

Spectroscopic studies of transition metal ions in spessartine garnet

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Abstract. From optical absorption studies at room and liquid air temperatures and from Mössbauer spectrum, the absorption bands of spessartine garnet are attributed to Mn^{2+} and Fe^{2+} ions. The energy matrices of d^5 and d^6 configurations are solved and the experimental data of Mn^{2+} and Fe^{2+} bands are fitted with the calculated values to solve for the Racah and crystal field parameters.

Keywords. Optical absorption; spessartine garnet; crystal field parameters; quadrupole splitting; isomer shift; Mössbauer spectrum.

1. Introduction

Manning (1967) and Langer (1977) investigated the optical absorption spectrum of spessartine garnet and concluded that the absorption bands are due to Mn^{2+} and Fe^{3+} or Fe^{2+} ions. However, the Mössbauer spectrum of spessartine garnet has not been reported. In order to confirm the ionic nature of the transition metal ions in spessartine garnet, the optical absorption and Mössbauer spectral studies have been undertaken and reported in this paper.

2. Experimental

The sample of pinkish red coloured spessartine garnet $[Mn_3Al_2(SiO_4)_3]$ was collected from Karnataka State, India. A crystal of 0.14 cm thickness was cut at random from the bulk sample and its optical absorption spectrum was recorded from $\lambda 1000$ nm to $\lambda 200$ nm on Hilger medium quartz spectrograph both at room and liquid air temperatures. The band maxima positions and oscillator strengths of the bands are calculated from the microphotometric profiles taken on a moll recording microphotometer. Spectrochemical analysis of the sample was carried out and it was found that manganese and iron were present in the sample, the former in large quantities.

3. Theory

In a cubic crystalline field, the ground state configuration for Mn^{2+} ion is written as $t_2^3e^2$. This gives rise to the electronic states 6A_1 , 4A_1 , 4E , 4T_1 , 4T_2 and a number of doublet states of which 6A_1 lies lowest and forms the ground state. The other electron configurations give rise to several doublet and quartet states.

The ground state configuration for Fe^{2+} ion in a cubic crystalline field is written as $t_{2g}^3 e_g^2$. This gives rise to electronic states 5T_2 , 3E , 3T_1 , 3T_2 and some triplet and singlet states of which 5T_2 forms the ground state. The other configurations give rise to several triplet and singlet states and one quintet state 5E .

4. Results and discussion

The microphotometric profiles of the bands of the sample recorded at liquid air temperature are shown in figure 1. Some of the bands could not be observed at room temperature. The observed energies, oscillator strengths along with the assignments of the bands are presented in table 1. From the nature and positions of the bands, they have been attributed to Mn^{2+} and Fe^{2+} ions. At room temperature, four bands have been recorded at 17222, 18800, 19727 and 24512 cm^{-1} . On cooling to liquid air temperature, the band at 18800 cm^{-1} exhibited a violet shift. At liquid air temperature, four extra bands have been recorded at 20227, 22806, 23335 and 24206 cm^{-1} .

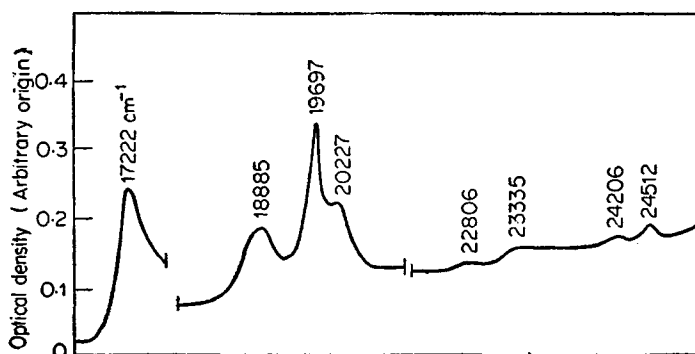


Figure 1. Microphotometric traces of the absorption bands of spessartine garnet at 80°K.

Table 1. Observed energies, oscillator strengths and assignments of the bands of spessartine garnet.

Band positions				Oscillator strengths ($f \times 10^8$)		Assignments
300K		80K		300 K	80 K	
λ (nm)	ν (cm^{-1})	λ (nm)	ν (cm^{-1})			
580.4	17222	580.4	17222	223.8	846.8	${}^5T_2 \rightarrow {}^3T_1 (H)$
531.7	18800	529.3	18885	7.4	124.3	${}^5T_2 \rightarrow {}^3T_2 (H)$
506.0	19727	507.5	19697*	66.6	105.7	${}^6A_1 \rightarrow {}^4T_1 (G)$
—	—	494.2	20227	—	8.5	${}^5T_2 \rightarrow {}^3T_1 (H)$
—	—	438.3	22806	—	5.0	${}^5T_2 \rightarrow {}^3E (H)$
—	—	428.4	23335*	—	10.2	${}^6A_1 \rightarrow {}^4T_2 (G)$
—	—	413.0	24206*	—	8.7	${}^6A_1 \rightarrow {}^4A_1 (G)$
407.8	24512	407.8	24512*	27.9	14.5	${}^6A_1 \rightarrow {}^4E (G)$

*Bands due to Mn^{2+} ; other bands due to Fe^{2+}

Of all the bands, the four sharp bands at 19697, 23335, 24206 and 24512 cm^{-1} are identified as due to Mn^{2+} ion and they are attributed to the spin forbidden transitions 4T_1 , 4T_2 , 4A_1 and 4E respectively (Manning 1967; Koide 1958; Lakshman and Reddy 1973; Tanabe and Sugano 1954). The two transitions ${}^6A_1 \rightarrow {}^4T_1$ and ${}^6A_1 \rightarrow {}^4T_2$ involve a change of configuration from $t_2^3e^2$ to $t_2^4e^1$ and are therefore expected to be broad. Moreover, the two energy levels have negative slopes in the energy level diagram for d^5 configuration and hence the bands should exhibit red shift at low temperature. In the present case, the two intense bands at 19697 and 23335 cm^{-1} are therefore attributed to ${}^4T_1(G)$ and ${}^4T_2(G)$ respectively. The red shift observed for the ${}^4T_1(G)$ band which is in accord with theory confirms our assignment. In the case of ${}^4T_2(G)$ measurements could not be recorded.

In d^5 configuration, since the electronic states ${}^4A_1(G) + {}^4E(G)$ and ${}^4E(D)$ are independent of Dq , the bands corresponding to these electronic levels should be sharp. The other two sharp and weak bands observed on the violet side at 24206 and 24512 cm^{-1} are therefore attributed to ${}^6A_1 \rightarrow {}^4A_1(G)$ and ${}^6A_1 \rightarrow {}^4E(G)$ transitions respectively.

The energy matrices for different states of d^5 configuration in a cubic crystalline field given by Tanabe and Sugano (1954) are solved on an IBM 370/155 computer. For different C/B values energy level diagrams are drawn between Dq/B and E/B to fit the experimental data with the theoretical values. The best fit of the observed bands is obtained for $C/B = 4.5$ with $B = 745 \text{ cm}^{-1}$ and $Dq = 633 \text{ cm}^{-1}$. The energy level diagram for Mn^{2+} with $C/B = 4.5$ along with the observed energies is shown in figure 2.

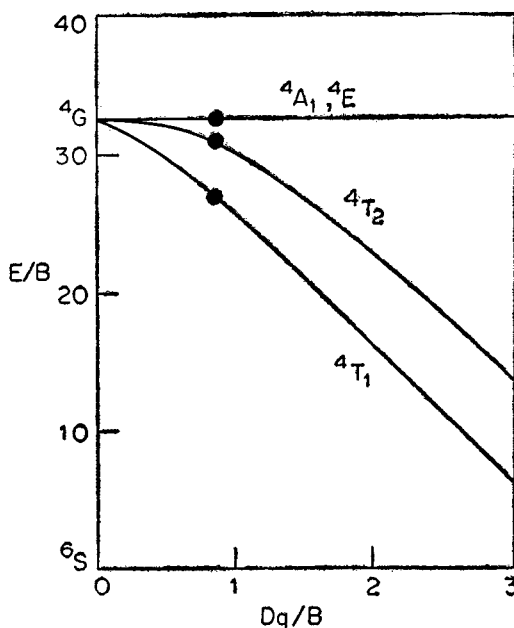


Figure 2. Energy level diagram of Mn^{2+} in cubic environment. E/B plotted as a function of Dq/B with $C/B = 4.5$. The solid circles show the experimental values at 80°K.

The remaining bands of the sample, from their nature, are attributed to Fe^{2+} ion. The band at 17222 cm^{-1} is assigned to ${}^5T_2 \rightarrow {}^3T_1$ transition. No change of energy is observed for this band at room and liquid air temperature as this is nearly field-independent. The band at 18800 cm^{-1} is assigned to ${}^5T_2 \rightarrow {}^3T_2$ transition. The other two weak bands at 20227 and 22806 cm^{-1} which are observed only at liquid air temperature are assigned to ${}^5T_2 \rightarrow {}^3T_1$ and ${}^5T_2 \rightarrow {}^3E$ transitions respectively. The intense band observed in the far infrared at 3500 cm^{-1} is assigned to ${}^5T_2 \rightarrow {}^5E$ transition as this is the only spin-allowed band expected for Fe^{2+} ion and as its energy is nearly equal to $10 Dq$.

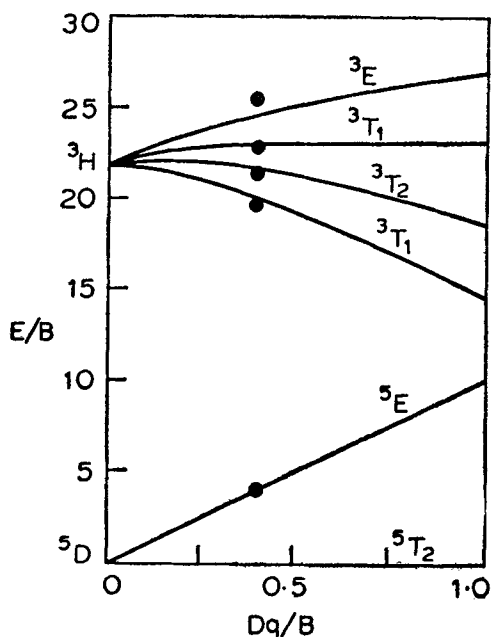


Figure 3. Energy level diagram for Fe^{2+} ($C/B = 4.5$) (Solid circles show the experimental values at 80°K).

Table 2. Comparison of crystal field parameters for Mn^{2+} and Fe^{2+} ions in different crystals

Sample	Ion	B (cm^{-1})	C (cm^{-1})	Dq (cm^{-1})	Reference
KCl	Mn^{2+}	760	2955	590	Mehra and Venkateswarlu (1966)
RbMnF_3	Mn^{2+}	840	3080	780	Mehra and Venkateswarlu (1967)
Rhodonite	Mn^{2+}	760	3290	750	Lakshman and Reddy (1973)
NaMnF_3	Mn^{2+}	845	3040	775	Srivastava and Mehra (1972)
Present sample (Spessartine garnet)	Mn^{2+}	745	3352	633	
Almandine	Fe^{2+}	890	4000	600	Moore and White (1972)
Present sample	Fe^{2+}	890	4005	356	

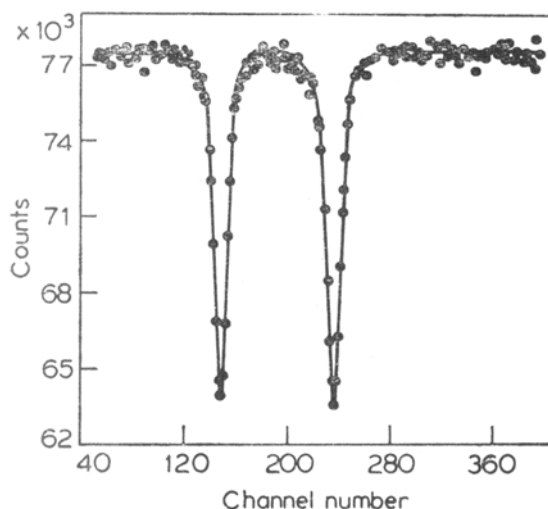


Figure 4. Room temperature Mössbauer spectrum of spessartine garnet.

The energy matrices for different states of d^6 configuration have been solved and the best fit is obtained for $C/B = 4.5$ with $B = 890 \text{ cm}^{-1}$ and $Dq = 356 \text{ cm}^{-1}$. The energy level diagram for Fe^{2+} with $C/B = 4.5$ along with the observed energies is shown in figure 3. Comparison of crystal field parameters for Mn^{2+} and Fe^{2+} ions in different crystals is given in table 2.

From the Mössbauer spectrum (figure 4) recorded at room temperature, the quadrupole splitting and the isomer shift for spessartine garnet were found to be 3.5772 mm/sec and 1.5447 mm/sec respectively. From these parameters the ionic nature of iron was confirmed as Fe^{2+} (Bancraft *et al* 1967).

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