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EPR and magnetic susceptibility studies of $x\mathrm{Cr_2O_3}-(1\text{-}x)\ 3\mathrm{B_2O_3}-\mathrm{PbO}$ glasses

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By using X-ray diffraction analysis, EPR and magnetic measurements, the chromium-ion distribution in $x\mathrm{Cr_2O_3}-(1-x)[3\mathrm{B_2O_3}-\mathrm{PbO}]$ glasses with $0 \leqslant x \leqslant 35$ mol% $\mathrm{Cr_2O_3}$ was studied. EPR investigation evidenced the presence of both $\mathrm{Cr^{3+}}$ and $\mathrm{Cr^{5+}}$ ions, the latter being in small proportion, in agreement with the atomic magnetic moment values.
For concentrations $x \leqslant 20$ mol% $\mathrm{Cr_2O_3}$ the isolated $\mathrm{Cr^{3+}}$ ions coexist with those coupled by super-exchange magnetic interactions, the isolated ones prevailing only for $x < 3$ mol% $\mathrm{Cr_2O_3}$. For $x > 20$ mol% $\mathrm{Cr_2O_3}$ microcrystalline precipitates were detected, giving rise to an antiferromagnetic transition with Néel temperature, $T_\mathrm{N} \simeq 310$ K and paramagnetic Curie temperature, $\theta_\mathrm{p} = -480$ K.

1. Introduction

Electron paramagnetic resonance (EPR) spectra of $\mathrm{Cr^{3+}}$ ions in a phosphate glass having a composition of 13 mol% $\mathrm{K_2O}$–30 mol% ZnO–7 mol% $\mathrm{Al_2O_3}$–50 mol% $\mathrm{P_2O_5}$ exhibit anistropic g-factors of $g_\perp = 1.78 \pm 0.015$ and $g_\parallel = 5.0 \pm 0.2$ [1]. In another phosphate glass containing 90 wt% $\mathrm{Al(PO_3)_3}$ + 10 wt% ZnO, the EPR spectrum, as well as the optical absorption of $\mathrm{Cr^{3+}}$ ions, has been studied systematically as a function of $\mathrm{Cr_2O_3}$ content in the range 0.098 to 8.69 wt% [2]. The EPR spectrum exhibits a marked concentration dependence. The spectrum at low field was assigned [2] to that of isolated $\mathrm{Cr^{3+}}$ ions. In high $\mathrm{Cr_2O_3}$-content glasses, the EPR spectrum is dominated by the build-up of a line in the vicinity of $g \sim 2.0$. This feature at high field has been attributed to exchange-coupled $\mathrm{Cr^{3+}}$ ion pairs. Thus, the gradual change in the EPR spectrum, from an initial low-field absorption to one at high field with increased $\mathrm{Cr_2O_3}$ concentration, implies the presence of more than one paramagnetic species in the glass. Since the optical spectrum remains essentially unchanged for the whole $\mathrm{Cr_2O_3}$ concentration range studied, the observed variation in the EPR spectrum has been attributed to a combination of isolated octahedrally co-ordinated $\mathrm{Cr^{3+}}$ ions and antiferromagnetic coupled pairs of $\mathrm{Cr^{3+}}$ ions, which are individually 6-fold co-ordinated. The antiferromagnetic nature of the coupling has further been elucidated by Fournier *et al.* [3], who derived an average coupling constant $J = 24 \pm 2\ \mathrm{cm^{-1}}$ from the temperature dependence of EPR intensity.

The resonance spectra of $\mathrm{Cr^{3+}}$ ions in borate and silicate glasses have been reported respectively in [4] and [5]. In sodium borate glasses [4] only a $g \sim 2$ resonance was observed, the shape of which is dependent on the alkali content. The absence of higher g resonances implies that the zero-field splitting of the observed chromium centre is considerably smaller in borate than in the phosphate glasses [6].

The EPR and magnetic susceptibility data [7] have shown that the Cr impurity atoms in chalcogenide glasses may exist in various valence states. $\mathrm{Cr^{3+}}$ ions may be incorporated into a glass network with different environments. Besides being incorporated into the glass network, $\mathrm{Cr^{3+}}$ ions may exist in microcrystalline inclusions, in which the phase transition of the $\mathrm{Cr^{3+}}$ spin system occurs.

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In order to obtain further information on the chromium in oxide glasses, the present paper will report results of EPR and magnetic susceptibility studies of chromium ions in lead–borate glasses.

2. Experimental procedure

2.1. Sample preparation

We have studied the $x\text{Cr}_2\text{O}_3$–$(1-x)[3\text{B}_2\text{O}_3$–$\text{PbO}]$ glasses, with $0 \leqslant x \leqslant 35$ mol%, maintaining the $\text{B}_2\text{O}_3/\text{PbO}$ ratio constant, that is, keeping the matrix structure unmodified. In this way, initially the glass matrix $3\text{B}_2\text{O}_3$–PbO was prepared by mixing H_3BO_3 and PbO and melting this admixture in a sintered corundum crucible. We used a technique previously reported [8], knowing that the B_2O_3–PbO system forms transparent and stable glasses in the concentration range 18 to 80 mol% PbO [9]. After cooling, the host glass was crushed and the resulting powder was mixed with appropriate amounts of Cr_2O_3, before final melting at $T_\text{M} = 1250°$ C for 1 h. The molten glass was poured onto a stainless-steel plate.

The structure of these glasses has been studied by X-ray diffraction analysis and did not reveal any crystalline phase up to 20 mol% Cr_2O_3. In the glasses with $x > 20$ mol% Cr_2O_3 the X-ray diffraction analysis reveals the microcrystalline precipitates of Cr_2O_3 [10]. For these glasses, the observed d-spacings are given in Table I. The crystallites are very small and X-ray lines are very weak and diffuse.

Chemical analysis reveals no sensible deviation from nominal composition.

2.2. Experimental details

The X-ray diffraction analyses were preformed using a model TUR-M61 X-ray diffractometer with filtered CuKα radiation (operating at 34 kV and 20 mA). The glasses were milled and then placed in the specimen holder provided. Peak maxima were determined using an Si polycrystalline standard.

TABLE I The observed d-spacings for glasses with $x >$ 20 mol% Cr_2O_3

d-spacing (nm)		
25 mol% Cr_2O_3	30 mol% Cr_2O_3	35 mol% Cr_2O_3
		0.402
		0.381
0.267	0.267	0.264
0.248	0.248	0.247
	0.211	0.213
0.166	0.167	0.165

The electron paramagnetic resonance studies were performed at 9.4 GHz (X-band), using a standard JEOL machine, in the temperature range 80 to 350 K. The calibration of the field was made by DPPH. For the EPR measurements we have used a powder of the glasses.

The magnetic data were obtained with a translation balance in the temperature range 80 to 750 K.

3. Results and discussion

3.1. EPR studies

EPR spectra for glasses of the system $x\text{Cr}_2\text{O}_3$–$(1-x)[3\text{B}_2\text{O}_3$–$\text{PbO}]$ with $0.5 \leqslant x \leqslant 35$ mol% are shown in Fig. 1. All samples had the same weight (0.1 g) and spectra were recorded at room temperature. For concentrations containing $\leqslant$ 10 mol% Cr_2O_3 the EPR spectra are generally characterized by the appearance of resonance absorption at $g \simeq 5.1$ and $g \simeq 1.97$, their intensities being strongly dependent on composition. The resonance absorption at $g \simeq 5.1$ is typical for isolated Cr^{3+} ion sites of rhombic symmetry subjected to strong crystal field effects [2]. The resonance absorption having $g \simeq 1.97$ results from contributions from both Cr^{3+} [2] and Cr^{5+} [2, 11–13] ions.

For concentrations containing 0.5 to 1 mol% Cr_2O_3, at the resonance absorption having $g \simeq$ 1.97, the predominant contribution is due to Cr^{5+} ions, the resonance line having all the characteristics already determined for these ions in oxidic glasses [2, 6, 11–13] and polycrystalline materials [14], especially a marked narrowness of the linewidth, $\Delta H \sim 3.18 \times 10^3$ A m^{-1}.

Although Loveridge and Parke [4] and Paul and Upreti [15] have assigned the resonance absorption at $g \simeq 1.98$ to the Cr^{3+} ions in sodium borate glasses with low concentration of chromium, this resonance is due to Cr^{5+} ions [6, 11–13]. Our results are in agreement with those obtained by Brückner *et al.* [12] for chromium ions in soda-lime–silicate glass fibres. In these glasses, at low concentration of chromium ions, both Cr^{3+} and Cr^{5+} are present as is shown by EPR spectra analysis. Studying some oxide glasses with chromium ions, Garif'yanov [13] showed by EPR that in these glasses Cr^{5+} ions are present. In the case of Cr^{5+} ions in oxide glasses [6, 12, 13], a narrow and asymmetric resonance with $g \simeq 1.98$ was evidenced. Asymmetry of EPR line-shape for

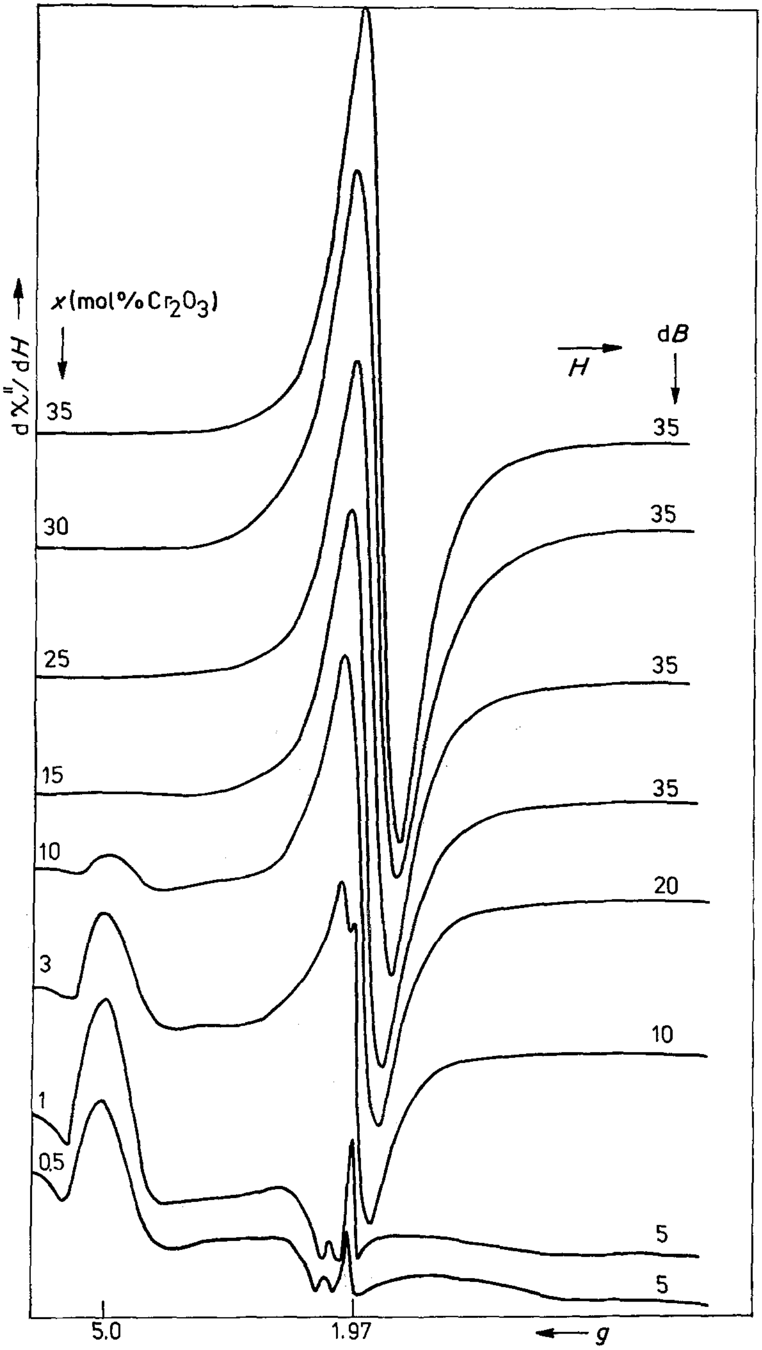

Figure 1 EPR spectra of $x\mathrm{Cr_2O_3}-(1-x)[3\mathrm{B_2O_3}-\mathrm{PbO}]$ glasses with $0.5 \leqslant x \leqslant 35$ mol%.

Cr^{5+} in these glasses is typical for centres with anisotropic g-factors. These results suggest that in our glasses Cr^{5+} ions are present, which are responsible for the asymmetric resonance absorption at $g \simeq 1.98$.

As the $\mathrm{Cr_2O_3}$ concentration increases, a broad resonance line due to Cr^{3+} ions is seen superposed upon the narrow one due to Cr^{5+}. At room temperature the resonance absorption having $g \simeq 1.97$ and due to Cr^{3+} ions is predominant for $x \geqslant 3$ mol% $\mathrm{Cr_2O_3}$, and the corresponding EPR parameters depend on the chromium content in glasses. At 78 K temperature all the glasses with $x \geqslant 3$ mol% $\mathrm{Cr_2O_3}$ present the resonance absorption at $g \simeq 1.98$ assigned to the Cr^{5+} ions, but this resonance is comparatively small compared to that assigned to the Cr^{3+} ions.

In order to analyse qualitatively the compo-

TABLE II ΔH_i, A_i and g factors corresponding to the resonance absorption due to Cr^{5+} ions for glasses with $x \leq 3$ mol% Cr_2O_3

x (mol% Cr_2O_3)	ΔH_i ($\times 10^3$ Am^{-1})	A_i (Arbitrary units)	g
0.5	3.37 ± 0.28	0.009 ± 0.001	1.970
1.0	3.27 ± 0.28	0.015 ± 0.002	1.973
3.0	3.74 ± 0.28	0.064 ± 0.003	1.974

sition dependence of the number of spins participating at the $g \simeq 1.97$ resonance absorption, the area, A_i, under the absorption curves was calculated. In terms of first derivatives,

$$A_i \simeq I_i(\Delta H_i)^2 \quad (1)$$

where I_i is the peak-to-peak height and ΔH_i is the line-width of the first derivative of the spectra. This analysis was used to interpret the composition dependence of the number of spins participating at resonances in the cases of Fe^{3+} [16] and Mn^{2+} [17] ions in oxidic glasses. Tables II and III summarize the calculated values for ΔH_i, A_i and the g-factors corresponding to the EPR spectra due to Cr^{5+} and Cr^{3+} ions, respectively.

Since the proportion of Cr^{5+} ions involved in the $g \simeq 1.97$ resonance absorption is small compared to those of the Cr^{3+} ions (see the A_i values in Tables II and III) for $x \geq 3$ mol%, they will not be taken into account in interpreting the magnetic properties of these glasses, which are not considerably affected.

The composition dependence of the intensity of the $g \simeq 1.97$ resonance, arising from Cr^{3+} ions, is plotted in Fig. 2. Analysing the intensity of these resonances, it can be observed that the number of Cr^{3+} ions participating in this resonance increases when the concentration of Cr_2O_3 increases up to about 25 mol%, the number of these ions remaining practically constant for higher concentrations.

TABLE III A_i and g factors for the resonance absorptions due to Cr^{3+} ions for glasses with $x \geq 3$ mol% Cr_2O_3

x (mol% Cr_2O_3)	A_i (Arbitrary units)	g
3	1.76	1.983
5	7.99	1.977
10	41.96	1.978
15	68.55	1.981
20	83.91	1.978
25	93.34	1.977
30	95.12	1.978
35	95.76	1.978

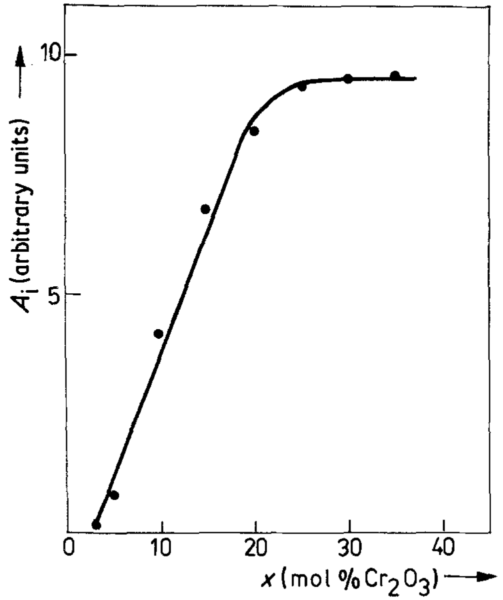

Figure 2 The composition dependence of the intensity of the $g \simeq 1.97$ resonance lines arising from Cr^{3+} ions.

The composition dependence of the line-width of the $g \simeq 1.97$ resonance, arising from Cr^{3+} ions, is plotted in Fig. 3. The $g \simeq 1.97$ resonance line-width increases linearly up to about 20 mol% Cr_2O_3 and after that decreases. Despite the fact that, for a Cr_2O_3 content of less than 20 mol% the line-width variation is linear, this does not satisfy the relation given by Kittel and Abrahams [18] for dipolar interactions according to which the line-width is proportional to the magnetic ion contents participating at resonance. Thus,

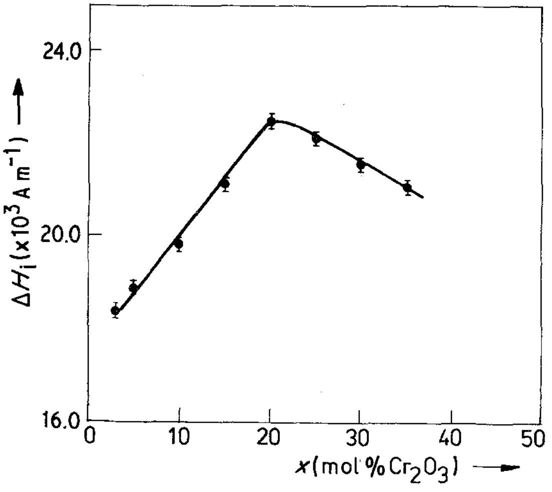

Figure 3 The composition dependence of the line-width for the $g \simeq 1.97$ resonance lines arising from Cr^{3+} ions.

$$\Delta H_{d\text{-}d} = (g \cdot \mu a^3)x. \qquad (2)$$

where $\Delta H_{d\text{-}d}$ is the dipolar line-width, a is some average "lattice" parameter, μ is the magnetic moment of the ion and x is its mole fraction. This relation was used by Moon *et al.* [19] to demonstrate the iron ion clustering in barium–borate glasses, and verified by Burzo and Ardelean [16] for Fe^{3+} ions in lead–borate glasses and by Ardelean *et al.* [17] for Mn^{2+} ions in lead–tellurate glasses, for composition ranges where these glasses contain isolated magnetic ions. In lead–tellurate glasses, for concentrations higher than 5 mol% MnO, where magnetic measurements evidenced super-exchange magnetic interactions, the resonance line-width at $g \sim 2.01$ deviate from the dependence predicted by the above mentioned relation, and this effect was attributed to the existence of clusters containing more than one ion participating in the magnetic interactions. Therefore, in case of the glasses investigated in the present work, this dependence may be interpreted as proving super-exchange magnetic interactions between the Cr^{3+} ions. Landry *et al.* [2] showed that Cr^{3+} ions in phosphate glasses, which are octahedrally co-ordinated giving rise to an absorption resonance at $g \sim 2$, are involved in super-exchange magnetic interactions of an antiferromagnetic nature, a result confirmed by Fournier *et al.* [3].

The line-width decreasing at concentrations above 20 mol% Cr_2O_3, may be related to the presence of Cr_2O_3 microcrystalline precipitates in these glasses, as evidenced by X-ray diffraction analysis. Because Cr_2O_3 is antiferromagnetic at room temperature (Neél temperature, $T_N = 310$ K) [26], the resonance line-narrowing, as a result of the antiferromagnetic order in the microcrystalline precipitates, becomes prevalent at these concentrations. The existence of Cr_2O_3 microcrystalline precipitates at concentrations higher than 20 mol% Cr_2O_3 may explain the fact that the number of spins involved in the $g \simeq 1.97$ resonance remain practically constant at these concentrations (see Fig. 2).

By following the variation of the number of spins participating at the $g \simeq 1.97$ resonance, as a function of temperature, it is found that, for glasses with $x > 20$ mol% Cr_2O_3, this number increases with temperature up to about 310 K. Figure 4 shows this dependence for the glasses containing 30 mol% Cr_2O_3. The gradual increasing of the Cr^{3+} ion proportion participating in the $g \simeq 1.97$ resonance as the temperature is increased up to T_N, is the results of their magnetic decoupling. Above T_N, when practically all the ions are magnetically decoupled, the number of spins participating at this resonance absorption should remain constant.

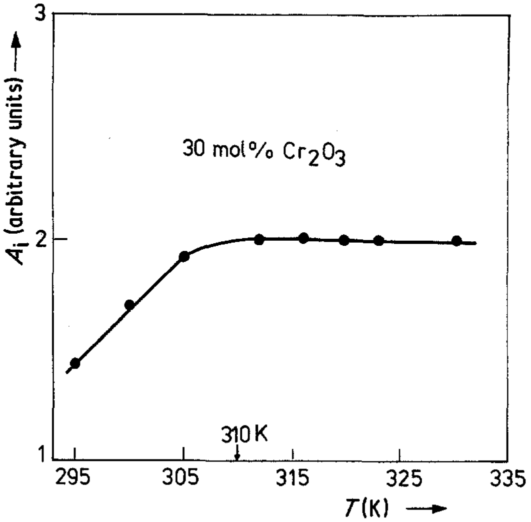

Figure 4 The temperature dependence of the intensity of the $g \simeq 1.97$ resonance lines arising from Cr^{3+} ions for glass containing 30 mol% Cr_2O_3.

Having in mind that Cr_2O_3 has a T_N value close to room temperature, the EPR measurements may represent a simple method for the rapid detection of Cr_2O_3 microcrystalline precipitates in oxide glasses.

3.2. Magnetic susceptibility studies

The temperature dependence of the reciprocal magnetic susceptibility of the various glasses is presented in Figs 5 and 6. For the glasses with a Cr_2O_3 content < 3 mol%, a Curie law is observed. This suggests that the predominant part of chromium ions are isolated and that no magnetic order is present. For a Cr_2O_3 content $\geqslant 3$ mol% the reciprocal magnetic susceptibility obeys a Curie–Weiss law behaviour, with a negative paramagnetic Curie temperature.

For glasses with $3 \leqslant x \leqslant 20$ mol% Cr_2O_3, the high-temperature susceptibility data indicate that the chromium ions in the glasses experience negative exchange interactions and are coupled antiferromagnetically. In this case, the antiferromagnetic order takes place only at short-range, and the magnetic behaviour of the glasses can be described by the so-called mictomagnetic [20] or speromagnetic [21] type order.

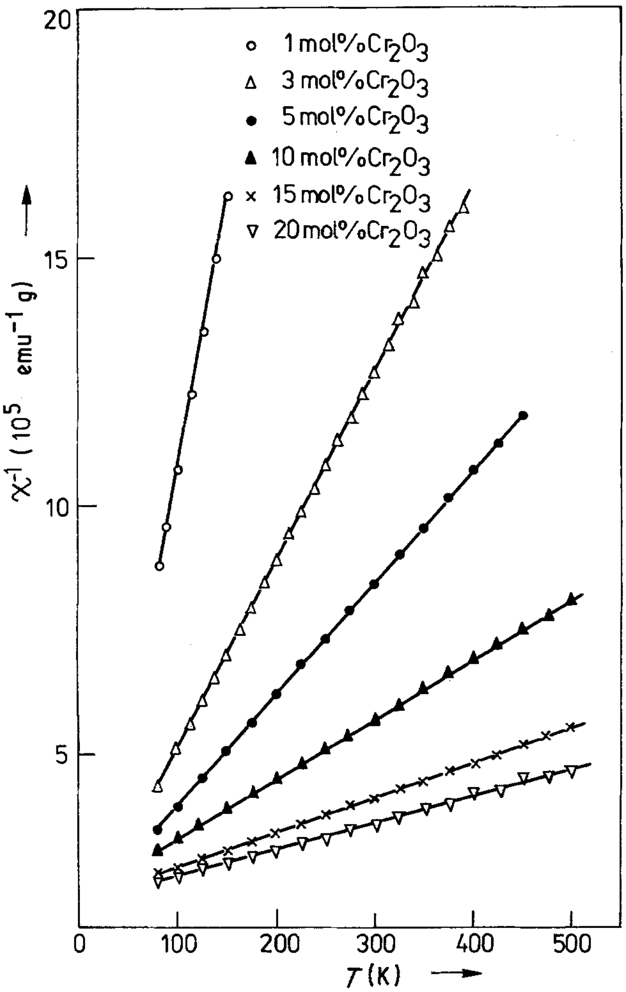

Figure 5 The temperature dependence of the reciprocal magnetic susceptibility for the glasses with $Cr_2O_3 \leqslant 20$ mol%.

This behaviour agrees with the EPR study conclusions. According to Fig. 2, for glasses having less than 3 mol% Cr_2O_3 the prevailing part of Cr^{3+} ions absorption is centred at $g \simeq 5.1$, corresponding to isolated ions, while at higher concentrations the resonance absorption at $g \simeq 1.97$, due to Cr^{3+} ions magnetically coupled by super-exchange interactions, becomes predominant. A similar conclusion was reached by Landry *et al.* [2] and confirmed by Fournier *et al.* [3] in their study of Cr^{3+} ions in phosphate glasses. Theoretical calculations [22–24] have shown that negative exchange interaction can occur in amorphous systems.

For glasses having Cr_2O_3 contents higher than 20 mol% (see Fig. 6), the temperature dependence of the reciprocal magnetic susceptibility shows an antiferromagnetic transition, with Neél temperature, $T_N \simeq 310$ K. In this way the magnetic measurements reveal the presence of Cr_2O_3 in the studied glasses, in agreement with the X-ray diffraction analysis and EPR studies. The shape of the curves in Fig. 6 below T_N can be accounted for in these glasses if there are chromium ions randomly distributed, together with those included in mircocrystalline precipitates, the number of the first being kept constant (Fig. 2). This means that increasing the Cr_2O_3 content in glasses with $x >$ 20 mol%, quantitatively increases the crystalline phase. This may explain the resonance line-width decreasing for $x > 20$ mol% (see Fig. 3).

The composition dependence of the paramagnetic Curie temperature, θ_p, is presented in Fig. 7. The absolute magnitude of the values of θ_p increases almost linearly for $3 \leqslant x \leqslant 20$ mol% Cr_2O_3. In general, the exchange integral increases as the concentration of the transition-metal ions is increased in the glass [25]. As a result, the magnitude of the paramagnetic Curie temperature increases. For Cr_2O_3 concentrations higher than 20 mol%, the paramagnetic Curie temperature is constant, and has the value 480 K.

This value is similar to that obtained for poly-

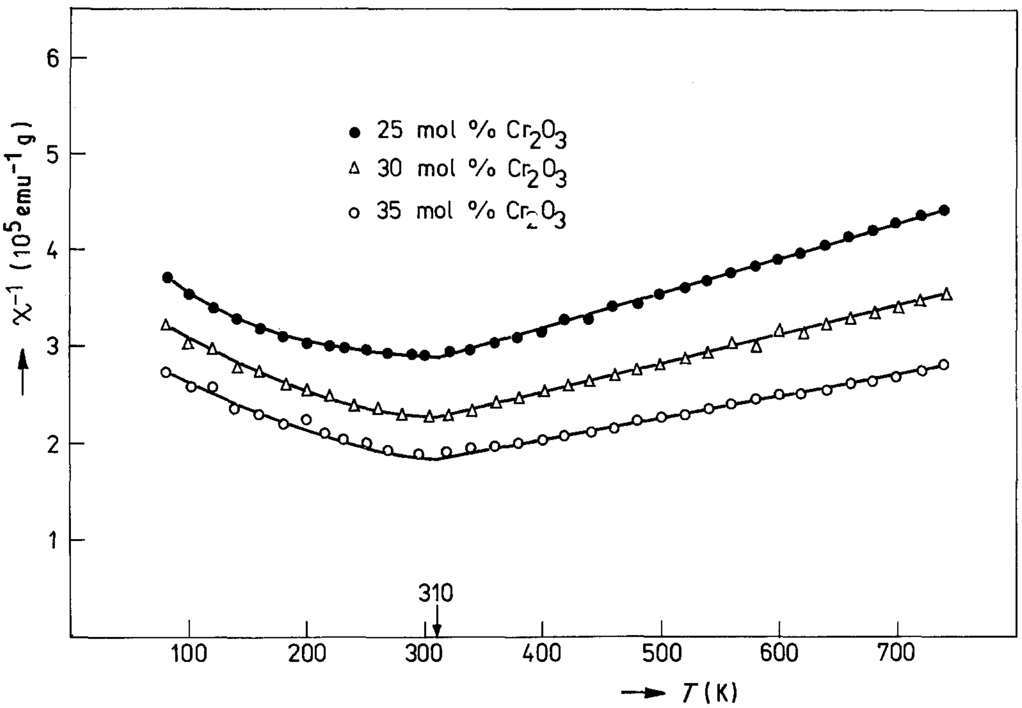

Figure 6 The temperature dependence of the reciprocal magnetic susceptibility for the glasses with Cr_2O_3 > 20 mol%.

crystalline Cr_2O_3 [26]. This confirms the idea, according to which, if the observed magnetic behaviour of the glasses is due to microcrystalline precipitates of the same nature, all the paramagnetic Curie temperatures would be the same [27, 28].

To determine accurately the values of the Curie constants, C, and atomic magnetic moments, μ, a correction due to the diamagnetism of the glass matrix and Cr_2O_3 was taken into account. The composition dependence of the Curie constants, C, is presented in Fig. 8. The values of the Curie constant, which is proportional to the ion concentration, vary linearly with the chromium ion concentrations. The experimental values obtained for the atomic magnetic moment $\mu = (3.82 \pm 0.07)\mu_B$, where μ_B is the Bohr magneton (see Table IV) are very close to the magnetic moment of Cr^{3+} cations in the free-ion state: $\mu_{Cr^{3+}} = 3.87\,\mu_B$ [29], in agreement with the behaviour usually observed in the paramagnetic salts [29] containing chromium ions. The smaller values obained for the atomic magnetic moments of glasses with $x \leqslant 20$ mol% Cr_2O_3 may be attributed to the presence of Cr^{5+} ions, for which the atomic magnetic moments in the free-ion state is $\mu_{Cr^{5+}} = 1.73\,\mu_B$ [29]. This results in the proportion of Cr^{5+} ions being small compared to the proportion of Cr^{3+} ions, in agreement with the EPR data.

From X-ray diffraction analysis, EPR and magnetic susceptibility studies it is concluded that the chromium ions seem to be randomly distribu-

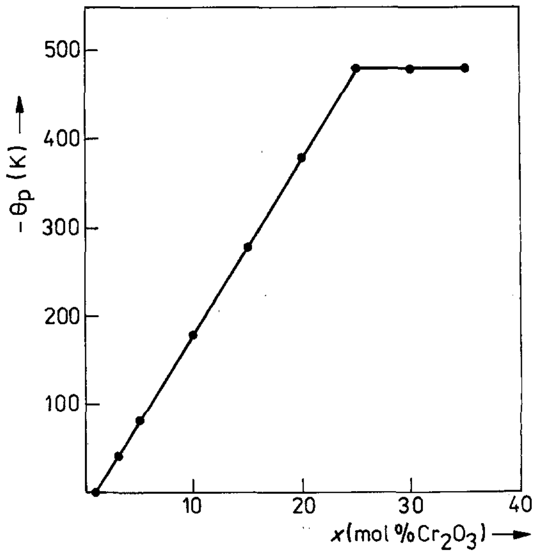

Figure 7 The composition dependence of the paramagnetic Curie temperature.

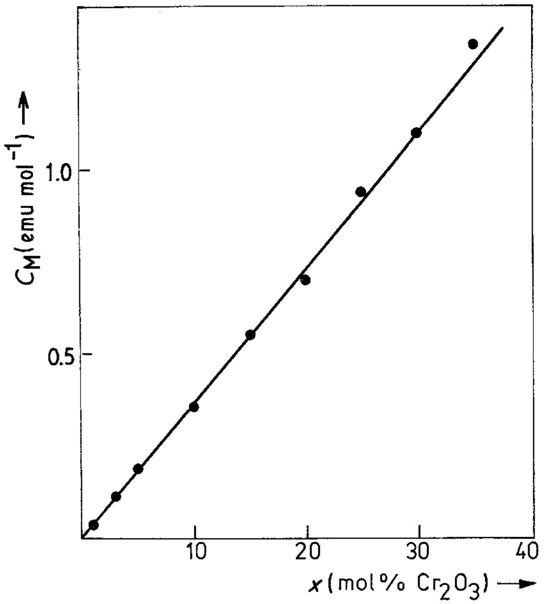

Figure 8 The composition dependence of the Curie constant.

ted in the glass matrix up to a concentration of 20 mol% Cr_2O_3.

4. Conclusions

By means of X-ray diffraction analysis, EPR studies and magnetic measurements, the $xCr_2O_3-(1-x)$ $[3B_2O_3-PbO]$ glasses with $0.5 \leqslant x \leqslant 35$ mol% were studied, obtaining information concerning the chromium ion distribution in the glass matrix, which explains their magnetic behaviour.

The EPR studies showed that in these glasses both Cr^{3+} and Cr^{5+} ions are present. These data correlated to magnetic susceptibility studies as evidence of the existence of Cr^{3+} ions simultaneously in two states, isolated ions and ions coupled by a magnetic super-exchange interaction. The isolated Cr^{3+} ions are predominant at concentrations less than 3 mol% Cr_2O_3, giving rise to the resonance absorption centred at $g \simeq 5.1$. Apart from this, for concentrations < 3 mol% Cr_2O_3, there is another resonance absorption, centred at $g \simeq 1.98$ due to Cr^{5+} ions. Their proportion, as compared to that of Cr^{3+} ions, is small enough not to affect considerably the magnetic properties of these glasses; this is also proved by the atomic magnetic moment values. With increasing Cr_2O_3 concentration, a broad resonance absorption, due to Cr^{3+} ions, superimposes at $g \simeq 1.97$ on that due to Cr^{5+} ions. From X-ray analysis, EPR and magnetic susceptibility studies we conclude that the chromium ions seem to be randomly distributed in the glass matrix up to 20 mol% Cr_2O_3.

TABLE IV Curie constants, magnetic moments and paramagnetic Curie temperatures

x (mol% Cr_2O_3)	C_M (emu mol^{-1})	μ (μ_B)	θ_p (K)
1	0.0357	3.82	0
3	0.110	3.83	−35 ± 2.5
5	0.1872	3.84	−79 ± 2.5
10	0.352	3.75	−180 ± 2.5
15	0.557	3.84	−281 ± 2.5
20	0.6963	3.76	−379 ± 2.5
25	0.940	3.86	−480 ± 2.5
30	1.100	3.85	−480 ± 2.5
35	1.336	3.89	−480 ± 2.5

For concentrations > 20 mol% Cr_2O_3, there are also Cr_2O_3 microcrystalline precipitates in our glasses, which determine their magnetic behaviour and the antiferromagnetic transition from $T_N \simeq 310$ K.

Because Cr_2O_3 has T_N value close to room temperature, the EPR spectrum or magnetic susceptibility measurements may provide a simple method for the rapid detection of Cr_2O_3 microcrystalline precipitates in oxidic glasses.

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