bands on strong background absorption.

All four minerals show an absorption band at $\sim$9,500 cm^{-1} that characterises octahedrally-bonded Fe(II). Pyroxmangite, bustamite and serandite have a band at $\sim$5,000 cm^{-1} that is characteristic of Fe(II) in tetrahedral sites. A band at 6,900 cm^{-1} in the rhodonite spectrum cannot be assigned unequivocally.

The interpretations of the absorption spectra advanced in this work are based on simple ligand field (*d-d* electronic transition) theory. The absorption bands characterise electronic transitions between electronic energy levels that arise as a result of the splitting, energywise, of the cation 3*d* orbitals.

INTRODUCTION

Ligand field theory (or, in its simpler electrostatic form, crystal field theory) has proved a useful tool in the hands of the inorganic chemist in the study of complex ions in solids and liquids. Unfortunately, the theory seems to have drawn little attention from the mineralogist or geochemist. Ligand field theory could prove useful in the study of structures of minerals for two good reasons. Firstly, the colours of transition metal complexes often can be interpreted in terms of *d-d* electronic transition theory and, secondly, minerals are often highly coloured. This does not mean that the colour of every coloured mineral is due to *d-d* electronic transitions, as other types of electronic transitions are possible (e.g. ligand → metal charge transfer).

A *d-d* band can usually be identified from its intensity (extinction coefficient) and energy. The extinction coefficient is defined by

$$\epsilon = A/Cl,$$

where A is the band absorbance at peak maximum, C is the concentration

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in moles/litre of the absorbing ion, and l is the crystal thickness in cm. In general, for octahedrally-bonded ions $\epsilon = 0.1$–100, and for tetrahedrally-bonded ions $\epsilon = 0.1$–1000. The *d-d* bands are usually observed in the energy range 4,000 cm^{-1}–30,000 cm^{-1} (25,000 Å–3,000 Å): the visible region of the spectrum is in this energy range.

The number of bands observed (and their energies) for a cation in a given environment can be correlated with a Tanabe-Sugano (1954) energy level diagram. These energy level diagrams are reproduced in simplified form in books by Cotton (1964) and Cotton & Wilkinson (1967). The Tanabe-Sugano (1954) energy level diagram for d^5 ions in a cubic field is shown in Figure 1. The diagram tells us that several relatively weak spin-forbidden bands should be observed in spectra of these ions, corresponding to the electronic transitions ${}^6A_1 \rightarrow {}^4T_1(G)$, ${}^6A_1 \rightarrow {}^4T_2(G)$, ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ etc. For d^5 ions, however, the observed energies of the absorption bands do not agree well with the Tanabe-Sugano (1954) energy level diagram, and some workers consider that this is due to a high degree of covalency (Ginsberg & Robin 1963; Wickersheim & Lefever 1962). For octahedrally-bonded Mn(II) in $Mn(OH_2)_6^{2+}$, the field-independent degenerate ${}^4A_1{}^4E(G)$ levels lie $\sim$24,000 cm^{-1} above the electronic ground state (Heidt, Koster & Johnson 1958), while for Fe(III) in garnets the corresponding figure is $\sim$22,000 cm^{-1} (Manning 1967).

In the present work, the absorption spectra of some Mn-containing chain silicates are reported. The silicates are pyroxmangite, rhodonite, bustamite and serandite. All show *d-d* bands characteristic of octahedrally-bonded Mn(II) and Fe(II). Pyroxmangite, in particular, also shows spin-forbidden bands in the visible region due to Fe(II). Pyroxmangite, bustamite and serandite show a band at $\sim$5,000 cm^{-1} due to tetrahedrally-bonded Fe(II).

The formulae of the Mn-containing silicates are:

pyroxmangite	$(Mn, Fe)SiO_3$
rhodonite	$(Mn, Fe, Ca)SiO_3$
bustamite	$(Mn, Ca, Fe)SiO_3$
serandite	$(Ca, Mn)_2NaH(SiO_3)_3$

In all these minerals, Mn is a principal constituent. Published chemical analyses of pyroxmangite (Deer, Howie & Zussman 1963), for example, show that the Mn is located principally in the octahedral sites. It would appear from these analyses that less than 5% of the total Mn is to be found in tetrahedral (Si) sites. In assigning absorption bands in the visible region in the spectra of the currently-studied minerals, it is logical to assume, initially, that octahedrally-bonded Mn(II) is the principal absorber. The energies of the absorption bands in the spectra of the Mn-containing minerals are also compared with the energies of bands in the spectra of materials known to contain octahedrally-bonded Mn(II).

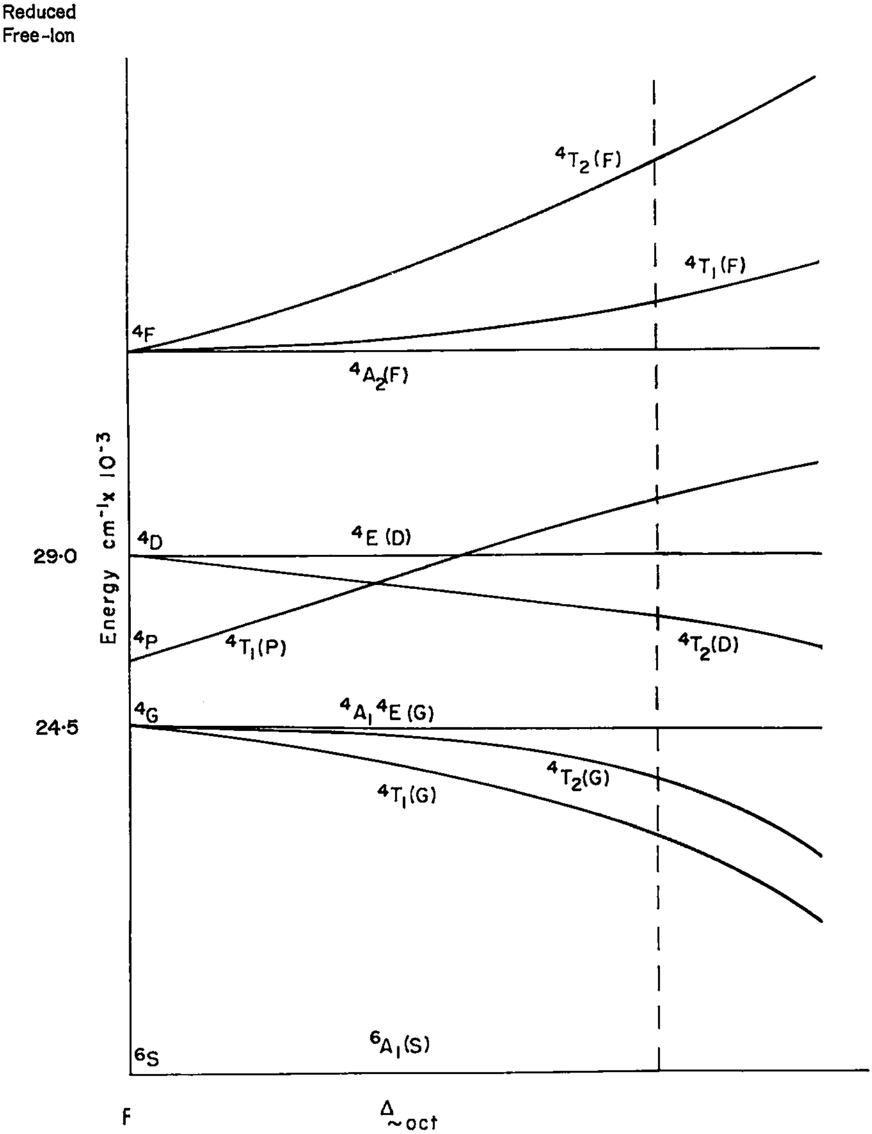

FIG. 1. Energy level diagram for d^5 ion in cubic field. Abscissa represents increasing strength of ligand field and dotted line represents inferred Δ value for the Mn-bearing silicates.

MATERIALS

The mineral specimens were obtained from Mr. H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada. The crystals came from the following locations: pyroxmangite, Shidosa, Aichi, Japan; rhodonite, Franklin, Sussex County, New Jersey; bustamite, Broken Hill, New South Wales; serandite, Mont St. Hilaire, Quebec.

The bustamite was light-brown in colour, and the other silicates were pink. Pyroxmangite and serandite crystals, of size 5 mm × 5 mm × 1 mm, were placed in one window of an aluminum crystal holder that had two variable-aperture windows. The holder fitted the cell compartment of a Beckman DK-2A spectrophotometer. Thin slivers of bustamite and rhodonite were mounted on quartz slides and masked with black masking tape to form "windows" of dimensions 2 mm × 2 mm. A similarly masked quartz slide was placed in the reference beam. All spectra were run at room temperature.

Discussion

Figures 2 to 5 present the absorption spectra of pyroxmangite, rhodonite, bustamite and serandite. In Table 1 are listed the energies of the absorption bands observed in the spectra of the above four minerals together with the energies of the absorptions due to octahedrally-bonded Mn(II) in $Mn(OH_2)_6^{2+}$ (Heidt, Koster & Johnson 1958) and KCl (Mehra & Venkateswarlu 1966). It is evident from the energies of the bands listed in Table 1 that most of the bands in the spectra of each of the four Mn-bearing chain silicates can be correlated with known spectra of octahedrally-bonded Mn(II). Chemical analyses of the minerals are given in Table 2.

Infrared spectra of pyroxmangite, rhodonite, bustamite and serandite

Let us first consider the absorption bands present in the infrared region of each spectrum shown in Figures 2 to 5. Each spectrum shows a band with $\epsilon \sim 2$ in the energy range 9,200 cm^{-1}–9,800 cm^{-1} that undoubtedly characterises octahedrally-bonded Fe(II). A band at ~10,000 cm^{-1} has been observed for octahedrally-bonded Fe(II) in MgO (Low & Weger 1960), in $Fe(OH_2)_6^{2+}$ (Holmes & McClure 1957) and also in actinolite, olivine and diopside (White & Keester 1966). For Fe(II) in cubic fields, the energy of the single spin-allowed absorption band is a linear function of the splitting (Δ) of t_{2g} and e_g orbitals. Therefore, assuming that a simple electrostatic point-charge model is valid, the absorptions for tetrahedrally-bonded Fe(II) should occur at $4/9 \times 9{,}500$ cm^{-1}, i.e. ~4,000 cm^{-1}. The absorption bands at 4,750 cm^{-1} in the pyroxmangite spectrum (Figure 2) and at 4,800 cm^{-1} in the serandite spectrum (Figure 5) could be due to Fe(II) in tetrahedral sites. A band in andradite spectra (Manning, unpublished work) at 5,600 cm^{-1} has also been attributed to tetrahedrally-bonded Fe(II), and we would suggest that the 5,600 cm^{-1} absorption in the bustamite spectrum (Figure 4) is due to

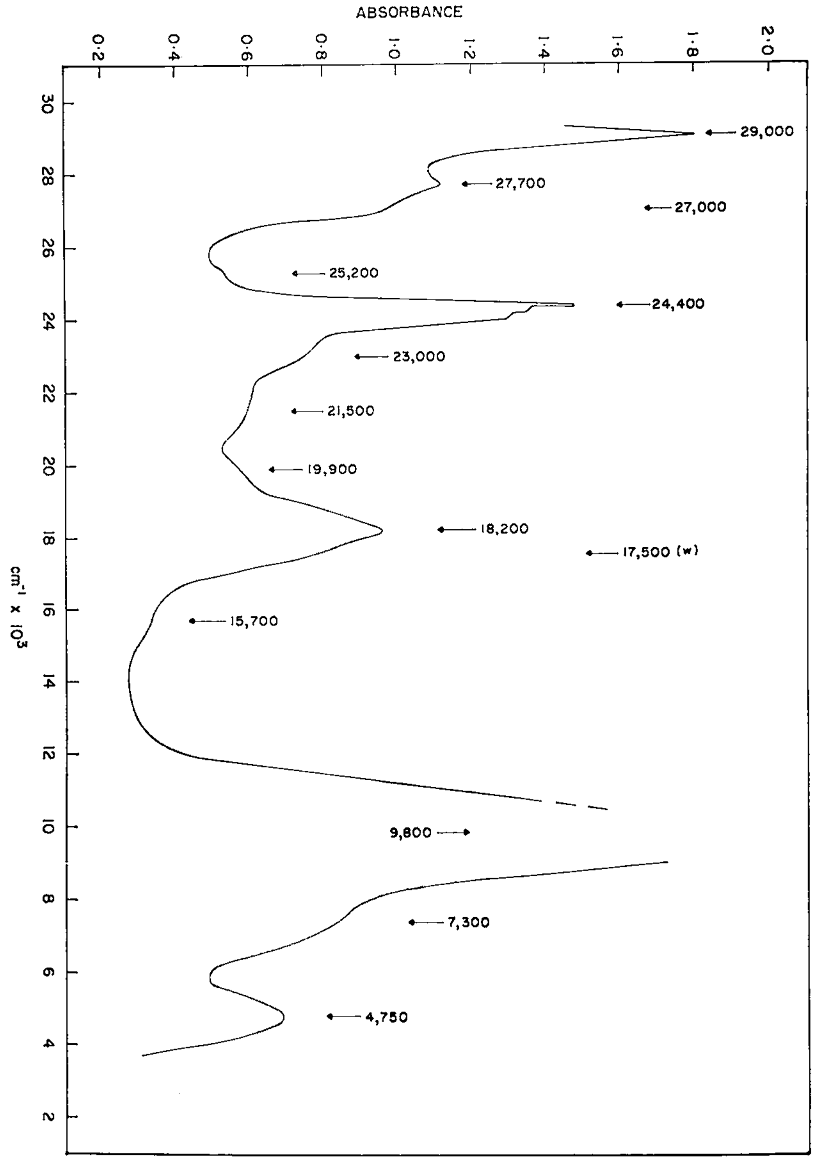

FIG. 2. Optical absorption spectrum of pyroxmangite. Crystal thickness = 1.35 mm.

Fe(II) in tetrahedral symmetry. Bates, White & Roy (1966) and Slack (1964) have attributed bands at ~4,500 cm^{-1} in the spectra of Fe-containing ZnO and $MgAl_2O_4$ to tetrahedrally-bonded Fe(II).

The spectra of pyroxmangite (Figure 2) and bustamite (Figure 4) exhibit absorptions at 7,300 cm^{-1} and 8,700 cm^{-1} that appear as shoulders

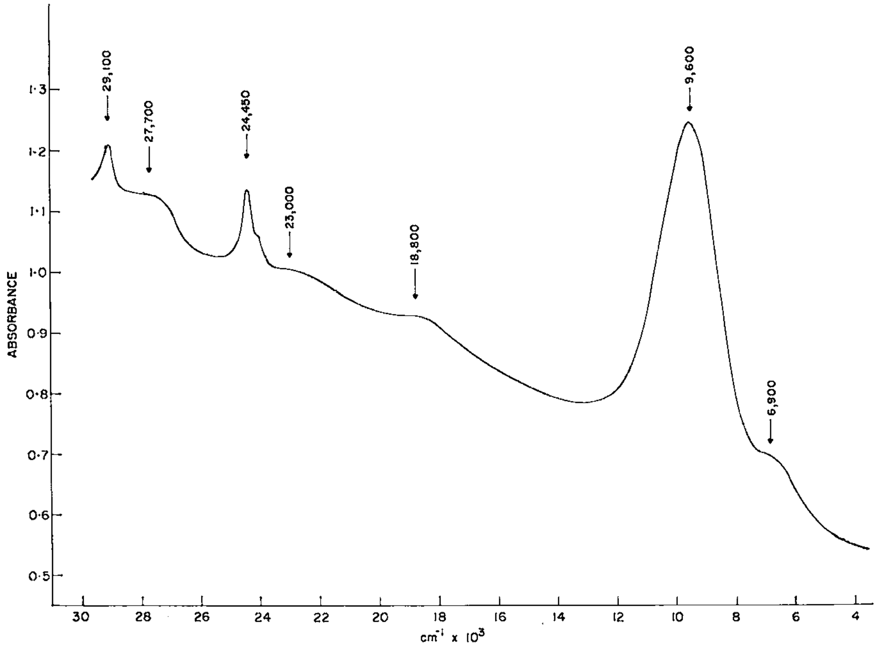

FIG. 3. Absorption spectrum of rhodonite. Crystal thickness = 0.3 mm.

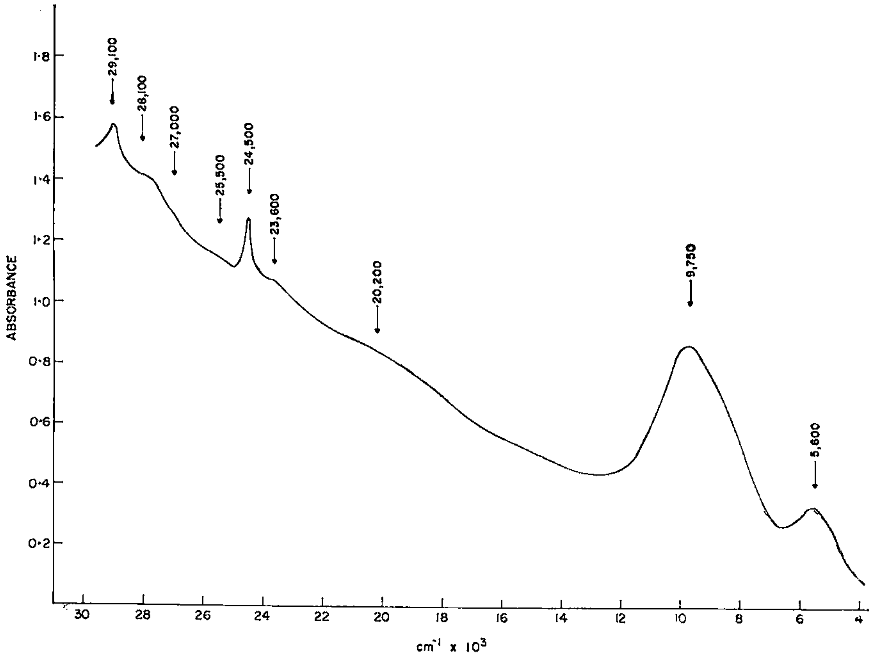

FIG. 4. Absorption spectrum of bustamite. Crystal thickness = 0.3 mm.

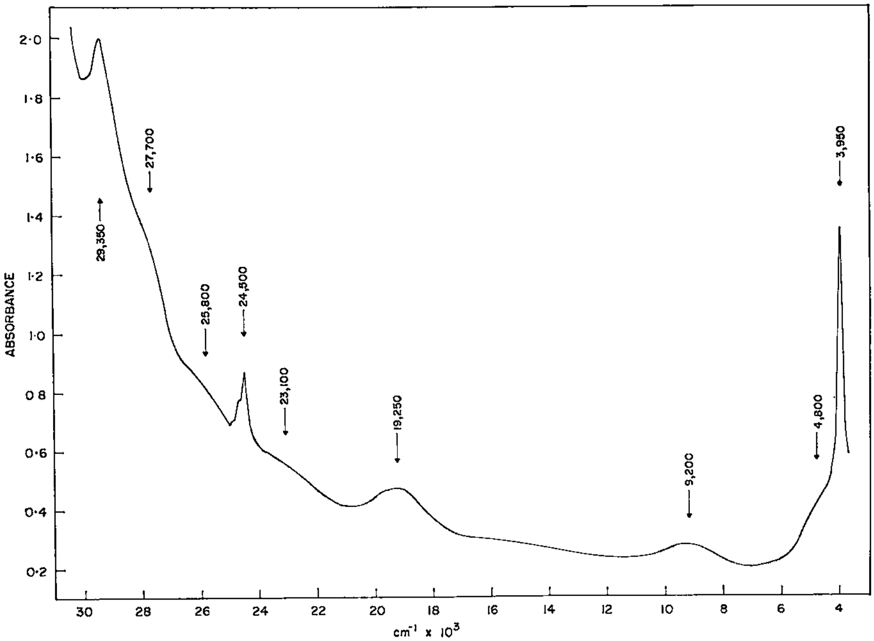

FIG. 5. Absorption spectrum of serandite. Crystal thickness = 0.9 mm.

on the low-energy limb of the major band attributed to octahedrally-bonded Fe(II). These shoulders are probably due to distortions in the O octahedron surrounding the Fe(II). The 7,300 cm^{-1} and 8,700 cm^{-1} bands are at too high an energy to be tetrahedrally-bonded Fe(II) bands, and in fact the tetrahedrally-bonded Fe(II) band is observed in pyroxmangite at

TABLE 1. A COMPARISON OF THE ENERGIES OF ABSORPTION BANDS IN SPECTRA OF CURRENTLY-STUDIED CHAIN SILICATES WITH ENERGIES OF Mn^{2+} BANDS IN WATER, KCl AND SPESSARTINE

$Mn(OH_2)_6^{2+}$	KCl	Spessartine	Pyroxmangite	Rhodonite	Bustamite	Serandite
			15,700			
18,870	19,400	20,800	18,200	18,800	20,200	19,250
			19,900			
			21,500			
23,120	22,700	23,500	23,000	23,000	23,600	23,100
			23,950			
25,100*	23,900*	24,500*	24,400*	24,450*	24,500*	24,500*
			25,200			25,800
			27,000		27,000	
27,980	27,200	27,000	27,700	27,700	28,100	27,700
29,750†			29,000†	29,100†	29,100†	29,350†

*Denotes very sharp absorption band.
†Denotes sharp absorption band.
In spessartine, Mn(II) is 8-coordinate.

TABLE 2. CHEMICAL ANALYSES OF Mn-BEARING SILICATES

	Serandite	Bustamite	Rhodonite
% Mn	28.5	17.4	23.2
% Fe	0.30	5.57	3.50
$\epsilon_{24,500}$	0.1	0.2	0.2
$\epsilon_{9,500}$	3	2	2

4,750 cm^{-1}. The 6,900 cm^{-1} band in rhodonite (Figure 3) cannot be assigned unequivocally, but it is very likely that it is also due to distortions in the octahedron. The 6,900 cm^{-1} rhodonite band is at a very similar energy to the 7,300 cm^{-1} band in pyroxmangite (Figure 2).

Spectra of octahedrally-bonded Mn(II)

The energy level diagram for a d^5 ion in a cubic field (Figure 1) affords an excellent base on which to begin the assignments of octahedrally-bonded Mn(II) bands. A notable feature of the energy level diagram in Figure 1 is that the $^4A_1{}^4E(G)$ and $^4E(D)$ excited states are parallel to the electronic ground state $^6A_1(S)$, i.e. the $^4A_1{}^4E(G)$ and $^4E(D)$ levels are field-independent. The absorption bands that characterise the electronic transitions $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ and $^6A_1 \rightarrow {}^4E(D)$ should therefore be sharper than the bands associated with transitions to other excited states derived from ^4G, ^4P and ^4D terms. Because the ligand atoms vibrate back and forth about a mean position, the strength of the ligand field (Δ) also oscillates about a mean value. Therefore, if the energy separation of the ground and excited states is relatively insensitive to Δ, only a narrow range of energy will be embraced over the range of the ligand vibration. Hence, in a qualitative fashion, the smaller the slope (of the excited state) the sharper the absorption band.

Let us now consider the relative widths of the absorption bands in Figures 2 to 5. It is readily apparent that the absorption bands at the approximate energies 24,500 cm^{-1} and 29,000 cm^{-1} in all four silicate spectra are considerably sharper than the other absorption bands in the visible region. The 24,400 cm^{-1} and 29,000 cm^{-1} bands in the pyroxmangite spectrum are impressively sharp. On the basis of the preceding discussion, therefore, we assign the absorption bands at the approximate energies 24,500 cm^{-1} and 29,000 cm^{-1} to the electronic transitions $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ and $^6A_1 \rightarrow {}^4E(D)$ respectively.

Referring to Figure 1, we find that three more absorption bands should be observed in the visible and near ultraviolet regions. The spectrum of rhodonite (Figure 3) shows five absorption bands in this energy range, and because the absorption bands at 24,450 cm^{-1} and 29,100 cm^{-1} have already been assigned, we may conclude that the 18,800 cm^{-1}, 23,000 cm^{-1}

and 27,700 cm^{-1} bands mark electronic transitions to the $^4T_1(G)$, $^4T_2(G)$ and $^4T_2(D)$ levels. The five absorption bands that characterise the Mn(II) in the spectra of pyroxmangite, bustamite and serandite (Figures 2, 4 and 5) are now evident, and the energies of the bands are listed in Table 1. The energies of the bands that we observe in our silicate spectra agree well with the energies of octahedrally-bonded Mn(II) bands in $Mn(OH_2)_6^{2+}$ (Heidt, Koster & Johnson 1958) and KCl (Mehra & Venkateswarlu, 1966). These workers also make similar assignments to ours. The currently-reported spectra for Mn(II) also agree with the spessartine spectra (Manning 1967) where Mn(II) is 8-coordinate.

Because the $^4A_1$ and ^4E states are not exactly degenerate, the absorption band marking the transition $^6A_1 \rightarrow {}^4A^4E(G)$ is split, and a shoulder is observed on the main band (Heidt, Koster & Johnson 1958). This weak shoulder is found in the pyroxmangite, rhodonite and serandite spectra (Figures 2, 3 and 5). The energy separation of peak and shoulder is 200 cm^{-1}, in agreement with the spectra of the octahedrally-bonded Mn(II) ions (e.g. Heidt, Koster & Johnson 1958). The 24,400 cm^{-1} band in pyroxmangite shows a second shoulder at 23,950 cm^{-1}, and the origin of this we shall discuss below.

Residual absorptions

The chain silicates studied here also exhibit absorption bands other than those attributable to octahedrally-bonded Mn(II) and octahedrally- and tetrahedrally-bonded Fe(II). Pyroxmangite has the following additional bands in the visible and near ultraviolet regions: 15,700 cm^{-1}, 17,500 cm^{-1} (weak), 19,900 cm^{-1}, 21,500 cm^{-1}, 23,950 cm^{-1}, 25,200 cm^{-1} and 27,000 cm^{-1}. Because no sharp bands are present in this group, it would seem that the amount of tetrahedrally-bonded Mn(II) in the currently-studied silicates is immeasurably small. A sharp band corresponding to the transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ (Figure 1) is also observed for tetrahedrally-bonded Mn(II) in other anionic environments (Cotton & Wilkinson 1967).

Other transition metal ions often present in silicate minerals are Ti(III) and Fe(III). The former ion exhibits an absorption band at $\sim$20,000 cm^{-1} in $Ti(OH_2)_6^{3+}$, and this band corresponds to the only allowed electronic transition $^2T_2 \rightarrow {}^2E(D)$. Spin-forbidden bands of octahedrally-bonded Fe(II) are also observed in the visible region (Manning, 1967), and this complicates the assignment of the residual absorptions in the pyroxmangite spectrum. The absence of sharp peaks among these residual absorptions further suggests that Fe(III), a d^5 ion, is unimportant. The 9,800 cm^{-1} Fe(II) band in the pyroxmangite spectrum (Figure 2) is very intense, and the intensities of the residual absorptions are certainly of the right order for spin-forbidden Fe(II) bands. The pyroxmangite crystal was too valuable a specimen to be destroyed for chemical analysis, but it is likely that most of the residual absorptions are spin-forbidden bands of Fe(II).

CONCLUSION

The optical absorption spectra of pyroxmangite, rhodonite and serandite show that the pink colours are due primarily to octahedrally-bonded Mn(II). The brown colour of bustamite can be attributed to octahedrally-bonded Mn(II) bands superimposed on a strong background absorption. Pyroxmangite has forbidden bands in the visible region due to Fe(II) in octahedral sites. All four silicates have bands in the infrared characteristic of Fe(II) in octahedral sites, while pyroxmangite, bustamite and serandite also show tetrahedrally-bonded Fe(II) bands.

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