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The local structure and interaction between Mn^{2+} and Mn^{3+} ions in borate glasses

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The oxide glasses are non–crystalline solid materials which atoms are disposed likewise crystals, but the arrangement is not steady they have only local order. Glasses may become host matrices for transition metal ions. The content of transition metal oxide dissolved in glass without separation of microcrystalline precipitates depends of the nature the involved ions, matrix composition and the equilibrium temperature of melting. Paramagnetic metal ions incorporated in borate glasses as a spectroscopic probe are studied in order to characterize the glass local structure. Magnetic susceptibility measurements have been performed on $xMnO\cdot(100-x)[2B_2O_3\cdot MO]$ glasses where MO→ SrO, CdO,As_2O_3 or PbO with $0< x \le 50$ mol%. The data give evidence that the manganese ions in this glasses are in Mn^{2+} and Mn^{3+} valence states, which explains their magnetic behaviors. This data are analyzed comparatively. The manganese ions provide information about many specific aspects like geometry of structural units of the glass network, the character of the chemical bonds in glasses as well as the polyhedral coordination (local symmetry) of paramagnetic metal ions. Manganese ions were detected as magnetically isolated for glasses with x < 20 mol % and as antiferromagnetic coupled when x ≥ 20 mol % MnO. Both Mn^{2+} and Mn^{3+} ionic species are responsible for the magnetic behavior of the investigated glasses. The paper aims to presented the results concerning: the temperature dependence of the reciprocal magnetic susceptibility, the composition dependencies of the molar Curie constant, C_M and the paramagnetic Curie temperature θ_p. The molar fraction of manganese ions in this two possible valence states were estimated in first approximation using relations: $x\mu_{eff}^2 = x_1\mu^2_{Mn^{2+}} + x_2\mu^2_{Mn^{3+}}$, $x = x_1 + x_2$ where x_1 and x_2 are the molar fraction of Mn^{2+} and Mn^{3+} ions, respectively. The obtained values are shown in tables in this paper. The studied materials present both practical and theoretical interest.

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1. Introduction

There are many reports concerning the investigation of the valence states and the distribution of transition metal ions (TMIs) in the network of oxide glasses, wich depend on the glass matrix nature [1], preparation conditions [2] and nature of the TMIs [3].

The ESR absorption spectra due to paramagnetic ions in vitreous matrices are recommended as valuable in revealing the structural details of the diamagnetic host, the coordination and valence state of these ions. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems. Many oxide glasses such as borate [4-6], alkali-silicate [7] aluminium-silicate or phosphate [8], tellurite [9] and also chalcogenide [10] or halide [11] containing Mn^{2+} ions have been investigated by ESR.

The magnetic properties of oxide glasses containing manganese have been investigated in potassium [3], lithium [12], strontium [13], lead [14], cadmium [15], borate and also in tellurite [16] and bismuthate [17-19] systems. The type and strength of magnetic interactions concerning manganese were determined in various concentration range. Besides Mn^{2+} ions, the Mn^{3+} species are often detected [13, 17, 20].

Magnetically susceptibility of glasses can be establish with:

$$M = m\chi H \,. \qquad (1)$$

We can express the magnetic moment of atom using the equation:

$$\mu_{at} = 2{,}827\sqrt{\frac{C_M}{x}} \qquad (2)$$

where
C_M represents molar Curie constant
X -represents the manganese ions concentration
As well if the value of recorded magnetic moment is between ($\mu_{Mn}^{2+} = 5{,}92\mu_B$ or $\mu_{Mn}^{3+} = 4{,}90\mu_B$) we can estimate the molar fraction using the relations:

$$x\,\mu^2_{\exp} = x_1\,\mu^2_{Mn^{2+}} + x_2\,\mu^2_{Mn^{3+}}\; x = x_1 + x_2\,, \qquad (3)$$

For the system $xMnO\cdot(100-x)[2B_2O_3\cdot PbO]$ of prepared samples we have determined also the electrical resistivity of volume ρ_V:

$$\rho_V = R_V\,\frac{S}{l}\,, \qquad (4)$$

where
l- probe wide
S- probe surface
We know that the electrical conductivity is given by:

$$\sigma = \frac{1}{\rho_V} = \frac{\nu n e^2 R^2}{kT}\, r(1-r)\exp(-2\alpha R)\exp(-\frac{W}{k_T}) \qquad (5)$$

Therefore

$$\rho_V = \rho_0 T \exp(\frac{W}{kT}) \cdot \qquad (6)$$

For activation energy determination we will use graphic representation: $\ln(\rho_V T^{-1}) = f(T^{-1})$.
The number of the total transitional ions is : $n = \frac{N_A}{V_M}$.

where:
N_A- Avogadro number
V_M-molar volume
$V_M = \frac{M}{d}$,
where:
d-probe density
M-molar mass

Knowing that $R = \sqrt[3]{\frac{1}{n}}$. and using $\sigma = n_0 e \mu$ we can estimate the value of carriers mobility; μ between [10^{-7} – 10^{-14}] cm^2/V s. Finally we conclude that the probes are semiconductors.

2. Experimental

Glasses of the $xMnO\cdot(100-x)[2B_2O_3\cdot MO]$ (where MO is CdO, SrO, PbO or As_2O_3), systems were prepared in the composition range 0 < x < 50 mol % for CdO, SrO and As_2O_3, 0 < x ≤ 80 mol % for PbO; using reagent grade $MnCO_3$, H_3BO_3, CdO, $SrCO_3$, PbO and As_2O_3 in suitable proportions. The mixture were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace at 1250°C. The molten materials was kept at this temperature for 30 min and quenched at room temperature by pouring onto a stainless-steel plate. Typical glass samples were obtained. The structure of samples was analyzed by means of X-ray diffraction. The patterns obtained did not reveal any crystalline phases up to x = 50 or 80 mol %.

Table 1

Studied system	Concentration domain x [% mol]													
$xMnO (1-x) [2B_2O_3\cdot CdO]$	0	0,1	0,5	1	3	5	10	20	35	50				
$xMnO (1-x) [2B_2O_3\ SrO]$	0	0,1	0,5	1	3	5	10	20	35	50				
$xMnO (1-x) [2B_2O_3\cdot PbO]$	0	0,1	0,5	1	3	5	10	20	30	40	50	60	70	80
$xMnO (1-x) [2B_2O_3\cdot As_2O_3]$	0	0,1	0,5	1	3	5	10	20	35	50				

2.1 Magnetic measurements

The magnetic susceptibility measurements were performed using a Faraday-type balance in the 80-300 K temperature range. For an accurate estimation of the molar Curie constant, C_M, corrections due to the diamagnetism of the vitreous matrix and MnO were taken into account.

2.2 Electric measurements

The electrical resistivity measurements were performed only for lead-borate glasses, using current-voltage techniques. Concerning the surface polarization no dependence on time was noted in dc conductivity after the voltage was applied. The thermoelectric power indicated that the current carriers are electrons. The samples have 1-1,5 cm^2 area and 0,5-3 mm thickness. For the control of the results we used also current-voltage techniques. The dc I-V characteristic was linear.

The glass samples density was determined using a picnometric technique.

3. Results and discussion

For all samples the temperature dependence of the reciprocal magnetic susceptibility are shown in Fig. 1 (a, b, c, d).

For the glasses with small concentration of MnO the magnetic susceptibility obeys a Curie law = C/T, suggesting that in this concentration range are predominant manganese ions which do not participate to the superexchange interactions. For higher concentrations of manganese a Curie-Weiss law, $\chi = C/(T - \theta_P)$, with negative paramagnetic Curie temperature was followed.

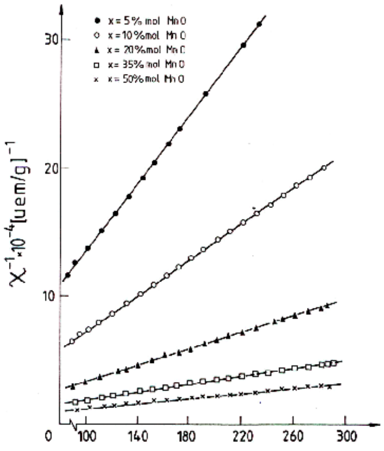

Fig. 1a) Temperature dependence of the reciprocal magnetic susceptibility of $xMnO\cdot(100-x)[2B_2O_3\cdot CdO]$ glasses

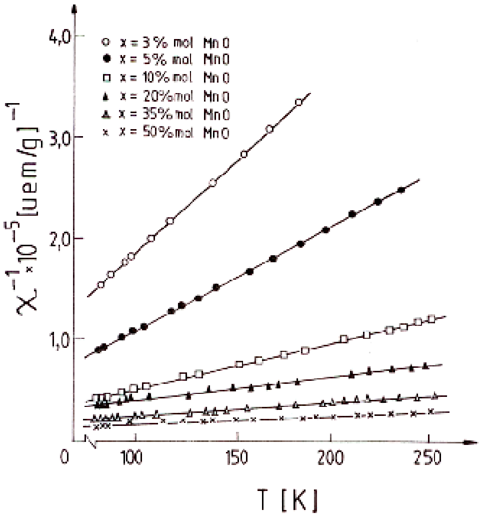

Fig. 1b) Temperature dependence of the reciprocal magnetic susceptibility of glasses in the system xMnO·(100-x)[$2B_2O_3$·SrO]

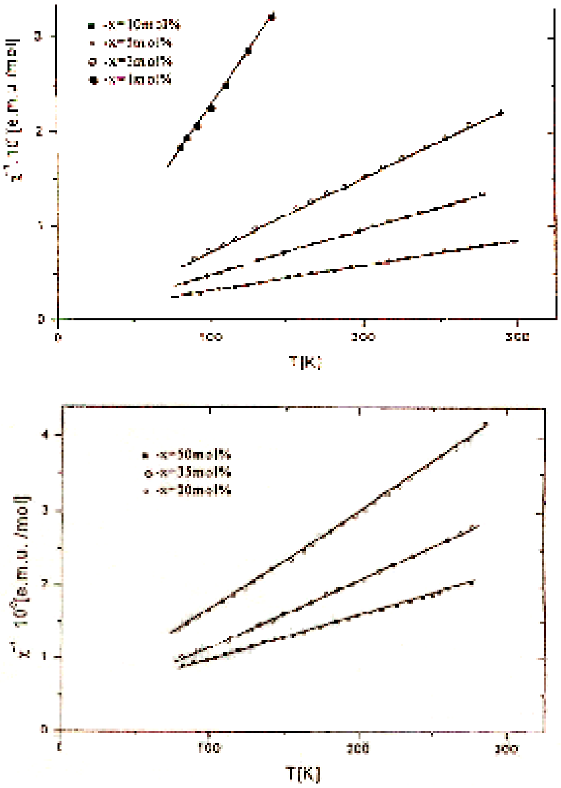

Fig. 1c) Temperature dependence of the reciprocal magnetic susceptibility of some glasses of the system xMnO·(100-x)[$2B_2O_3$·As_2O_3] for 1≤x≤10 mol% (a) and 20≤x≤50 mol% (b) concentration range

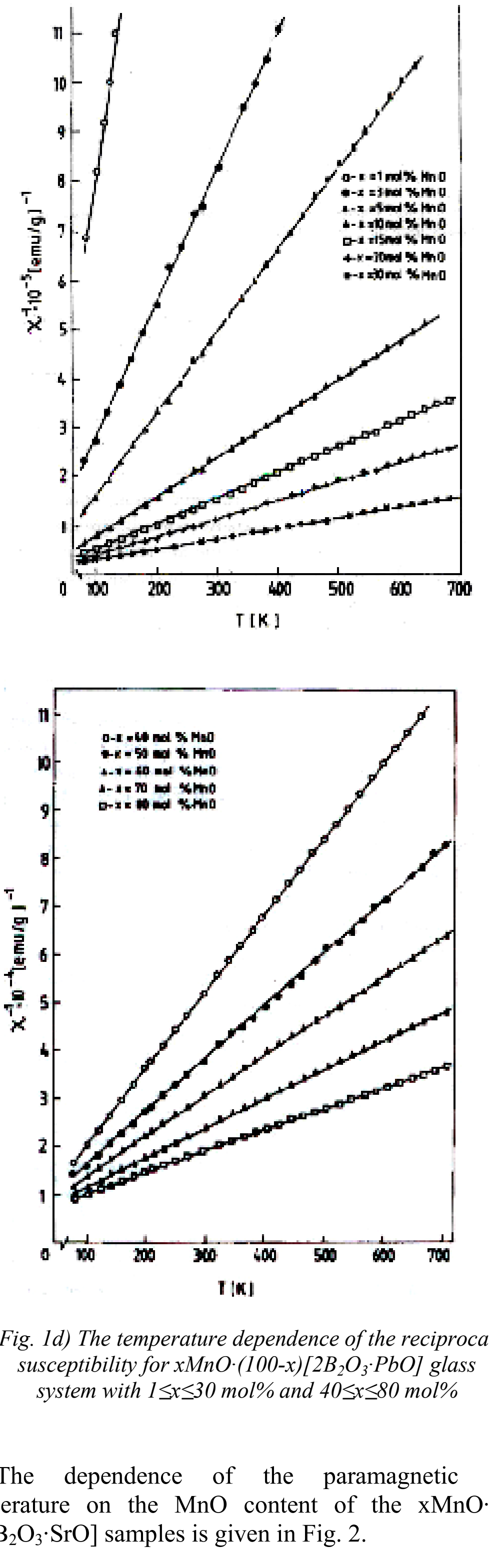

Fig. 1d) The temperature dependence of the reciprocal susceptibility for xMnO·(100-x)[$2B_2O_3$·PbO] glass system with 1≤x≤30 mol% and 40≤x≤80 mol%

The dependence of the paramagnetic Curie temperature on the MnO content of the xMnO·(100-x)[$2B_2O_3$·SrO] samples is given in Fig. 2.

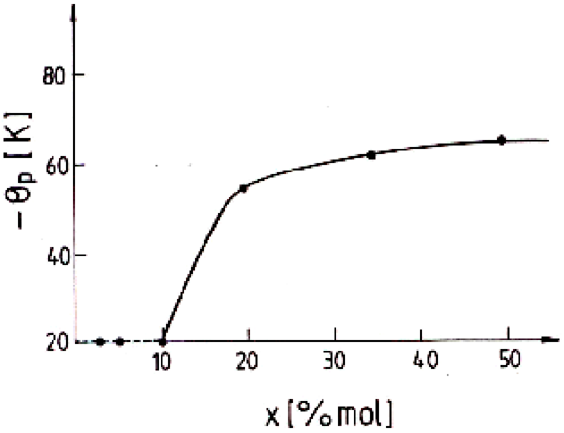

Fig. 2. The dependence of the paramagnetic Curie temperature on the MnO content of samples in the system $xMnO \cdot (100-x)[2B_2O_3 \cdot SrO]$.

The absolute value of θ_P increases non – linearly with the manganese ions content increasing. For these compositions, the high temperature susceptibility data indicate that the manganese ions in glasses experience negative interactions, are coupled predominant antiferromagnetically. In this case, the magnetic order takes place only at short-range and the magnetic behavior of the glasses can be described by the mictomagnetic type order. The exchange integral generally increases as the concentration of the magnetic ions is increased in the glass. As a result the magnitude of the paramagnetic Curie temperature increases.

To determine accurately the values of the molar Curie constants, C_M, correction due to the diamagnetism of the glass matrix and MnO were taken into account. Observing the experimental data, we consider that in these glasses are present both Mn^{2+} and Mn^{3+} ions. In this case, using the atomic magnetic moment values in free ion state (μ_{Mn}^{2+} = 5,92μ_B or μ_{Mn}^{3+} = 4,90μ_B), we estimate in a first approximation the molar fraction of these ions in the investigated samples from the previous relations.

Table 2. Molar curie constants and molar fractions of $Mn^{2+}(x_1)$ şi $Mn^{3+}(x_2)$ ions in $xMnO \cdot (100-x)$ $[2B_2O_3 \cdot CdO]$ glasses

x [% mol MnO]	C_M [uem / mol]	x_1 [% mol $Mn^{2+}O$]	x_2 [% mol $Mn^{3+}O$]
1	0,0451	1,0	-
3	0,1223	2,3	0,7
5	0,1889	2,8	2,2
10	0,3430	3,1	6,9
20	0,6897	6,4	13,6
35	1,2048	11,3	23,7
50	1,7101	15,1	34,9

There are different distributions of manganese valence states in the studied matrices, due to valence and ionic radius differences.

The composition dependencies of the molar Curie constant, C_M, and the paramagnetic Curie temperature, θ_p, are given in following tables.

Theoretical study regarding the possibility to realize a magnetically order in disorder magnetic materials is presented in the Gubanov [4] theory. He predicted the magnetically order sprouting at distance in amorphous and liquid materials. As well Simpson [5] demonstrate that in amorphous negative magnetically change interaction sprouting. According to Simpson model we can express the dependence of the magnetically susceptibility with temperature

Table 3. Molar fractions of the $Mn^{2+}(x_1)$ and $Mn^{3+}(x_2)$ ions in glasses of the system $xMnO \cdot (100-x)[2B_2O_3 \cdot SrO]$

x [% mol MnO]	x_1 [% mol $Mn^{2+}O$]	x_2 [% mol $Mn^{3+}O$]
3,0	3,0	0,0
5,0	5,0	0,0
10,0	10,0	0,0
20,0	15,0	5,0
35,0	12,3	22,7
50,0	6,3	43,7

Table 4. Molar curie constants effective magnetic moments, molar fractions of Mn^{2+} and Mn^{3+} ions for $xMnO \cdot (100-x)[2B_2O_3 \cdot As_2O_3]$

x %molMnO	C_M 10^2 emu/mol	μ_{exp} [μ_B]	x_1 % mol	x_2 % mol
1	4.39	5.92	1	-
3	12.83	5.84	2.73	0.27
5	29.90	5.76	4.13	0.87
10	39.35	5.6	6.6	3.4
20	75.22	5.48	10.74	9.26
35	123.44	5.31	12.88	22.12
50	164.89	5.14	10.22	39.78

Table 5. Molar curie constant, C_M, molar fractions of manganese ions of $xMnO\cdot(100-x)[2B_2O_3\cdot PbO]$ glass systems

x [mol %]	C_M [emu mol^{-1}]	x_1 [mol % $Mn^{2+}O$]	x_2 [mol % $Mn^{3+}O$]
1	0.04233	1.0	-
3	0.12274	2.8	0.2
5	0.2087	4.5	0.5
10	0.4089	8.1	1.9
20	0.7838	13.7	6.3
30	1.1596	19.9	10.1
40	1.5346	25.2	14.8
50	1.8985	30.6	19.4
60	2.2140	32.5	27.5
70	2.5712	35.1	34.9
80	2.9025	38.9	41.1

Table 6. Sample density (d), number of Mn^{2+} (n_0), ions per volum unit ($r=Mn^{2+}/Mn_{tot}=x_1/x$) , average intersite separation (R), hopping activation energy (W), for glasses of the system $xMnO\cdot(100-x)[2B_2O_3\cdot PbO]$

X %mol MnO	d [g/cm^3]	n_0 x 10^{-21} [cm^{-3}]	R [Å]	W [eV]	r
3	3.62	0.17	17.65	1.62	0.93
5	3.63	0.28	14.80	1.44	0.90
10	3.66	0.54	11.45	1.02	0.81
20	3.72	1.01	8.79	0.94	0.69
30	3.71	1.61	7.44	0.78	0.66
40	3.73	2.32	6.48	0.67	0.63
50	3.73	3.17	5.78	0.59	0.61
60	3.72	3.91	5.17	0.51	0.54
70	3.72	4.96	4.66	0.44	0.50
80	3.72	6.69	4.17	0.37	0.48

$$x = x_I = \frac{C}{T+\theta_p} + x_0 , \qquad (7)$$

where: $\theta_p = \frac{\mu_0^2}{k}|\vec{\gamma}|\bar{z}$ is paramagnetic Curie temperature.

Kobe and Handrich [25] elaborated an other model which include the structural fluctuation in the magnetically susceptibility calculation. Hasegawa [26] elaborated also a model which predicted a $T_N > T_N^o$ and depend by the relatively distribution of the first and second order neighbor.

All these models based on the effective (molecular) field theory, which imply a collective order for the spins identical located in the systems. This not corresponds to the reality facts in the disorder materials. All homogenous non-crystalline materials present a paramagnetic behavior. Therefore the magnetically susceptibility is well approximated by the Curie-low:

$$\chi = \chi_{I_z} = \frac{C}{T} + x_0 . \qquad (8)$$

For non-crystalline materials with higher concentration of the magnetically ions the magnetically susceptibility is better expressed with Curie-Weiss low

3.1 Electrical conductivity in dc of the oxide semiconductor glasses

Oxide glasses containing transition metal ions (TMIs) are known to be electronic semiconductors. It is of course necessary that ions in more than one valence state should be present. Austin and Mott and Schnakenberg have discussed the conduction process in terms of hopping between ions in two valence states. Mott [9] has proposed for the electric conductivity an expression of the form:

$$\sigma = \frac{\nu_0 n e^2 R^2}{kT} r(1-r)\exp(-2\alpha R)\exp\left(-\frac{W_D}{kT}\right) \qquad (9)$$

were R is the average intersite separation; n-is the number of sites of TMIs in low valence state per unit volume; r – the fraction of sites occupied by an electron; - the photon frequency; T – the absolute temperature; exp (2α R) – the tunneling probability; W – the hopping activation energy. The variation of conductivity with glass composition is difficult to interpret since the parameters n, r, R and W vary with the nature and the proportion of the TMIs and with the preparation conditions. The results obtained by Sayer et al. [10] for high concentration of TMIs in phosphate glasses suggest that the term exp(-2 α R) arising from electron tunneling is not observed.

3.2 Conductivity data

In order to analyze the conductivity data we have considered a polaronic model.

The values of the conductivity activation energy are shown in the previous tables. The activation energies have been calculated by using the method of least squares. One remarks that the activation energy increases if the MnO content is decreased. The results are similar to those found for iron, vanadium, manganese phosphate oxide glasses.

4. Conclusions

Magnetic susceptibility and electric conductivity measurements performed on the presented glass systems indicate that in the glasses with x>30 mol% the manganese ions participate to negative magnetic superexcenge interactions. The curie constant values allow to establish that in the glasses both Mn^{2+} and Mn^{3+} ions are present and the and the molar fraction of these ions is estimated between 100 and 48,62% for Mn^{2+}. The presence of the Mn^{2+} and Mn^{3+} ions determined the semiconducting behavior of these glasses. The semiconduction processes occurring in lead borate glasses containing manganese ions suggest that a polaron model is applicable.

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