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Electron paramagnetic resonance and optical absorption spectra of Cr³⁺ ions in fluorophosphate glasses

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Abstract. Electron paramagnetic resonance and optical absorption studies of Cr³⁺ ions in fluorophosphate glasses have been carried out at room and low temperatures. The EPR spectra exhibit two resonances at $g \approx 4.67$ and $g \approx 2.0$. These resonances are attributed to isolated Cr³⁺ ions and exchange coupled Cr³⁺ pairs respectively. The EPR spectra were also studied at various low temperatures. The numbers of spins are found to be increasing with decreasing temperature. For the first time, the magnetic susceptibility χ was calculated from the EPR data. It was also observed that as temperature decreases χ increases in accordance with Curie's law. The line width of the $g \approx 2.0$ resonance was found to be decreasing with increasing temperature which confirms the pairing mechanism between Cr³⁺ ions. The exchange coupling constant J between Cr³⁺ ions was calculated from the relative intensities of $g \approx 2.0$ resonance line at various temperatures. The optical absorption spectrum exhibits four bands, characteristic of Cr³⁺ ions in octahedral symmetry. The crystal field parameter Dq and the Racah interelectronic repulsion parameters B and C were evaluated.

1. Introduction

Fluorophosphate glasses are promising host materials for optical applications because of their optical properties, low refractive indices, low dispersion and good transparency from the ultraviolet to the infrared regions of the optical spectra [1, 2]. Seeber *et al* [3] studied, in detail, the spectroscopic and laser properties of Cr³⁺ ions in fluoride phosphate and phosphate glasses. Gan Fuxi *et al* [4] studied the EPR spectra of Cr³⁺ ions in fluoride phosphate glasses at room temperature only. Since the variation of EPR line intensity with temperature allows us to calculate the exchange-interaction energy between Cr³⁺ pairs, the present investigation has been undertaken to study the EPR spectra from the room temperature to low temperature regions. Also this paper presents an attempt to calculate the magnetic susceptibility and Curie constant from low temperature EPR data.

2. Experiment

Glasses studied in the present work were kindly provided by Professor W Seeber (Germany). Table 1 gives the composition of the glasses studied in the present work as given by Seeber *et al* [3]. Approximately 100 mg of the finely powdered samples of the glasses were used for EPR measurements. The EPR spectra at room temperature were recorded on a JEOL-FE-1X ESR spectrometer operating in the X-band frequency of 9.205 GHz with a field modulation of

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Table 1. Composition of glasses studied in the present work.

Glass	\sum fluorides (mol%)	\sum phosphates (mol%)	Cr	Nd	Ce
WS FP 6*	94	6	0.1	0.9	0.08
WS FP 10*	90	10	>5	—	—

100 kHz. The magnetic field was scanned from 0 to 500 mT and the field was swept at a rate of 125 mT min^{-1} . A polycrystalline DPPH with a g value of 2.0036 was used as a standard field marker. The EPR spectrum of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powdered substance was recorded at 9.205 GHz as a reference to calculate the number of spins.

EPR spectra were also recorded at different temperatures. The temperature was varied using a JES-UCT-2AX variable temperature controller. A temperature stability of $\pm 1 \text{ K}$ was easily obtained by waiting for about 30 minutes at the set temperature before recording the spectrum.

The optical absorption spectra of the Cr^{3+} doped fluoride phosphate glasses were recorded at room temperature on a Perkin–Elmer spectrophotometer in the wavelength range of 390 to 850 nm.

3. Results and analysis

3.1. EPR spectra

Figure 1 shows the EPR spectra of two glass samples (WS FP 6*: 0.1 Cr–0.9 Nd–0.08 Ce and WS FP 10*: Cr) at room temperature. The EPR spectrum of the WS FP 6* glass sample shows two resonance signals at $g \approx 4.67$ and $g \approx 2.0$, while the EPR spectrum of the WS FP 10* glass sample is characterized by a strong resonance in the vicinity of $g \approx 4.67$ along with a weak resonance at $g \approx 2.0$.

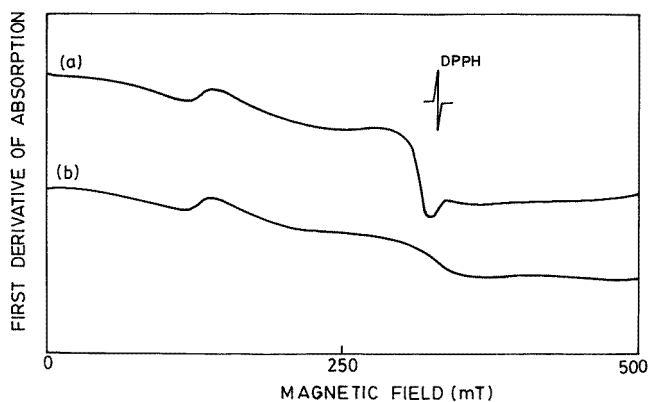


Figure 1. X-band EPR spectra of (a) WS FP 6* and (b) WS FP 10* glass samples at room temperature.

Figure 2 shows the EPR spectra of the WS FP 6* glass sample at various low temperatures. The EPR spectrum of the WS FP 10* glass sample was recorded at 123 K also and no significant changes were observed in intensity, linewidth and g values.

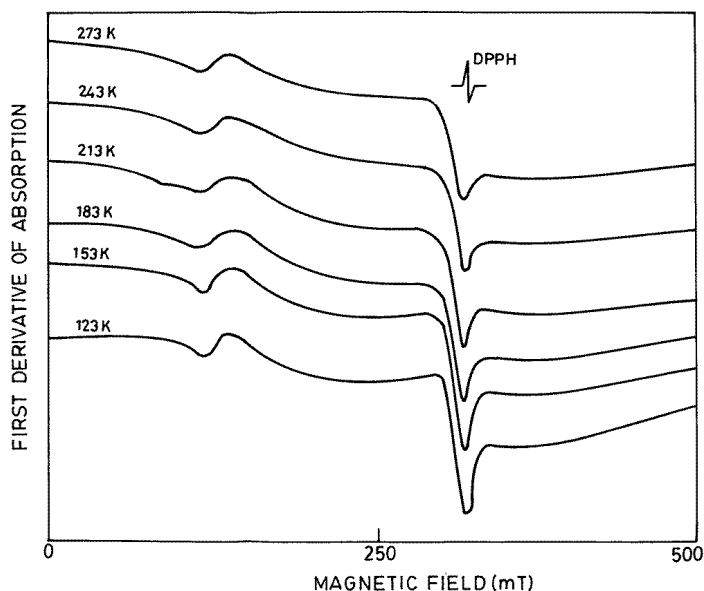


Figure 2. X-band EPR spectra of WS FP 6* glass sample at various low temperatures.

3.2. Number of spins

The number of spins can be calculated with the help of a reference ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in this study) by using the formula [5]

$$N = \frac{A_x (\text{Scan}_x)^2 G_{std} (B_m)_{std} (g_{std})^2 [S(S+1)]_{std} [\text{Std}]}{A_{std} (\text{Scan}_{std})^2 G_x (B_m)_x (g_x)^2 [S(S+1)]_x} \quad (1)$$

where A is the area under the absorption curve which can be obtained by double integration of the first derivative absorption curve; Scan is the magnetic field corresponding to unit length of the chart; G is the gain; B_m is the modulation field width; g is the g factor; S is the spin of the system in its ground state. The subscripts x and std represent the corresponding quantities for the Cr^{3+} sample and the reference ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) respectively. $[\text{Std}]$ represents the concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the reference taken.

The number of spins is calculated according to equation (1) as a function of temperature. Figure 3 shows a plot of $\log N$ against $1/T$.

3.3. Paramagnetic susceptibility from EPR data

EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula

$$\chi = \frac{Ng^2\beta^2 J(J+1)}{3k_B T} \quad (2)$$

where N is the number of spins per m^3 ; the rest having their usual meanings. N can be calculated from equation (1) and g is taken from EPR data. Paramagnetic susceptibility was calculated at various temperatures. A plot of the susceptibility χ as a function of the reciprocal of temperature is shown in figure 4.

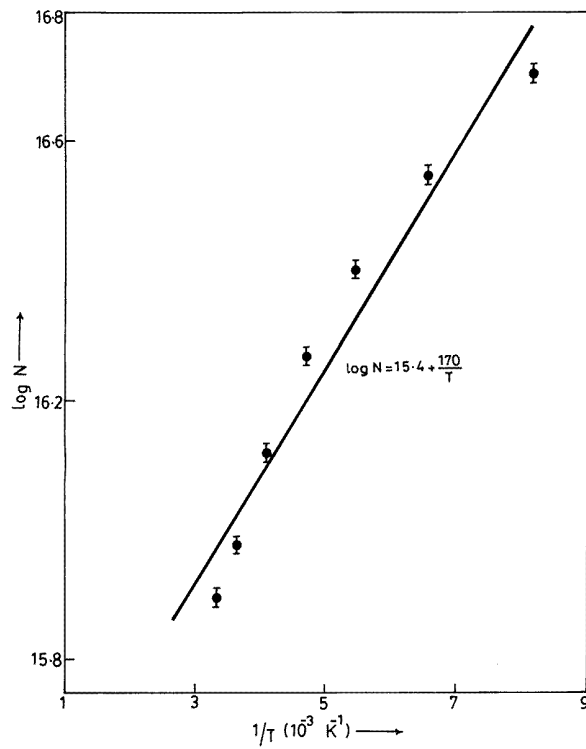


Figure 3. Variation of $\log N$ against $1/T$ for 100 mg of WS FP 6* glass sample.

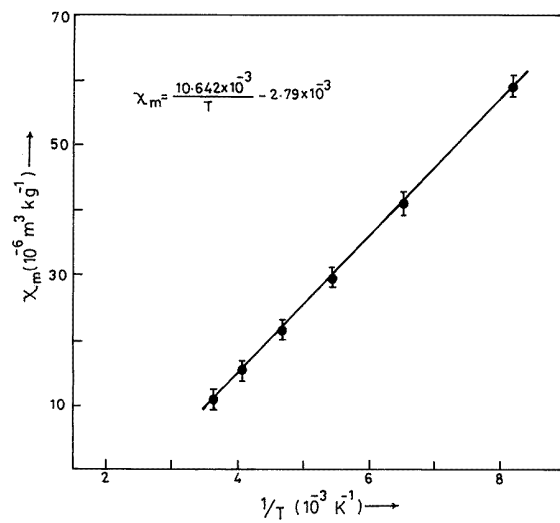


Figure 4. A plot of χ as a function of reciprocal of temperature ($1/T$) for the WS FP 6* glass sample.

The line width of the $g \approx 2.0$ resonance line was measured as a function of temperature. Figure 5 shows the variation of the line width ΔH as a function of absolute temperature T .

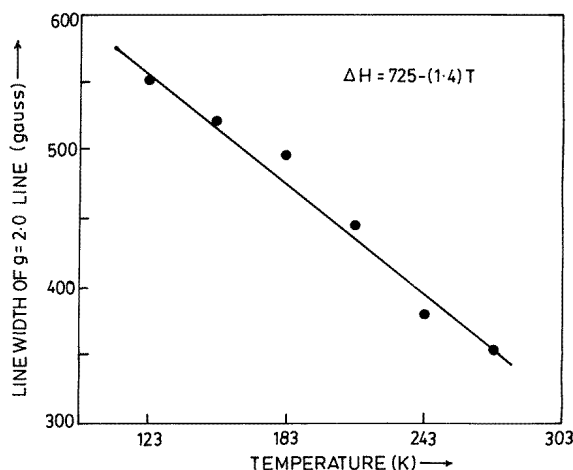


Figure 5. Variation of linewidth ΔH as a function of absolute temperature T for the $g \approx 2.0$ resonance line of the WS FP 6* glass sample.

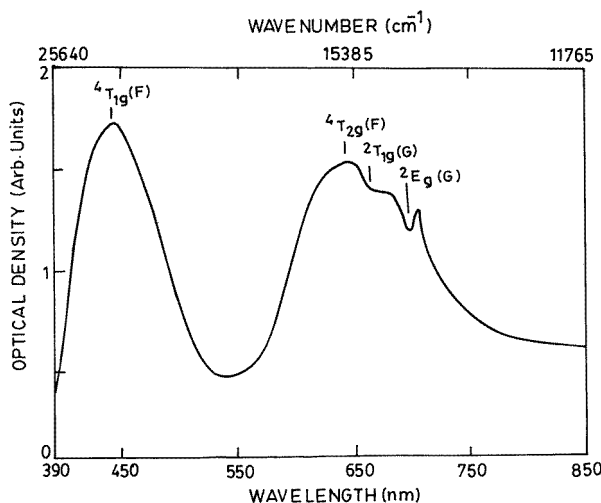


Figure 6. Optical absorption spectrum of the WS FP 6* glass sample at room temperature.

3.4. Optical absorption spectrum

The optical absorption spectrum of the glass sample WS FP 6* was recorded in the wavelength range from 390 nm to 850 nm. Figure 6 shows the optical absorption spectrum of this sample at room temperature.

The optical absorption spectrum shows two broad bands at 445 nm (22470 cm^{-1}) and 643 nm (15550 cm^{-1}) along with one weak band centred at 671 nm (14900 cm^{-1}) and a sharp band at 717 nm (13945 cm^{-1}). The observed bands are characteristic of Cr^{3+} ions in octahedral symmetry. The two broad bands are assigned to the spin-allowed transitions ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ in decreasing order of energy, while the weak

Table 2. Observed and calculated band positions along with their assignments for Cr³⁺ ions in fluorophosphate glasses ($Dq = 1555 \text{ cm}^{-1}$, $B = 720 \text{ cm}^{-1}$ and $C = 2904 \text{ cm}^{-1}$).

Transition	Observed wavelength (nm)	Observed wavenumber (cm ⁻¹)	Calculated wavenumber (cm ⁻¹)
⁴ A _{2g} (F) →			
⁴ T _{1g} (F)	445	22 470	22 462
⁴ T _{2g} (F)	643	15 550	15 550
² T _{1g} (G)	671	14 900	14 390
² E _g (G)	717	13 945	13 525

band is assigned to ⁴A_{2g}(F) → ²E_g(G) and the sharp band is assigned to ⁴A_{2g}(F) → ²E_g(G) respectively. The observed band positions along with their assignments are given in table 2.

4. Discussion

4.1. EPR spectra

Cr³⁺ ions belong to the d³ configuration with a large octahedral site preference energy (OSPE) [6]. In an octahedral field, its ground state is ⁴A_{2g}. In the presence of a low symmetry component and spin-orbit coupling, the fourfold degeneracy spin states split into two Kramers doublets. In glasses, a large separation between the two doublets leads to the resonance at $g = 2$ to 6 [7]. The Cr³⁺ ions may exist in glasses as both isolated Cr³⁺ ions in the glassy network and antiferromagnetic exchange coupled Cr³⁺-Cr³⁺ pairs aggregating together [7].

EPR spectra of Cr³⁺ ions in phosphate [4, 7, 8], fluorophosphates [4], borosulphates [9], fluoroberyllates [4], fluoroaluminates [10], fluorozirconates [11] and silicates [12] were reported by many authors. In all these glasses two resonances were observed at $g \approx 5.0$ and $g \approx 2.0$; they have been attributed to isolated Cr³⁺ ions in strongly distorted sites and Cr³⁺ ion pairs [4, 8–12] respectively.

Gan Fuxi *et al* [4] studied the EPR spectra of Cr³⁺ ions in fluorophosphate glasses at room temperature only. They reported resonances at $g \approx 4.89$ and $g \approx 4.97$ for fluorophosphate glasses. In the present work, we observed resonances in the vicinity of $g \approx 4.7$ and $g \approx 2.0$.

The resonance in the high field region ($g \approx 2.0$) is observed in the high Cr³⁺ content [7]. Landry *et al* [7] attributed this phenomenon as arising due to the presence of both exchange coupled Cr³⁺ ion pairs and isolated Cr³⁺ ions. This general change in the EPR spectrum, from an initial low field absorption to one at high field with increased Cr³⁺ content implies the presence of more than one paramagnetic species in the glass. On the other hand, they found the optical absorption spectrum independent of the Cr³⁺ ion content for the whole Cr₂O₃ concentration range studied. Hence they attributed the variation in the EPR spectrum to a combination of isolated octahedrally coordinated Cr³⁺ ions and antiferromagnetic coupled pairs of Cr³⁺ ions which are individually sixfold coordinated.

Despite this, Paul and Upreti [13] observed an entirely different EPR pattern in Na₂O-B₂O₃ glasses. They observed $g_{\parallel} \approx 1.938$ and $g_{\perp} \approx 1.986$ for the entire Cr³⁺ content range studied (0.019 wt% of Cr to 1.870 wt% of Cr). Also they observed the EPR line becoming asymmetric with increasing alkali content.

In the present study, as shown in figures 1 and 2, we observed two resonances, at $g \approx 2.0$ and $g \approx 4.67$. The resonance at $g \approx 4.67$ was assigned to the isolated Cr³⁺ ions. The resonance at $g \approx 2.0$ may be due to both exchange coupled Cr³⁺ ions and isolated Cr³⁺ ions. The temperature dependent linewidth of this resonance confirms the pairing of Cr³⁺ ions (see figure 5) and hence the resonance at $g \approx 2.0$ may be attributed to exchange coupled Cr³⁺

ions. The intensities of both the resonance lines were increasing with decreasing temperature. The EPR results indicate that not all the Cr³⁺ ions are truly diluted in the glass but there is some coupling. The coupling may also appear for complex aggregates having more than two chromium ions.

Figure 3 shows the variation of the logarithm of number of spins ($\log N$) in 100 mg of the WS FP 6* glass sample as a function of $1/T$. From the figure, we can observe that the $\log N$ is varying linearly with $1/T$. The data are fitted to a straight line $\log N = 15.4 + (170/T)$ by the method of least squares.

Figure 4 shows a plot of the paramagnetic susceptibility (χ) of Cr³⁺ ions in the WS FP 6* glass sample as a function of $1/T$. The data is fitted to the straight line $\chi_m = (10.64 \times 10^{-3})/T - (2.79 \times 10^{-3})$. From the figure, it is clear that as temperature is increased, the susceptibility of the sample decreases obeying the Curie law. Further, the slope of the line gives the Curie constant (10.64×10^{-3}) which is of the same order expected for a paramagnetic ion [14].

Figure 5 shows the variation of the linewidth with temperature for the $g \approx 2.0$ resonance in the WS FP 6* glass sample. From the figure, it is clear that as temperature is increased, the line width decreases. Since the $g \approx 2.0$ resonance line is attributed to the Cr³⁺ pairs, a dipolar broadening may affect the linewidth as temperature is varied. In fact, this is observed in the present work. Further it may be noted that the spin–spin relaxation causes an increase of ΔH when the temperature decreases while spin–lattice relaxation normally leads to an increase of ΔH when temperature increases [15]. Similar observations in temperature dependent linewidths were reported by Baiocchi *et al* [16] and Stober and Nofz [17] for Fe³⁺ ions in glasses.

4.2. Coupling constant J between Cr³⁺ pairs

Fournier *et al* [18] gave the following expression to calculate the relative intensity at various temperatures:

$$I(T) = \frac{4 \exp(-J/kT) + 20 \exp(-3J/kT) + 56 \exp(-6J/kT)}{1 + 3 \exp(-J/kT) + 5 \exp(-3J/kT) + 7 \exp(-6J/kT)} \quad (3)$$

where J is the coupling constant between the Cr³⁺ ion pairs, k is the Boltzmann constant and T is the absolute temperature.

Fournier *et al* [18] observed that the intensity of the resonance signal at $g \approx 2$ increases with increasing temperature if exchange is antiferromagnetic. In the present case we observed, in contrast to Fournier *et al* [18], a decrease in signal intensity with increasing temperature. Haouari *et al* [8] also observed a similar phenomenon where they assigned the $g \approx 2$ resonance to the isolated Cr³⁺ ions. From the variation of linewidth of the $g \approx 2.0$ resonance line (figure 5) with temperature, we can attribute the resonance as arising due to exchange coupled Cr³⁺ ions. The decrease in intensity with increase in temperature is possible only if the exchange interaction between Cr³⁺ ion pairs is ferromagnetic in nature. Hence, in the present case the $g \approx 2.0$ resonance line is attributed to the Cr³⁺ pairs coupled through ferromagnetic interaction.

The intensities were determined by double integration of the ESR first derivative curves. The relative intensities were measured with respect to the intensity at room temperature. Figure 7 shows the relationship between relative intensity, $I(T)$, and kT for different J values calculated using equation (3). Figure 7 also shows the experimental values superimposed on the theoretical curves. Fournier *et al* [18] has taken a spin 1/2 sample as standard for measuring the relative intensities. In the present work, the relative intensities were measured with respect

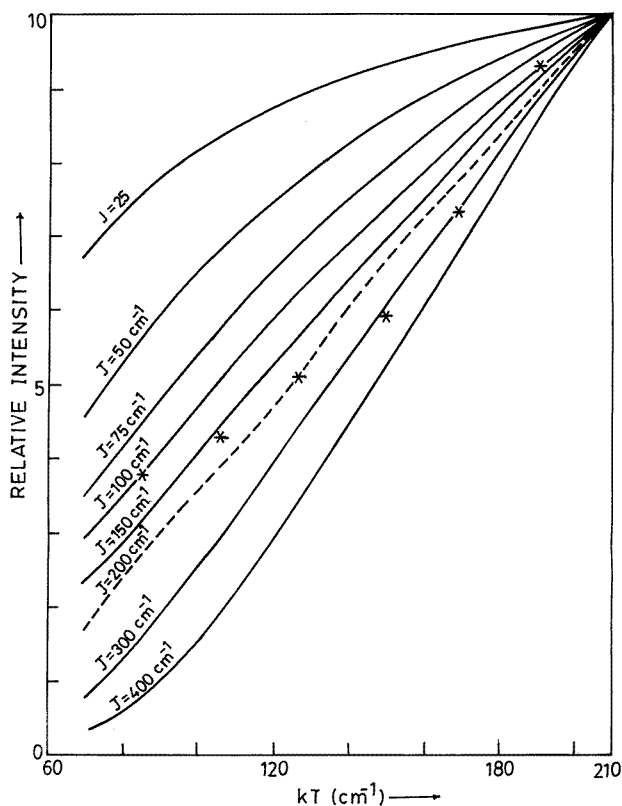


Figure 7. Variation of relative intensity (equation (3)) of EPR spectra with kT for various J values. The experimental points are superimposed. The dashed line shows the curve that fits best for the experimental values.

to the intensity at room temperature. Hence, all the curves have been scaled to a factor of 10 at room temperature (corresponding to $kT \approx 209 \text{ cm}^{-1}$). The experimental data is fitted to the theoretical curves by the method of the χ^2 -test [19] (for goodness of fit—shown by the dashed line in figure 7). The best fit was found for a coupling constant of $J = 200 \text{ cm}^{-1}$. The value is very much higher than the value reported ($J = 24 \pm 2 \text{ cm}^{-1}$) by Fournier *et al* [18] but is of the same order as for Cr^{3+} ions in ruby reported by Statz *et al* [20] and Mollenauer and Schawlow [21].

4.3. Optical absorption spectra

In general, the Cr^{3+} ions in octahedral symmetry are characterized by three spin-allowed transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$. In the present study, only two bands corresponding to the first two transitions are observed. The absorption spectrum also shows fine structure in the ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ band which is due to the transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^2E_g(\text{G})$ ($13\,945 \text{ cm}^{-1}$) and ${}^4A_{2g}(\text{F}) \rightarrow {}^2T_{1g}(\text{G})$ ($14\,900 \text{ cm}^{-1}$). These transitions are interpreted as Fano antiresonances and the transition energies are assigned to the minima rather than to the spectral peaks [22]. The crystal field parameter Dq is evaluated from the band position of ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ and found to be $Dq = 1555 \text{ cm}^{-1}$. The Racah

interelectronic repulsion parameter B can be evaluated using the relations [12]:

$$\frac{Dq}{B} = \frac{15(x-8)}{x^2-10x} \quad (4)$$

where $x = (E_1 - E_2)/Dq$.

Here E_1 and E_2 represent the energies of ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively. Using equation (4), the Dq/B -ratio was found to be ≈ 2.16 which leads to a B -value of about 720 cm^{-1} . The C -value is evaluated using the relation given by Rasheed *et al* [23]:

$$\frac{C}{B} = \frac{1}{3.05} \left[\frac{E(^2E)}{B} - 7.9 + 1.8 \left(\frac{B}{Dq} \right) \right] \quad (5)$$

which results in a value of $C \approx 2904 \text{ cm}^{-1}$. Adam *et al* [24] gave the expressions to solve the above parameters. Table 2 lists the band positions calculated using the Adam equations [24] for $Dq = 1555 \text{ cm}^{-1}$, $B = 720 \text{ cm}^{-1}$ and $C = 2904 \text{ cm}^{-1}$ along with the observed band positions. These values are consistent with the values reported by Seeber *et al* [3].

Table 3 gives the crystal field parameter Dq and Racah parameters B and C for Cr³⁺ ions in different glasses reported in the literature. The ratio Dq/B for all the glasses is also shown. From the table, it is evident that the Dq/B -value is smaller for silicate glasses than the fluorophosphate, sulphate and lead silicate glasses.

Table 3. Crystal field parameters (Dq) and Racah parameters (B and C) for Cr³⁺ ions in different host glasses.

Glass system ^a	Dq (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)	Dq/B	Reference
FP 10	1552	734	—	2.11	[3]
FP 20	1553	721	—	2.15	[3]
PBaK	1522	708	3356	2.15	[8]
LiZBS	1569	641	3095	2.45	[9]
Silicate	1565	855	2904	1.83	[12]
NRC-7	1543	810	2932	1.9	[22]
SLS7b/7	1555	759	2609	2.05	[23]
ZBLA	1531	721	3461	2.12	[24]
BIZYT	1563	728	3438	2.15	[24]
Sulphate	1595	585	3189	2.73	[25]
Fluorophosphate (3)	1552	770	3165	2.02	[26]
WSFP6*	1555	720	2904	2.16	Present work

^a Notations are those used in the references cited.

The free ion B -value [27] of Cr³⁺ ion is $B = 918 \text{ cm}^{-1}$. In the present case, we observed a B -value of 720 cm^{-1} , which suggests that the bonding between the transition metal ion (Cr³⁺) and the ligand is an ionic one.

The bonding can also be predicted from the expression given by Seeber *et al* [3].

$$h = [(B_{free} - B)/B_{free}]/k_{Cr^{3+}} \quad (6)$$

where h and k are nephelauxetic functions of the ligands and central metal ion respectively. For the Cr³⁺ ion, the value of $k = 0.21$ [28]. In the present work, we obtained a value of $h = 1.08$. This value is close to the value reported for Cr³⁺ ions surrounded by six H₂O molecules [28] which also suggests that the bonding between Cr³⁺ and the ligands in the present work is ionic.

5. Conclusions

(1) EPR spectra of Cr^{3+} ions in fluorophosphate glasses were studied at room and low temperatures. The EPR spectra exhibit two resonances at $g \approx 4.67$ and $g \approx 2.0$ which are attributed to the isolated Cr^{3+} ions and exchange coupled Cr^{3+} pairs respectively.

(2) The absolute number of spins were calculated using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a standard reference. A linear relationship between $\log N$ and $1/T$ was established.

(3) The magnetic susceptibility χ was calculated from EPR data. A linear relationship was observed between χ and $1/T$ for Cr^{3+} ions.

(4) The variation of linewidth ΔH with temperature T was studied. It is found that as T increases ΔH decreases. This confirms the dipole interaction between the paired Cr^{3+} ions.

(5) The relative intensities of the EPR signal were measured at various temperatures to evaluate the exchange coupling constant J . The fit between observed and theoretical values were performed using a χ^2 -test and the best fit is found for $J = 200 \text{ cm}^{-1}$.

(6) The optical absorption spectrum shows four bands characteristic of Cr^{3+} ions in octahedral symmetry. From the analysis of the optical absorption bands, the crystal field and Racah parameters were evaluated.

(7) From the EPR and optical absorption spectra, it is concluded that Cr^{3+} ions have octahedral symmetry in the fluorophosphate glasses.

Acknowledgments

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