

Magnetic susceptibility studies of lead oxyhalide glasses containing transition metal oxides†

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Abstract. Magnetic susceptibility studies of lead oxyhalide glasses containing high concentrations of transition metal oxides such as MnO and Fe_2O_3 have been performed. While they exhibit predominantly antiferromagnetic interactions, the low temperature ($< 100\text{K}$) region is dominated by paramagnetic contributions. The behaviour in these glasses is found to be similar to that of covalent oxide glasses and is different from that of purely ionic sulphate glasses.

Keywords. Magnetic susceptibility; oxyhalide glasses; transition metal oxides.

1. Introduction

Lead oxyhalide glasses in the systems, PbO-PbF_2 and PbO-PbCl_2 can be prepared with high concentrations of transition metal (TM) ions such as Fe_2O_3 and MnO (Rao and Rao 1985a). We have earlier investigated these glasses containing TM ions by ESR and optical spectroscopies (Rao and Rao 1985a, 1985b). It was found that Fe^{3+} ions prefer non-substitutional 4-coordinated sites of their own whereas Mn^{2+} ions acquire a slightly distorted octahedral coordination of the type, $[\text{MnO}_2\text{X}_4]$, ($\text{X} = \text{F, Cl}$) similar to the sites of Pb^{2+} ions in these glasses (Rao and Rao 1984; Rao *et al* 1984a, 1984b). It was also found that part of the added Mn^{2+} ions gets oxidized to Mn^{3+} state during glass preparation. In glasses containing high concentrations of Fe_2O_3 or MnO , magnetic interaction between TM ions is dominantly dipolar. But even then we observed (Rao and Rao 1985a) that a significant fraction of Fe^{3+} and Mn^{2+} ions are present in magnetically isolated sites.

We therefore consider that a study of the temperature dependence of magnetic susceptibilities is in order, since it provides information about the nature of the interaction between the TM ions. Additionally the curie constants evaluated from susceptibility measurements give information about the valence state of the TM ions. Further, the influence of non-magnetic (lead oxyhalide) host glass in which the ionicity of bonding increases with halide concentration is also worth investigating, because in purely ionic sulphate glasses the interaction between TM ions was found to be weakly ferromagnetic (Rao and Sundar 1981), whereas in most (covalent) oxide glasses the interaction was found to be antiferromagnetic (Shinkel and Rathenau 1965; Simpson and Lucas 1971; Hasegawa 1971; Egami *et al* 1972, 1973; Wilson *et al* 1973; Friebel and Koon 1974; Burzo *et al* 1982).

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In this short communication we present the results of our magnetic susceptibility studies of lead oxyhalide glasses containing high concentrations of MnO and Fe_2O_3 . Our results suggest that the nature of interaction in these glasses is dominantly antiferromagnetic. We have discussed the possible origin of this effect.

2. Experimental

PbO-PbF_2 and PbO-PbCl_2 glasses containing various quantities of Fe_2O_3 and MnO were prepared by the procedure reported earlier (Rao and Rao 1985a). In this method, melts of appropriate composition containing 5 to 10 mol % of Fe_2O_3 or MnO (added as MnC_2O_4 which decomposes to MnO) were quenched into thin disks between two steel plates. The glasses so prepared were found to be homogeneous and no phase separation was noticed.

Magnetic susceptibility of these glasses in the temperature region of 15–300 K was measured by the Faraday method using a Cahn RG vacuum recording electrobalance. Specially shaped pole pieces are used for generating a constant field gradient. The maximum field used was around 4000G. $\text{Hg}[\text{Co}(\text{NCS})_4]$ was used as calibrant. A closed cycle helium cryostat (model CS 202) manufactured by Air Products Inc., USA, was used for low temperature measurements. The molar magnetic susceptibilities reported here are corrected for diamagnetic contributions of the constituent ions in the glasses.

3. Results and discussion

Temperature variation of the inverse molar magnetic susceptibility, χ_M^{-1} , for various glasses containing different concentrations of Fe_2O_3 is shown in figure 1. Similar χ_M^{-1} vs T plots for glasses with different concentrations of MnO are presented in figure 2.

The temperature variations of the inverse susceptibilities exhibit the following interesting features: (1) There appears to be two linear temperature regions, one below 100 K (low temperature, LT region) and the other above 100 K (high temperature, HT region) in all glasses though this is only weakly apparent in MnO-containing glasses; (2) the susceptibility increases by almost an order of magnitude for a two-fold increase of Fe_2O_3 concentration while the increase is almost proportional to the concentration in the case of MnO; (3) the susceptibility increases enormously for heat treated glasses containing 0.5 mol % of Fe_2O_3 . When the glass was heated above its crystallization temperature ($\simeq 600$ K) for 2 hours; (4) the LT and HT regions in MnO doped glasses possess considerably smaller differences in slopes as compared to Fe_2O_3 -doped glasses, in fact, Fe_2O_3 -doped glasses exhibit distinctly large curvature in the region of 100 K, (5) the slope of the HT region of glass containing a higher concentration of MnO is lower than the corresponding slope in the glass containing lower concentration.

The two linear regions were visually identified and were least square fitted. The temperature variation of χ_M^{-1} in the two regions may be described by the Curie-Weiss law,

$$\chi_M = C/(T + \theta_p) \quad (1)$$

where C is the Curie constant and θ_p is an effective Curie temperature. Effective

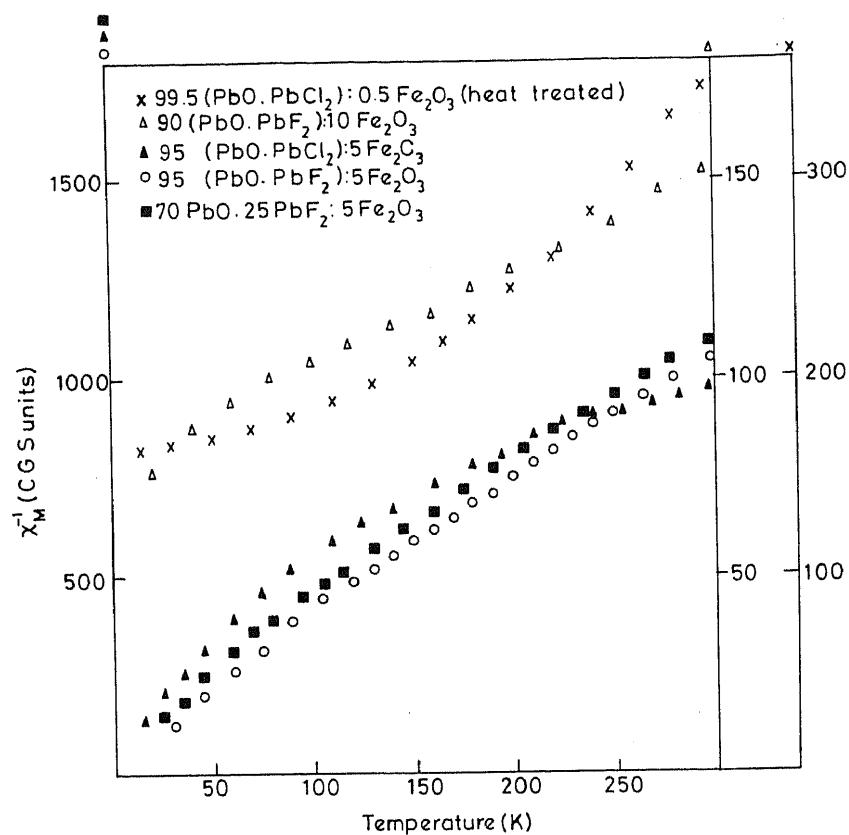


Figure 1. Temperature variation of inverse magnetic susceptibility for various glasses containing Fe_2O_3 . The y-axes for different curves in the figure are identified by the symbols at the top.

magnetic moment, μ_{eff} can be calculated from χ_M by the following formula

$$\mu_{\text{eff}} = 2.83(C/x)^{1/2} \quad (2)$$

where x is the mole fraction of the transition metal ions in the glass. The calculated values of θ_p and μ_{eff} are given in table 1. The values of θ_p for the high temperature regions in all cases suggest that interactions are predominantly antiferromagnetic in these glasses. It may also be noted that glasses containing Fe_2O_3 give rise to larger θ_p values as compared to glasses containing MnO . Further, θ_p is higher for glasses with higher concentration of TM ions in the case of Fe_2O_3 whereas it is lower in the case of MnO . The magnitudes of θ_p suggest that the manganese ions are weakly coupled in the glass matrices in comparison to Fe^{3+} ions which are quite strongly coupled. This is quite in keeping with the structural features of these glasses in that the substitutional octahedral positions taken up by $\text{Mn}^{2+}/\text{Mn}^{3+}$ ions are spatially separated by larger distances than the tetrahedral positions preferred by Fe^{3+} ions. The spatial closeness of Fe^{3+} positions in these glasses is likely to be due to the tendency of Fe^{3+} ions to cluster together (Bandyopadhyay *et al* 1980). This clustering attains its limits when the glass is

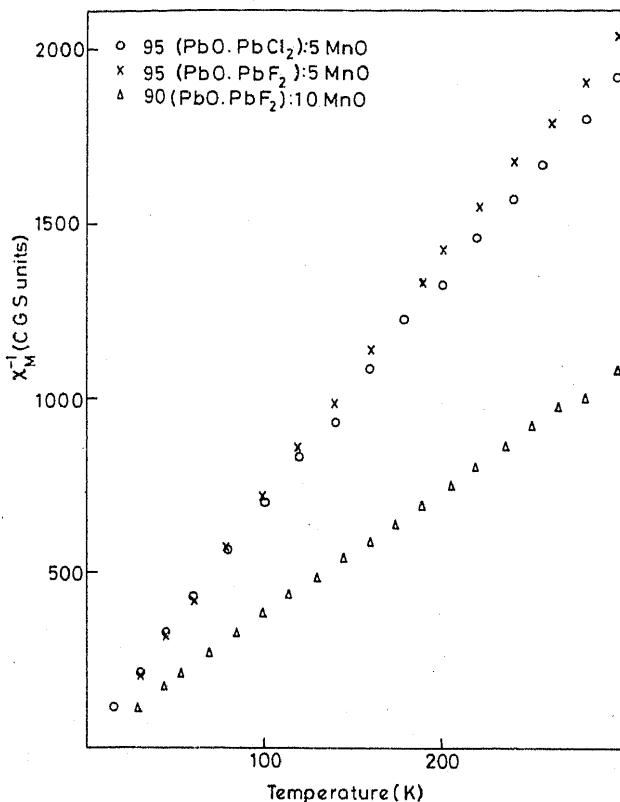


Figure 2. Temperature variation of inverse susceptibilities of various glasses containing MnO.

Table 1. Values of θ_p and μ_{eff} obtained from the high temperature (HT) region and θ_p values obtained from the low temperature (LT) region.

No.	Glass composition	LT region		HT region	
		θ_p	θ_p	μ_{eff}	μ_{eff}
1.	47.5 PbO:47.5 PbCl ₂ :5 MnO	1.9	4.6	4.93	
2.	47.5 PbO:47.5 PbF ₂ :5 MnO	1.9	9.3	4.92	
3.	45.0 PbO:45.0 PbF ₂ :10 MnO	0.9	5.9	4.72	
4.	47.5 PbO:47.5 PbCl ₂ :5 Fe ₂ O ₃	12.0	116.4	7.84	
5.	47.5 PbO:47.5 PbF ₂ :5 Fe ₂ O ₃	2.6	35.0	5.04	
6.	70 PbO:25 PbF ₂ :5 Fe ₂ O ₃	9.5	45.3	4.99	
7.	45.0 PbO:45.0 PbF ₂ :10 Fe ₂ O ₃	—	132.3	13.83	

crystallized by annealing at ≈ 600 K. The clustered Fe³⁺ ions behave ferromagnetically with high χ_M values (figure 1).

In the LT region (15–100 K) we observe that χ_M^{-1} vs. T plots possess higher slopes in

all cases, and is particularly large for Fe_2O_3 -containing glasses. This is reflected in decreased θ_p values. Such behaviour for an amorphous antiferromagnet was predicted by Simpson (1970) in his effective field model. This model assumes the presence of isolated magnetic ions in addition to those which interact with their magnetic neighbours. As the isolated ions do not interact with their neighbours (which are structurally far away) they contribute a small paramagnetic component to the total susceptibility which obeys the Curie law. This explains the susceptibility behaviour of these glasses in the LT region. The existence of isolated ions is a natural concomitant of the glassy state. A fraction of Mn^{2+} and Fe^{3+} ions are indeed present always in magnetically isolated sites even in glasses containing high concentrations of transition metal ions (as evidenced by characteristic low field ESR resonances) (Rao and Rao 1985a). Hence the LT region is dominated by paramagnetic interactions in almost all compositions. However, the nature of the interaction can be slightly different. In the glass containing 10 mol % MnO , the concentration of Mn^{3+} ions can be considerable (see later). This leads to Mn^{2+} - Mn^{3+} interactions which can result at the least in ferromagnetic interactions. This necessarily brings down θ_p even for the HT region. As it was noted earlier (table 1) θ_p is lower for glass containing 10 mol % MnO as compared to glass containing 5 mol % MnO .

In the case of $\text{PbO} \cdot \text{PbCl}_2$ glass containing 5 mol % Fe_2O_3 , another essentially linear HT region with a different slope above 225 K was observed (figure 1). This may possibly arise from strongly antiferromagnetically coupled near-neighbour Fe^{3+} ions present in the glass.

It may be noted from table 1 that μ_{eff} values for glasses containing 5 mol % MnO obtained from the analysis of the HT region are much lower than the free ion μ_{eff} value for Mn^{2+} ($5.92 \mu_B$) and are closer to that of Mn^{3+} ($4.90 \mu_B$). This value is even lower for the glass containing 10 mol % MnO , which suggests that the fraction of Mn^{3+} ions increases with added manganese concentration. These observations are quite in agreement with the results of our ESR and earlier optical spectroscopy studies. The μ_{eff} values for glasses containing 5 mol % Fe_2O_3 show that most of the ions are present as Fe^{3+} . However, it is not likely that Fe^{2+} ions are also produced during equilibration at melting temperature like in other lead oxide containing glasses (Burzo *et al* 1980). Nevertheless, Fe^{2+} ions may not aggregate into regions dominated by Fe^{3+} ions. Hence Fe^{2+} ions, if any, make contributions only to paramagnetic susceptibility and not to ferromagnetic type as expected in manganese containing glasses. The μ_{eff} value for the glass containing 10 mol % Fe_2O_3 is very high ($13.83 \mu_B$) and may be due to the onset of dominant ferromagnetic interactions in isolated clusters.

The results discussed above point to the fact that magnetic interactions in lead oxyhalide glasses containing transition metal ions are essentially antiferromagnetic as in other covalent oxide glasses and they are different from the type of interactions in purely ionic sulphate glasses. In fact the θ_p value for a PbO -rich glass ($70\text{PbO} \cdot 25\text{PbF}_2 \cdot 5\text{Fe}_2\text{O}_3$) is higher than that of PbO -poor ($47.5\text{PbO} \cdot 47.5\text{PbF}_2 \cdot 5\text{Fe}_2\text{O}_3$) glass in the case of glasses containing 5 mol % Fe_2O_3 (glass nos. 5 and 6 in table 1). Since the magnetic interactions are most likely mediated by oxygen atoms in a super-exchange type of interaction we feel that the covalency of oxygen bonding dictates an antiferromagnetic spin orientation in these glasses. We have also noted elsewhere (Rao *et al* 1984a) that in PbO - PbF_2 glasses fluorine tends to occupy network positions with an apparently covalent Pb-F interaction. This is also likely to play a role in the covalency effect on magnetic interactions in these glasses.

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