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EPR and magnetic susceptibility studies of Cr_2O_3–Bi_2O_3–GeO_2 glasses

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Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements have been performed on $xCr_2O_3(1-x)[Bi_2O_3 \cdot GeO_2]$ glasses with $0 < x \leqslant 20$ mol%. These data show that the chromium ions are in Cr^{3+} valence state and for $x \leqslant 5$ mol% they are isolated or experience dipole–dipole interactions. For higher Cr_2O_3 content the Cr^{3+} ions participate to the dipole–dipole and superexchange type interactions.

1. Introduction

Data on degree of short-range ordering in disordered solids may be provided by electron paramagnetic resonance (EPR) which is well known to supply valuable information about the local site symmetry. 3d ions are used as paramagnetic probes of the local order in diamagnetic vitreous matrices, the fine structure parameters of their EPR absorption spectra being very sensitive to local structure.

There is a great variety of vitreous systems for which Cr^{3+} EPR spectra were reported. In phosphate glasses of complex composition Zacharov *et al.* [1] detected Cr^{3+} ion EPR resonances with anisotropic g factors having the values $g_\perp = 1.78$ and $g_\parallel = 5.0$. The EPR spectrum and the optical absorptions of Cr^{3+} ions were studied as a function of Cr_2O_3 content in another phosphate system by Landry *et al.* [2]. They evidenced that the EPR spectrum gradually changes with increasing Cr_2O_3 concentration, from an initial low-field absorption assigned to isolated, octahedrally co-ordinated Cr^{3+} ions, to one at high field with a $g \approx 2.0$ attributed to exchange coupled pairs of Cr^{3+} ions, which are individually six-fold co-ordinated. The antiferromagnetic nature of the coupling was elucidated by Fournier *et al.* [3].

In sodium borate glasses studied by Loveridge *et al.* [4] only a $g \approx 2.0$ resonance was observed, the shape of which is dependent on the alkali content. The absence of higher g resonances was interpreted as proving a zero field-splitting of the observed chromium centre considerably smaller in borate than in phosphate glasses [5].

In chalcogenide glasses chromium impurity atoms may exist in various valence states according to the EPR and magnetic susceptibility data reported by Chepeleva *et al.* [6]. Besides being incorporated into the glass network Cr^{3+} ions may exist in microcrystalline inclusions.

In $3B_2O_3 \cdot PbO$ glasses studied by Ardelean *et al.* [7] using EPR, X-ray diffraction, and magnetic measurements, both Cr^{3+} and Cr^{5+} species were detected. For lower concentrations than 3 mol% Cr_2O_3 the EPR spectrum consists in absorptions centred at $g \approx 5.1$ caused by isolated Cr^{3+} ions and a narrow, asymmetric resonance at $g \approx 1.98$ caused by Cr^{5+} ions. With increasing the chromium oxide concentration a broad absorption due to Cr^{3+} ions coupled by magnetic superexchange interactions superimposes at $g \approx 1.97$ the Cr^{5+} EPR absorption line. For concentrations higher than 20 mol% Cr_2O_3 microcrystalline precipitates of Cr_2O_3 were detected, which change the magnetic behaviour of the glass.

The $g \approx 1.98$ absorptions caused by Cr^{5+} ions were also detected in soda-lime–silicate glass fibres [8] and other oxide glasses containing chromium ions [9–13].

Cr^{3+} ions were used as local probes in fluoride glasses [14–17] because they adopt octahedral co-ordination in a fluoride medium, and the network is built up from corner-shared octahedra. Dance *et al.* [15] studied the EPR spectrum of Cr^{3+} ions in a fluoro-aluminate glass and considered the large absorption centred at $g = 1.98$ as caused by exchange within the pair of Cr^{3+} ions. The X-band Cr^{3+} EPR spectrum exhibits two broad resonances at $g = 5.0$ and $g = 1.97$ as reported for chromium fluoride glasses studied by Leigh *et al.* [18]. The $g = 5.0$ resonance was attributed to isolated Cr^{3+} ions in strongly distorted sites characterized by $\Delta > h\nu$ values, Δ being the zero field splitting between the two Kramer doublets. The $g = 1.97$ resonance attributed to isolated Cr^{3+} ions, is related to weakly distorted sites characterized by $\Delta < h\nu$. The resonance at $g = 2.0$ generally observed in fluoride glasses was assigned to Cr^{3+} ions pairs [2, 14, 15]. From the frequency dependence of the spectra studied in [17] it was proved that Cr^{3+} ions are characterized by a continuous fine structure parameter distribution in the range 0.06–0.55 cm^{-1}, which was taken into account for simulations of these spectra.

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Cr^{3+} ion alkali–zinc–borosulfate glasses were investigated by Rao *et al.* [18]. The EPR spectra exhibit an intense resonance line centred at $g = 1.99$ and two less intense resonance lines at $g = 4.93$ to 4.97 and $g = 5.26$. The low-field spectral resonance lines were attributed to isolated Cr^{3+} ions. From the EPR and optical data it was concluded an octahedral site symmetry around Cr^{3+} ions, and a predominantly covalent character of the bonds.

The glasses based on heavy metal oxides (bismuth and/or lead) were intensively investigated [19]. These glasses are characterized by high density, high refractive index, high thermal expansion, low transformation temperature and excellent infrared transmission [20, 21]. Since the network bond strengths of heavy metal oxide glasses are relatively weak compared to those of silicate and borate glasses, the glass forming regions are comparatively limited [19, 22, 23]. There have been several works on the formation of Bi_2O_3 containing multi-component glasses from the point of view of practical applications. The local structure around bismuth in Bi_2O_3-containing glasses has been discussed in [20, 24]. The glass formation and structure of $xBi_2O_3 \cdot yGeO_2$ system have been investigated by Lottici *et al.* [25]. Ardelean *et al.* [26–29] have studied the glass formation, structure and magnetic properties of $xMO \cdot (1-x)[Bi_2O_3 \cdot GeO_2]$ glasses with $MO = Gd_2O_3$, CuO, MnO and Fe_2O_3.

This paper aims to investigate Cr_2O_3–Bi_2O_3–GeO_2 glasses having in view the above mentioned interest for glasses based on heavy metal ions and the possibility to use chromium dopant ions as local probes in vitreous matrices. EPR and magnetic susceptibility data allow to establish correlations between their bulk properties as determined by susceptibility measurements and their local properties as determined by EPR investigation.

2. Experimental procedure

We investigated the $xCr_2O_3 \cdot (1-x)[Bi_2O_3 \cdot GeO_2]$ glasses with $0 < x \leq 20$ mol % Cr_2O_3. The starting materials were reagent grade purity Cr_2O_3, Bi_2O_3 and GeO_2. The samples were prepared by oxides mixing in suitable proportion and melting in sintered corundum crucibles at 1250 °C for 10 min. The melts were poured on stainless steel plates. The structure of the samples was studied by X-ray analysis and did not reveal any crystalline phase up to 20 mol % Cr_2O_3. In glasses with $x > 20$ mol % Cr_2O_3, the X-ray diffraction patterns evidenced microcrystalline precipitates of Cr_2O_3 [7].

The EPR measurements were realized at room temperature, in X-band (9.4 GHz) and 100 kHz field modulation, with a Jeol-type equipment.

The magnetic data were obtained with a Faraday-type balance in the temperature range 80–300 K.

3. Results and discussion

3.1. EPR results

3.1.1. Theoretical approach

Most of the above mentioned papers assign the low-field resonance absorptions of Cr^{3+} ($3d^3$; ${}^4F_{3/2}$) ions in glasses to isolated ions subjected to a strong orthorhombic crystal field arising from a slightly distorted octahedral environment. The ${}^4F_{3/2}$ state splitting in strong crystalline field of rhombic symmetry may be obtained by using the spin Hamiltonian

$$\mathscr{H} = g\beta HS + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

where β is the Bohr magnetron, H the magnetic field, S the effective electronspin and the parameters D and E represent the axial and the rhombic distortions of the octahedron, respectively. Cr^{3+} ions have a d^3 ($L = 3$, $S = 3/2$) electron configuration (where L is orbital moment). Their interaction with the crystalline field is strong and is the principal term determining the energy levels. Since the spin–orbit interaction and the crystalline field distortions act on the singlet orbital, the Zeeman term will split the two Kramers doublets and the energy levels will depend on the magnetic field and consequently on D and E. Several transitions may occur between the doublet levels for each direction of the magnetic field. According to Wickman *et al.* [30] the spin Hamiltonian (Equation 1) may be written as

$$\begin{aligned}\mathscr{H} &= S_z^2 - \tfrac{1}{3}S(S+1) + \lambda(S_x^2 - S_y^2) + g\beta HS \\ &= \mathscr{H}_0 + g\beta HS \qquad (2)\end{aligned}$$

introducing the parameter $\lambda = E/D$ with distinct values within $0 \leq \lambda \leq 1/3$. Only positive values of λ are taken into account.

In zero magnetic field, the crystalline field term, after diagonalization, introduces the ground state splitting into two Kramers doublets

$$\psi_i(\pm) = a_i|\pm 3/2\rangle + b_i|\mp 1/2\rangle \qquad i = 1;2 \quad (3)$$

corresponding to the energy levels (in units of D)

$$\varepsilon_i = (-1)^{i+1}[3\lambda^2 + 1] \qquad i = 1;2 \quad (4)$$

The coefficients a_i and b_i

$$a_i = \left(\frac{\varepsilon_i + 1}{2\varepsilon_i}\right)^{1/2} \qquad b_i = \left(\frac{\varepsilon_i - 1}{2\varepsilon_i}\right)^{1/2} \quad (5)$$

are functions of the parameter λ, according to Equation 4.

The principal values of the effective g tensor are calculated as

$$\begin{aligned}g_i(x) &= 4[3^{1/2}a_ib_i + b_i^2] \\ g_i(y) &= 4(-1)^{i+1}[3^{1/2}a_ib_i - b_i^2] \qquad (6) \\ g_i(z) &= 2(-1)^{i+1}(3a_i^2 - b_i^2)\end{aligned}$$

For $\lambda = 0$ corresponding to a pure axial field, one obtains $g_1(x) = 0$, $g_1(y) = 0$, $g_1(z) = 6$ (forbidden transitions), and $g_2(x) = g_2(y) = 4$, $g_2(z) = 2$ resulting in absorptions characterized by $g_\parallel = 4$ and $g_\perp = 2$ values. For $\lambda = 1/3$, corresponding to a pure rhombic field, one obtains $g_1(x) = 2$, $g_1(y) = 1.46$, $g_1(z) = 5.46$ and $g_2(x) = 2$, $g_2(y) = 5.46$, $g_2(z) = 1.46$. Consequently, for Cr^{3+} ions in rhombic vicinities the resonance absorptions occur at 5.46, 2 and 1.46 values of g_{eff}.

According to Equation 6 one may represent the g_{eff} variation as a function of λ, for the two doublets, and obtain diagrams which allow to determine the values of λ characterizing the Cr^{3+} ions vicinity for any value of experimentally detected g. Such diagrams were used by Trif *et al.* [31] to identify the sites involving Cr^{3+} in molecular sieves (zeolites).

Because of the crystalline field parameters distribution in glasses the absorption lines are generally broadened and often appear as a superposition of more contributions. In other materials, as silicalites [32] or aluminas [12], where the structural units are better defined, the absorption lines are sharper and therefore easier to be localized on both spectra and diagrams.

3.1.2. Experimental results

The investigated $xCr_2O_3 \cdot (1-x)[Bi_2O_3 \cdot GeO_2]$ glasses show EPR absorption spectra due to Cr^{3+} ($3d^3$) ions within $1 \leq x \leq 20$ mol % Cr_2O_3. The spectra are presented in Fig. 1.

At the lowest limit of concentration ($x = 1$ mol %) the spectrum consists of two absorption lines centred at $g \approx 4.8$ and $g \approx 2.0$. At higher concentrations ($x > 1$ mol %) the high-field absorption line is overlapped by a more intense one with $g \approx 1.98$, increasing in intensity as the Cr_2O_3 content of the sample rises up to 20 mol % Cr_2O_3. In contrast to this increase, the low-field absorption line decreases, disappearing for $x > 5$ mol % Cr_2O_3. This absorption is detailed in Fig. 2 for the best resolved spectrum. The line-width of the $g \approx 1.98$ absorption line increases within the investigated concentration range but the slope of this increasing changes for samples containing more than 5 mol % Cr_2O_3. The line-width dependence on the Cr_2O_3 content is presented in Fig. 3 for the high-field absorption line.

As presented in Section 1, the low-field resonances at $g \approx 5.0$ evidenced in the Cr^{3+} EPR spectra in glasses, were generally attributed to isolated Cr^{3+} ions in distorted sites, characterized by large zero field splitting of the ground state energy level. The most intense low-field absorption was detected in our spectra for $x = 1$ mol % Cr_2O_3. As shown in Fig. 2 the line is centred at $g \approx 4.8$ and extends from $g \approx 5.6$ to $g \approx 4.3$. According to the previously presented theory these absorptions may be attributed to isolated Cr^{3+} ions subjected to a strong orthorhombic crystalline field arising from a slightly distorted octahedral environment. Because of the fine-structure parameter distribution they are broad and may be regarded as a superposition of contributions from sites with slightly different axial distortions. There is another

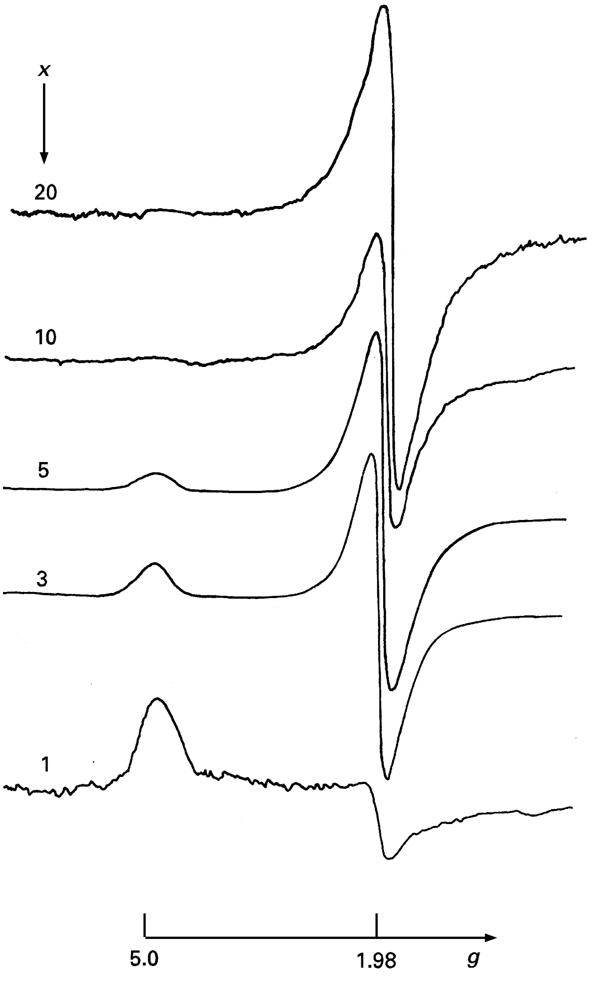

Figure 1 EPR absorption spectra of Cr^{3+} in glasses of $xCr_2O_3 \cdot (1-x)[Bi_2O_3 \cdot GeO_2]$ system.

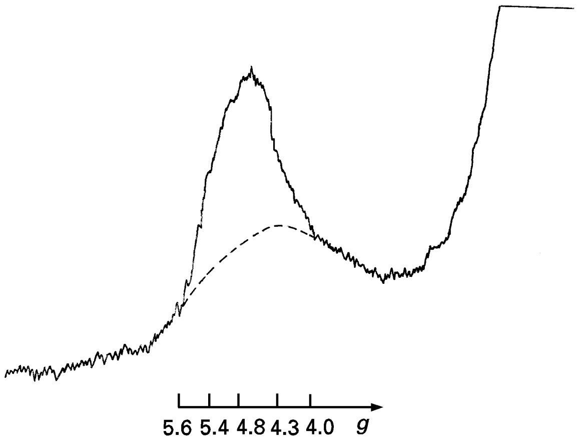

Figure 2 The low-field absorption corresponding to the samples with $x = 1$ mol % Cr_2O_3.

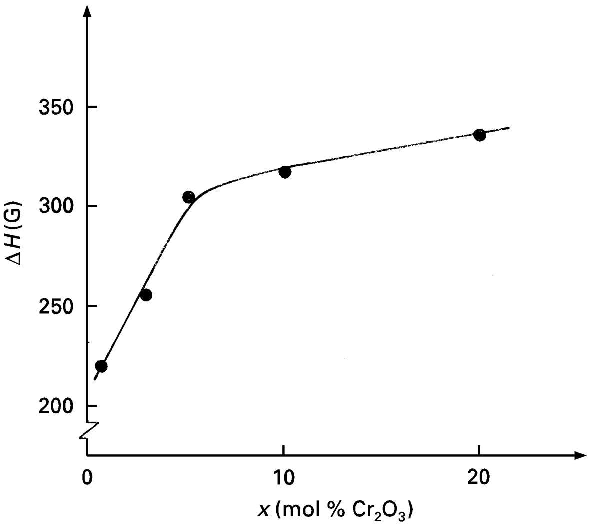

Figure 3 The composition dependence of $g = 1.98$ line-width for $xCr_2O_3 \cdot (1-x)[Bi_2O_3 \cdot GeO_2]$ glasses.

broad absorption as background of the previous one, centred at $g \approx 4.0$, approximated by the dotted line in Fig. 2, which may be attributed to sites with a predominantly axial character. According to the g_{eff} dependence on λ expressed by Equation 6 small variations of λ from the 0 value give greater differences between $g_1(z)$ and $g_2(y)$ values than those between $g_1(z)$ and $g_2(y)$ when λ deviates from 1/3. This explains the great extension of the absorption at $g \approx 4.0$ due to λ fluctuations, comparatively to that corresponding to the $g \approx 4.8$ absorption arising from sites with a predominantly rhombic character. For both $g \approx 4.8$ and $g \approx 4.0$ resonances, there is the corresponding $g \approx 2.0$ absorption line, theoretically justified in Section 3.1.1, so the EPR absorption spectrum for samples with $x = 1\,\mathrm{mol\%}$ Cr_2O_3 may be regarded as arising from isolated Cr^{3+} ions, characterized by $\Delta > h\nu$. The structural units involving Cr^{3+} in sites of strong crystalline field become less represented as the Cr_2O_3 content of the sample increases, the corresponding absorption intensity decreases, and the line disappears for $x > 5\,\mathrm{mol\,\%}$ Cr_2O_3 (Fig. 1). When Cr^{3+} ions accumulate glass matrix in the neighbourhood of the initially isolated ions is progressively disturbed so that their former vicinity has no more a well defined symmetry.

The high-field absorption at $g \approx 1.98$ increases when the Cr_2O_3 on the sample rises within $1 \leq x \leq 20\,\mathrm{mol\,\%}$ Cr_2O_3. The line-width evolution presented in Fig. 3 indicates a linear increase up to $x = 5\,\mathrm{mol\,\%}$ Cr_2O_3 because of dipolar interactions. This variation satisfies the relation given by Kittel and Abrahams [33] for dipolar interactions according to which the line-width is proportional to the magnetic ions content participating at resonance. Thus

$$\Delta H_{\text{d-d}} = (g\mu/a^3)x \tag{7}$$

where $\Delta H_{\text{d-d}}$ is the dipolar line-width, a is some average "lattice" parameter, μ is the magnetic moment of the ion and x is its molar fraction. This relation was used by Moon *et al.* [34] to demonstrate the iron ions clustering in barium borate glasses, and verified by Burzo *et al.* [35] for Fe^{3+} ions in lead borate glasses and by Ardelean *et al.* [36] for Mn^{2+} ions in lead tellurite glasses.

For samples having $x > 5\,\mathrm{mol\,\%}$ Cr_2O_3 the line-width evolution illustrated in Fig. 3 shows exchange interaction narrowing. At these concentrations the dipole–dipole and magnetic superexchange interactions coexist. For the high-field absorptions of these samples a slight shift of g values to 1.97 was also noticed. One may conclude that in our glasses, within $1 \leq x \leq 5\,\mathrm{mol\,\%}$ Cr_2O_3, the high-field resonances at $g \approx 1.98$ are caused by isolated Cr^{3+} ions in weakly distorted sites characterized by $\Delta < h\nu$ and dipole–dipole interacting ones. For samples containing $x > 5\,\mathrm{mol\,\%}$ Cr_2O_3 the absorptions are caused by Cr^{3+} ions pairs, simultaneously coupled by dipole–dipole and exchange-type mechanisms. The dipolar broadening of the absorption line is affected by narrowing due to the exchange interactions within the Cr^{3+} ion pairs.

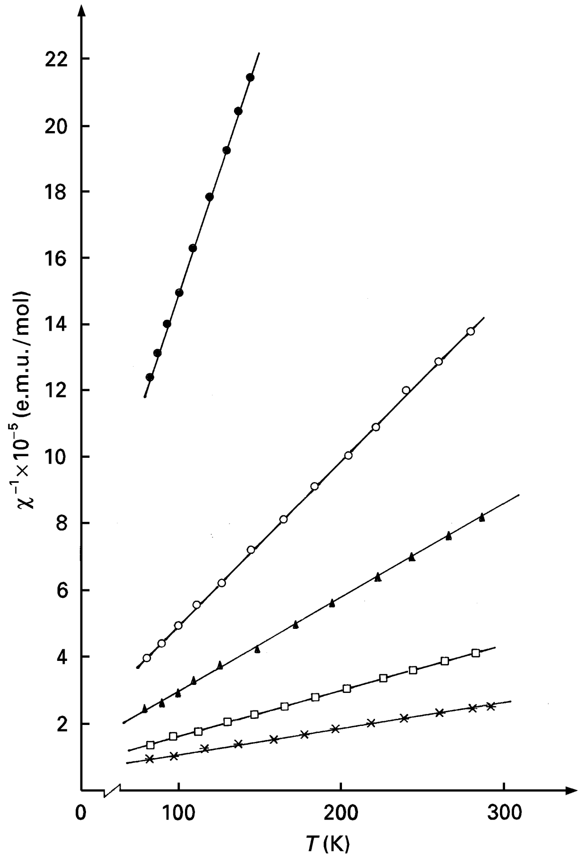

Figure 4 Temperature dependence of the reciprocal magnetic susceptibility for glasses of $x\mathrm{Cr_2O_3}\cdot(1-x)[\mathrm{Bi_2O_3}\cdot\mathrm{GeO_2}]$ system. mol % Cr_2O_3: x = (●) 1; (○) 3; (▲) 5; (□) 10; (*) 20.

3.2. Magnetic susceptibility data

The $Bi_2O_3 \cdot GeO_2$ glass matrix exhibits temperature independent diamagnetism ($\chi_d \approx -0.21 \times 10^{-6}$ e.m.u./g). Adding of Cr_2O_3 to the $Bi_2O_3 \cdot GeO_2$ glass matrix leads to paramagnetic behaviour in the studied temperature range.

The temperature dependence of the reciprocal magnetic susceptibility of some glasses from the studied system are presented in Fig. 4. For glasses with $x \leq 5\,\mathrm{mol\,\%}$ Cr_2O_3, the Curie law is observed. This suggests that chromium ions are magnetically isolated in this composition range. On the other hand the EPR data indicated that Cr^{3+} ions are electrically isolated or experience dipole–dipole interactions. For $x > 5\,\mathrm{mol\,\%}$ Cr_2O_3 the reciprocal magnetic susceptibility obeys the Curie–Weiss law with a negative paramagnetic Curie temperature θ_p. For these glass compositions the high temperature magnetic susceptibility data indicate that the chromium ions are predominantly antiferromagnetically coupled. In this case, the magnetic interactions take place only at short range and can determine the micromagnetic type behaviour [37, 38]. These results are in agreement with the EPR study conclusions which indicated that for $x > 5\,\mathrm{mol\,\%}$ Cr_2O_3 the Cr^{3+} ions experience superexchange-type interactions. A similar conclusion was reached by Landry *et al.* [2] and confirmed by Fournier *et al.* [3] for phosphate glasses containing Cr^{3+} ions, and by Ardelean *et al.* in their studies of

TABLE I Magnetic moment, paramagnetic Curie temperature and molar Curie constant for $x\mathrm{Cr_2O_3}\cdot(1-x)[\mathrm{Bi_2O_3}\cdot\mathrm{GeO_2}]$ glasses

x (mol % Cr_2O_3)	μ_{eff} (μ_B)	θ_p (K)	C_M (e.m.u./mol)
1	3.87	0	0.03738
3	3.86	0	0.11158
5	3.86	0	0.18566
10	3.86	− 18	0.37226
20	3.84	− 42	0.73753

chromium ions in $3B_2O_3\cdot PbO$ [7], $2B_2O_3\cdot Li_2O$ [13] and $Bi_2O_3\cdot PbO$ [39] glasses.

The composition dependence of the paramagnetic Curie temperature, θ_p, is presented in Table I. The absolute magnitude of the θ_p values increases for $x > 5$ mol % Cr_2O_3. In general, the θ_p and exchange integral values increase with the magnetic ions content of the sample [7, 40]. Therefore, the magnitude of the paramagnetic Curie temperature increases with the Cr_2O_3 content.

The composition dependence of the molar Curie constant, C_M, is also presented in Table I. The values of the Curie constant, which are proportional to the Cr^{3+} ions concentration, vary linearly with the chromium oxide concentration. The experimental values obtained for the effective magnetic moment $\mu_{eff} = (3.86 \pm 0.02)\,\mu_B$, where μ_B is the Bohr magneton (Table I) are very close to the magnetic moment of Cr^{3+} in the free ion state: $\mu_{Cr^{3+}} = 3.87\,\mu_B$ [41], in agreement with the values usually observed in the paramagnetic salts [41] containing chromium ions.

4. Conclusions

In $x\mathrm{Cr_2O_3}\cdot(1-x)[\mathrm{Bi_2O_3}\cdot\mathrm{GeO_2}]$ glasses only Cr^{3+} species were detected by means of EPR and magnetic susceptibility measurements, for $0 < x \leq 20$ mol % Cr_2O_3.

For samples containing $0 < x \leq 5$ mol % Cr_2O_3 magnetically isolated Cr^{3+} ions were detected, in octahedral symmetric sites subjected to various distortions. For strongly distorted sites EPR absorptions at $g \approx 4.8$ and $g \approx 4.0$ were detected. These absorptions may be attributed to isolated Cr^{3+} ions in sites subjected to strong crystal field effects, having a predominantly rhombic, respectively axial, character. For the slightly distorted sites absorptions at $g \approx 1.98$ were detected. These may be attributed to Cr^{3+} ions involved in dipole–dipole coupling.

For samples containing $x > 5$ mol % Cr_2O_3 the high-field resonances were attributed to Cr^{3+} ions magnetically coupled by superexchange mechanisms and dipole–dipole interactions.

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