

MAGNETIC BEHAVIOUR OF SOME LEAD-BORATE GLASSES WITH MANGANESE IONS

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Abstract. – The magnetic susceptibility measurements have been performed on $x\text{MnO} \cdot (1-x)[2\text{B}_2\text{O}_3 \cdot \text{PbO}]$ glasses with $0 < x \leq 80$ mol %. These data suggests that for $x > 30$ mol %, the manganese ions experience magnetic interactions. From Curie constant values and qualitative chemical analysis we have established that in these glasses Mn^{2+} and Mn^{3+} ions are present, which explains their magnetic behaviour.

Introduction

In the past few years there are many reports on the investigations of the valence states and distribution mode of the transition metal (TM) ions in the network of the oxide glasses [1, 2]. Up to now, the EPR [3-5] and magnetic susceptibility [6] studies of the oxide glasses with manganese ions suggest the presence only of Mn^{2+} ions. In the papers [7, 8], we have evidenced that in the potassium and lithium borate glass matrix for $x \geq 10$ mol % MnO and respectively $x > 5$ mol % MnO both, Mn^{2+} and Mn^{3+} ions are present. These ions may participate in magnetic superexchange interactions.

Experimental

We have studied the $x\text{MnO} \cdot (1-x)[2\text{B}_2\text{O}_3 \cdot \text{PbO}]$ glasses, with $0 < x \leq 80$ mol %, using the magnetic susceptibility measurements. The samples were prepared using the technique previously reported [1]. The X-ray diffraction analysis showed that the samples are homogeneous glasses up to $x = 80$ mol %. The qualitative chemical analysis of these glasses indicates the presence of both, Mn^{2+} and Mn^{3+} ions. The preliminary EPR measurements indicated that in all samples are present Mn^{2+} ions.

The magnetic measurements were made between 80 K and 700 K using a Faraday type balance.

Results and discussion

The temperature dependence of the reciprocal magnetic susceptibility of some glasses from studied system is presented in figure 1. For the glasses with $x \leq 30$ mol % a Curie law is observed. This suggests that in this concentration range are predominant the isolated manganese ions and no magnetic order is present. For $x > 30$ mol %, the reciprocal magnetic susceptibility obeys a Curie-Weiss behaviour with a negative paramagnetic Curie temperature $-\theta_p$. For these compositions, the high temperature susceptibility data indicate that the manganese ions in the

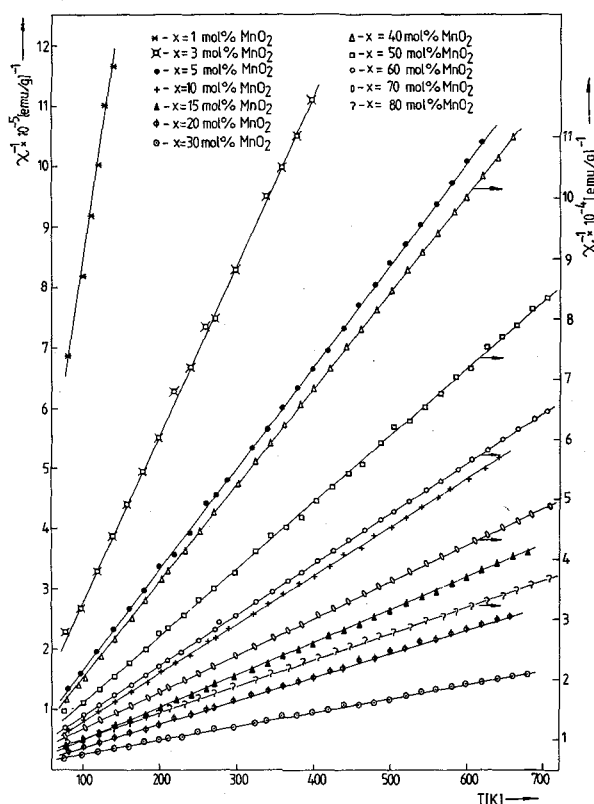


Fig. 1. – The temperature dependence of the reciprocal magnetic susceptibility.

glasses experience negative interactions and are coupled antiferromagnetically. In this case, the magnetic order takes place only at short-range and the magnetic behaviour of the glasses can be described by the so-called mictomagnetic [9] type order.

The absolute magnitude of the values of θ_p increases for $x > 30$ mol % (Fig. 2). In general the exchange integral increases as the concentration of the magnetic ions increases in the glass [10]. As a result the magnitude of the paramagnetic Curie temperature increases.

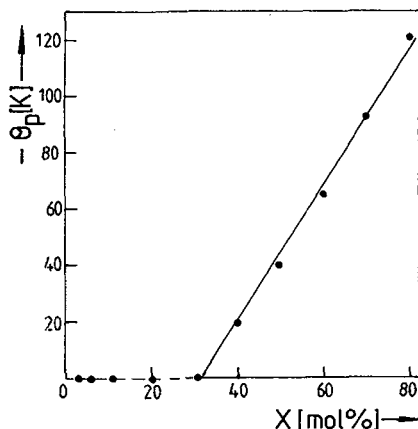


Fig. 2. — The composition dependence of the paramagnetic Curie temperature.

To determine accurately the values of the Curie constants, C_M , correction due to the diamagnetism of the matrix and MnO were taken into account. The composition dependence of the Curie constant is presented in table I. For the glasses with $x \geq 3$ mol %, the experimental values obtained for Curie constant and consequently for atomic magnetic moments are lower than those which correspond to MnO content, considering that all manganese ions are in Mn^{2+} valence state. In this way, having in view the qualitative chemical analysis and EPR studies, we consider that in these glasses are present both, Mn^{2+} and Mn^{3+} ions. In this case, using the atomic magnetic moment values $\mu_{Mn^{2+}} = 5.92 \mu_B$ and $\mu_{Mn^{3+}} = 4.90 \mu_B$ [11], we have estimated the molar fraction of these ions in the glasses from relations

$$x\mu_{exp}^2 = 2.83^2 C_M = x_1 \cdot \mu_{Mn^{2+}}^2 + x_2 \cdot \mu_{Mn^{3+}}^2 \quad (1)$$

and

$$x = x_1 + x_2 \quad (2)$$

where μ_{exp} is the experimental atomic magnetic moment, x_1 and x_2 the molar fraction of manganese in Mn^{2+} and Mn^{3+} valence states. The results are

Table I. — Curie constant and the molar fraction of manganese ions in Mn^{2+} and Mn^{3+} valence state.

x [mol %]	C_M [emu/mol]	x_1 [mol % Mn^{2+}]	x_2 [mol % Mn^{3+}]	θ_p [K]
1	0.04332	1	—	0
3	0.1274	2.8	0.2	0
10	0.4089	8.1	1.9	0
15	0.5949	11.1	3.9	0
20	0.7838	13.7	6.3	0
30	1.1596	19.9	10.1	0
40	1.5346	25.2	14.8	-20
60	2.214	32.5	27.5	-65
80	2.9025	38.9	41.1	-121

presented in table I. From these data it results that the molar fraction of the both, Mn^{2+} and Mn^{3+} ions in these glasses increases up to $x = 80$ mol %. A similar result was obtained in the case of lithium-borate glasses [8]. In the case potassium-borate glasses, the molar fraction of the Mn^{2+} ions increases up to 40 mol % and after that decreases [7]. This fact indicate that the matrix structure play an important role in the distribution mode and valence states of manganese ions in oxide glasses. Having in view these results, the magnetic data may be explained if one accepts the participation of the $Mn^{2+} - Mn^{2+}$, $Mn^{3+} - Mn^{3+}$ and $Mn^{2+} - Mn^{3+}$ magnetic exchange pairs.

Conclusions

From magnetic susceptibility data performed on $xMnO \cdot (1-x)[2B_2O_3 \cdot PbO]$ with $0 < x \leq 80$ mol %, we conclude that these results depend on the MnO content and matrix structure. For the glasses with $x > 30$ mol % the manganese ions experience negative magnetic exchange interactions and are coupled antiferromagnetically. Having in view EPR data and qualitative chemical analysis which indicates the presence of Mn^{2+} and Mn^{3+} ions, from Curie constant values we have estimated the molar fraction of these ions. The magnetic data may be explained if one accepts the participation of the $Mn^{2+} - Mn^{2+}$, $Mn^{3+} - Mn^{3+}$, $Mn^{2+} - Mn^{3+}$ magnetic exchange pairs.

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