Eur. Phys. J. B **20**, 235–240 (2001)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Structural and magnetic studies of CuO-TeO$_2$ and CuO-TeO$_2$-B$_2$O$_3$ glasses

F. Ciorcas[1,2], S.K. Mendiratta[1,a], I. Ardelean[2], and M.A. Valente[1]

[1] Physics Department, University of Aveiro, 3810 Aveiro, Portugal
[2] Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania

Received 23 October 2000 and Received in final form 1st February 2001

Abstract. The glass systems xCuO$\cdot(1-x)$TeO$_2$ and xCuO$\cdot(1-x)[75$TeO$_2\cdot25$B$_2$O$_3]$ with $0 < x \leq 50$ mol% were investigated by means of X-ray diffraction, electron paramagnetic resonance (EPR) and a.c. magnetic susceptibility ($\chi_{\mathrm{a.c}}$) measurements, the principal aim of the investigation being the study of the structural modifications in the tellurite glasses introduced by the addition of boron oxide. In the case of first glass system, *i.e.* without B$_2$O$_3$, EPR spectra of Cu^{2+} ions undergo changes with the increasing concentration of CuO. At very low concentrations, spectra are due to isolated Cu^{2+} ions in axially distorted octahedral sites. The EPR signal for samples with $3 \leq x \leq 20$ mol% can be explained as being the superposition of two EPR absorptions, one showing the hyperfine structure typical for isolated Cu^{2+} ions and the other consisting of a symmetric line typical for clustered ions. The broadening of the absorption band is due to dipolar as well exchange interaction. The susceptibility data show that for $x > 20$ mol%, the Cu^{2+} ions are predominantly clustered and are coupled through antiferromagnetic exchange interaction. A comparative study of amorphous X-ray diffraction pattern of the glasses indicates a structural modification in the TeO$_2$ network with increasing CuO concentration; the effect is quite visible in the samples with CuO concentrations higher than 20 mole percent. Measurements of density corroborate the conclusions drawn from the X-ray diffraction. Additionally, we show that our data validates a model in which CuO rich regions are surrounded by a buffer boundary which separates them from the tellurite glassy network; effect of introducing B$_2$O$_3$ can be best described as breaking these regions into smaller size regions.

PACS. 61.43.Fs Glasses – 76.30.Fc Iron group (3d) ions and impurities (Ti-Cu)

1 Introduction

TeO$_2$ based glasses have been widely studied due to their possible applications in optoelectronic devices [1,2]. The relation between the properties and the structure as well as the effect of structural inhomogenity on the properties has been extensively investigated [3–10]. The addition of TM ions confers them semiconducting properties and the applications in switching and memory devices have been explored [11,12]. The local environment of a TM ion can be easily probed by EPR techniques; the paper of Griscom [13] provides an interesting example of a study using this technique.

We have reported before the results of our study on the behaviour of ternary tellurite glasses containing Cu^{2+} ions introduced as CuO [14–17]. These glasses contained B$_2$O$_3$ and PbO as network modifier. The experimental data, EPR and magnetic susceptibility obtained from Faraday balance (fields up to 8 tesla), was interpreted as indicating the presence of monovalent Cu ions in significant proportions. The conclusions were based on the behaviour of the linewidth and the intensity of the EPR absorption as well as on the magnetisation data obtained in the balance. Magnetic measurements – zero field a.c. susceptibility and low temperature magnetization M *vs.* H (fields up to 20 tesla) – on the system xCuO-PbO-2B$_2$O$_3$ show [18] that though the measured effective spin per magnetic ion is less than the theoretical value for a free divalent Cu ion, there is an effective antiferromagnetic interaction between the Cu ions for as low a concentration as 10%. The aim of the present study is to verify whether some of conclusions drawn in the previous studies on the behaviour of Cu ions in tellurite glasses also hold good in a simple binary system *i.e.* CuO-TeO$_2$ and to see how the behaviour changes with the addition of another network former -B$_2$O$_3$. We also included the data on density and the X-ray diffraction to gather further evidence on the role of structure of the glass on the magnetic properties. Another difference from the previous studies is that the susceptibility measurements were done by zero field a.c. method; we think that the magnetic response for the very low fields applied in the a.c. method is a more accurate direct measurement of the susceptibility. Our analysis of the data of the measurements from four different techniques allows us to infer

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[a] e-mail: `skm@fis.ua.pt`

Table 1. 2θ values corresponding to the first maximum in X-ray diffraction spectrum and mass density values for xCuO·(1−x)TeO$_2$ and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] systems. $(\Delta\rho)_{\mathrm{exp}}$ is experimentally measured density increment referred to the density of the glass without CuO. For Cu-Te glass $\rho_{\mathrm{th}} = x \times 6.135 + (1-x) \times 4.77$; 6.135 is taken as the density of CuO. $(\Delta\rho)_{\mathrm{th}} = \rho_{\mathrm{th}} - 4.77$. Calculations for the Cu-Te-B glasses were done similarly.

x	xCuO·(1−x)TeO$_2$				xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$]			
(mol%)	2θ (°)	ρ_{exp} (g/cm^3)	$\Delta\rho_{\mathrm{exp}}$	$\Delta\rho_{\mathrm{th}}$ (g/cm^3)	2θ (°)	ρ_{exp} (g/cm^3)	$\Delta\rho_{\mathrm{exp}}$	$\Delta\rho_{\mathrm{th}}$ (g/cm^3)
3	27.225	4.848	0.078	0.045	26.075	4.150	−0.016	0.062
5	27.225	4.843	0.073	0.076	26.725	4.129	−0.037	0.105
10	27.125	4.751	−0.020	0.153	26.825	4.166	0.000	0.213
20	27.925	5.075	0.304	0.307	28.475	4.461	0.294	0.428
30	29.025	5.217	0.447	0.462	28.075	4.630	0.464	0.642
50	31.025	5.418	0.548	0.771	30.525	4.924	0.758	1.072

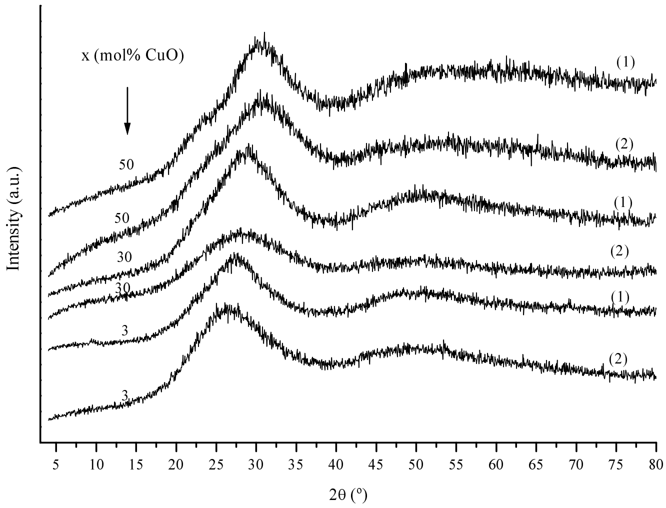


Fig. 1. X-ray diffraction patterns of xCuO·(1−x)TeO$_2$ (1) and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] (2) glasses for x = 3, 30 and 50 mol% CuO.

a feature of the structure that we believe has not been reported before in these glasses.

2 Experimental

The tellurite vitreous systems xCuO·(1−x)TeO$_2$ and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] with $0 < x \leq 50$ mol% were prepared. The powder admixtures of suitable proportions of pure reagents CuO, TeO$_2$ and H$_3$BO$_3$ were introduced into the sintered corundum crucibles. The melting was performed in an electrical furnace at 1000 °C during 10 minutes. The molten material was quenched by pouring it onto a copper plate held at room temperature. Glasses had the characteristic coloration of copper containing glasses. X-ray diffraction patterns were recorded using a Philips X'Pert MPD Diffractometer at Cu K$_\alpha$ wavelength. The EPR measurements were recorded at room temperature in the X-band (9.45 GHz) with a Bruker ESR 300E EPR spectrometer. The magnetic susceptibility $\chi_{\mathrm{a.c.}}$ measurements were carried out in the temperature range 80–300 K by applying sinusoidal fields of frequency 119 Hz and amplitude less than 1 mT.

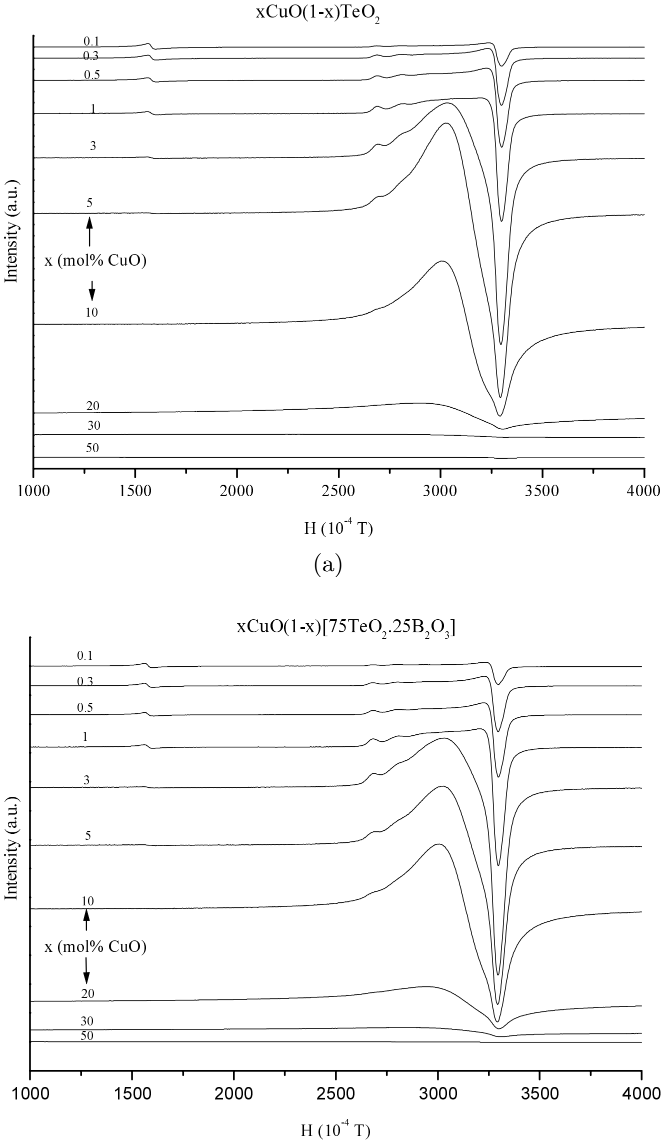
3 Results and discussion

3.1 X-Ray diffraction and density measurements

The X-ray diffraction pattern for some representative samples are plotted in Figure 1. No crystalline phase was detected and the X-ray patterns are characteristic of a vitreous solid up to 50 mol% CuO for both the tellurite systems investigated. But it was noticed that the 2θ position of the most intense amorphous peak shifted with increasing concentration of copper in both the systems. These values are shown in Table 1 along with the densities measured by Archemedies principle. We notice that up to 10 mole percent of CuO the shifts are insignificant and fall within the measurement error. However, in the glasses with larger concentrations a shift towards larger 2θ values with increasing Cu content is clearly noticeable in both the glass systems. Also, a comparison between the two glass systems indicates that the introduction of some borate in the tellurite network shifts this peak towards lower values. Since this is the most prominent peak in almost pure (3 mole percent CuO) tellurite network glass, it is definitely due to Te-O bonds. A shift towards higher 2θ values indicates shortening of the length of this bond. Table 1 shows the 2θ values of the X-ray diffraction peak corresponding to the Te-O bond in various glasses. In the column adjacent to the density column in the table we show the increase $\Delta\rho$ in the experimentally measured density with the increasing Cu concentration. In the next column we indicate theoretically expected $\Delta\rho$ calculated with the assumption that all the CuO is in the isolated regions and has the theoretical density of the crystalline form. Of course this is a gross assumption but it does not alter our final argument so long as we suppose a constant density of the pure CuO regions. We propose to interpret the results in the following way. For low concentrations the Cu ions go into the available rather open spaces of the Te-O network without straining the bonds too much. This leads to the fact that the experimentally measured increments in the Cu tellurite glasses

Table 2. EPR parameters for xCuO·(1−x)TeO$_2$ and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] glasses with $0.1 \leq x \leq 0.5$ mol%.

	xCuO·(1−x)TeO$_2$				xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$]			
x (mol% CuO)	A_1 (10^{-4} T)	A_2 (10^{-4} T)	$g_\parallel$	$g_\perp$	A_1 (10^{-4} T)	A_2 (10^{-4} T)	$g_\parallel$	$g_\perp$
0.1	120.821	140.763	2.35	2.06	108.503	121.994	2.37	2.07
0.3	120.821	138.417	2.35	2.06	120.235	123.165	2.36	2.07
0.5	120.821	140.763	2.35	2.06	129.032	137.830	2.35	2.07



(a)

(b)

Fig. 2. (a) EPR absorption spectra of Cu^{2+} ions in xCuO·(1−x)TeO$_2$ glasses and (b) EPR absorption spectra of Cu^{2+} ions in xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] glasses.

for low concentrations (less than approximately 5 percent) are higher than those theoretically expected. With the increasing concentration, Cu ions begin to strain and distort locally the surrounding the Te-O network and then the increase is not so pronounced and as a matter of fact there is a levelling of the tendency up to 10 mol percent. The experimentally measured 2θ values, indicative of the Te-O bond length, in this concentration region do not show discernible variation. However, for larger concentrations, *i.e.* more than ten mol percent, the Cu ions cluster and a sort of demixing occurs. In these Cu rich regions the density is higher, being closer to the theoretical density of the CuO. These tendencies are clearly shown by the numbers in the table for the two glass systems. The process of demixing implies emerging of the Cu ions from the strained Te-O network and forming almost pure amorphous CuO regions. Around these regions is a buffer layer where the density is in between that of CuO and TeO$_2$ and the Te-O bonds are shorter. As a consequence the *average* length of the Te-O bond is smaller. This tendency is clearly implied by the increase in the 2θ values for concentrations larger than ten percent as shown in the data of the table. We are undertaking the calculation of the radial distribution function to further confirm our hypothesis. Our data indicates that the mixed tellurite-borate network is relatively more open but more importantly the CuO rich regions in boro-tellurite are smaller resulting in more volume of the buffer layer with shorter Te-O bonds.

3.2 EPR-results

In Figures 2a and 2b, we show the typical EPR spectra. In the spectra corresponding to lower concentrations of CuO, hyperfine structure due to $I = 3/2$ of Cu^{2+} ion is easily seen. For glasses containing less than 0.5 mol% of CuO we could calculate values of the parameters $g_\parallel$, $g_\perp$ and A; these are shown in Table 2. For both the systems, values of $g_\parallel$ and $g_\perp$ satisfy the relation $g_\parallel > g_\perp > g_e = 2.0023$ indicating that the Cu^{2+} ions are coordinated by six ligand atoms in an axially distorted octahedron [15]. In this relation g_e represents the g-factor for a free electron. The anisotropic HFS is due to pronounced ligand field fluctuations present in the vitreous matrices that broaden the line. Over this anisotropy a broadening of the spectral lines appears which is caused by the long-range interactions that become stronger with the increasing CuO concentration.

Analysis of the spectral structure in the range $3 \leq x \leq 20$ mol% for both the systems shows that the absorption spectrum is a superposition of two bands. This superposition is illustrated for 0.05CuO-0.95TeO$_2$ glass in Figure 3. The first signal is due to isolated Cu^{2+} ions in axial neighborhood and the second is a large EPR signal presenting a high symmetry. The latter absorption indicates the interaction between neighboring Cu^{2+} ions. Thus we conclude

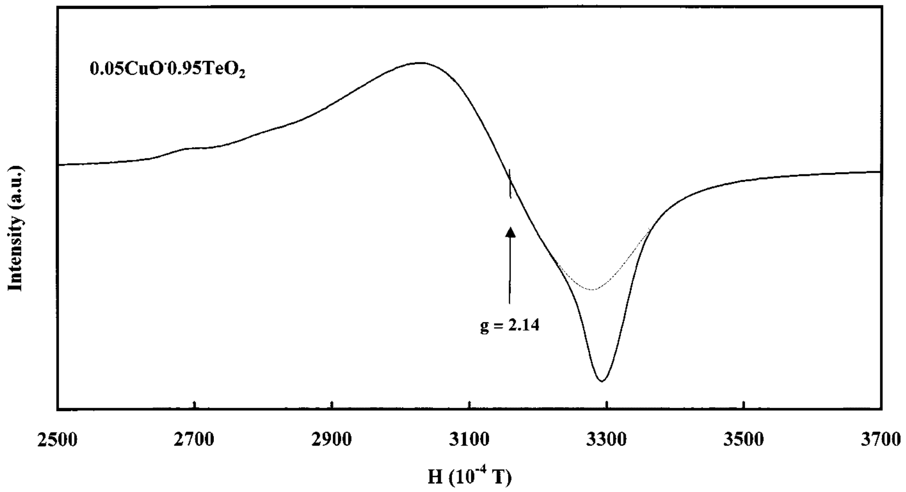


Fig. 3. Superposition of two absorption signals illustrated for 0.05CuO-0.95TeO$_2$ glass.

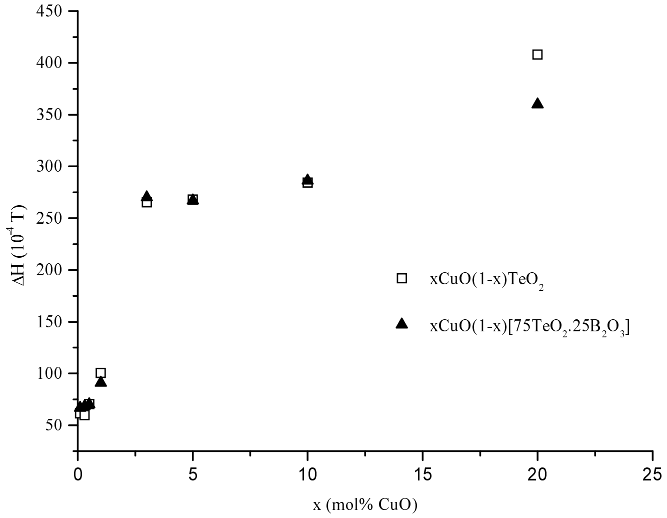


Fig. 4. Linewidth evolution of the $g \cong 2.07$ resonance due to Cu^{2+} ions for xCuO·(1$-x$)TeO$_2$ and xCuO·(1$-x$)[75TeO$_2$·25B$_2$O$_3$] glasses with $0.1 \leq x \leq 20$ mol% CuO.

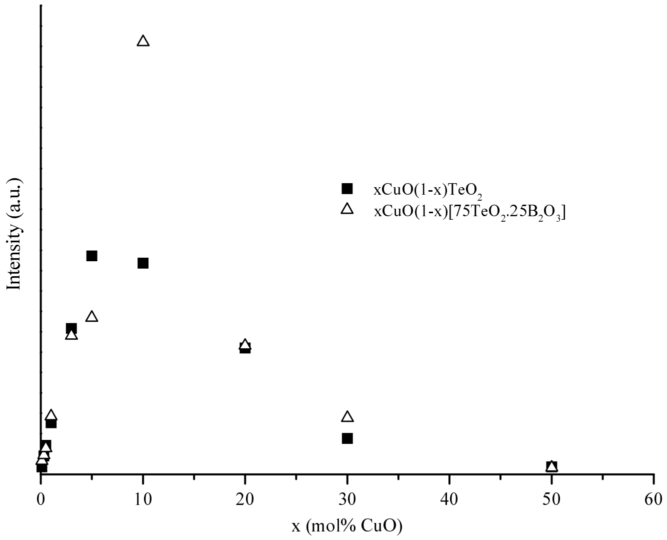


Fig. 5. Concentration dependence of the resonance line intensity for xCuO·(1$-x$)TeO$_2$ and xCuO·(1$-x$)[75TeO$_2$·25B$_2$O$_3$] systems.

that either the neighborhood symmetry of the isolated ions and the interacting ions (forming a cluster of mutually interacting ions) is basically the same or not all the ions are in some cluster and there are always some isolated ions. It is clear that the population density of the isolated ions decreases with the increasing concentration. Existence of isolated Cu^{2+} ions in axially distorted neighborhood in the glasses with concentration up to 20 mol% suggests that the clustered ions in our vitreous matrices probably cause the distortion but do not destroy the fundamental symmetry of the neighborhood. The line-width ΔH of the absorption band of the isolated ion considered as the peak-to-peak width of the first derivative could be calculated for the samples with $0.1 \leq x \leq 20$ mol%. At higher concentrations ($20 < x \leq 50$ mol%) line-width could not be estimated because of very broad absorption due to interaction. Evolution of the line-width ΔH as a function of concentration of CuO in the range $0.1 \leq x \leq 20$ mol% presented in Figure 4 supports the hypothesis presented above. Thus the line-width ΔH at first increases in this concentration range due to dipolar interactions, but at about 5 mol% the slope of the curve changes. The values of ΔH beyond 5 percent concentration include the broadening due to exchange coupling.

In the glasses with $x > 20$ mol%, intensity of the EPR signal is very weak (Figs. 2a, b). In this concentration range, for both the systems, the Cu^{2+} ions responding to EPR absorption are clustered and have their unpaired electron spins coupled predominantly in antiparallel configuration by superexchange-type mechanism. Intensity of the absorption spectra was determined by numerical integration of the EPR signal. The concentration dependence (Fig. 5) shows an increasing of the intensity up to 5 mol% for xCuO·(1$-x$)TeO$_2$ and 10 mol% for xCuO·(1$-x$)[75TeO$_2$·25B$_2$O$_3$]. At higher concentrations, for both the systems, the intensity decreases reaching to

Table 3. Magnetic parameters obtained from $\chi_{\text{a.c.}}$ measurements for xCuO·(1−x)TeO$_2$ and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] glasses with $20 \le x \le 50$ mol%.

	xCuO·(1−x)TeO$_2$			xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$]		
x (mol% CuO)	$\theta_p \pm 1$ (K)	$C_\mathrm{M} \pm 0.0005$ (emu/mol)	μ_eff (μ_B)	$\theta_p \pm 1$ (K)	$C_\mathrm{M} \pm 0.0005$ (emu/mol)	μ_eff (μ_B)
20	0	0.0378	1.298 ± 0.002	0	0.0350	1.288 ± 0.001
30	−16	0.0607	1.221 ± 0.005	−7	0.0559	1.273 ± 0.007
50	−63	0.1037	1.183 ± 0.004	−42	0.1053	1.229 ± 0.002

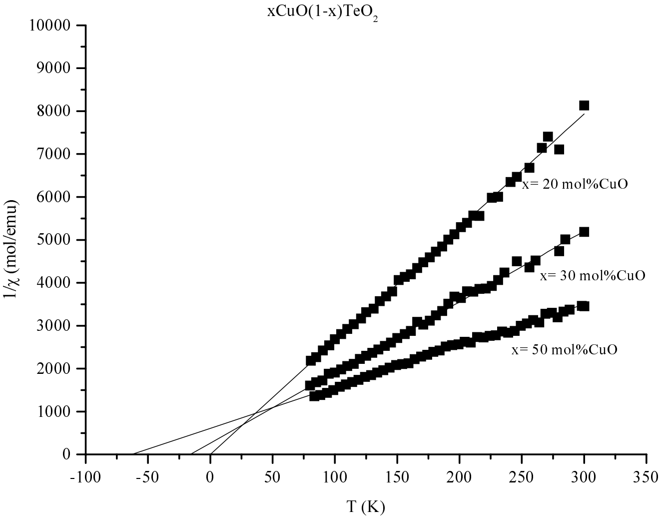


Fig. 6. Temperature dependence of the reciprocal magnetic susceptibility for xCuO·(1−x)TeO$_2$ glasses with $20 \le x \le 50$ mol% CuO.

a negligibly small value for $x = 50$ mol%. At high concentrations decreasing of the intensity can be attributed to the presence of the Cu$^+$ and Cu^{2+} ions in the system, larger spatial disorder or the magnetic coupling between the ions.

Addition of B$_2$O$_3$ to the copper tellurite glasses affects the intensity variations indicating that comparatively speaking the Cu ions in these glasses have less tendency to cluster and therefore the critical concentration beyond which most of the ions are magnetically coupled is higher. Since the number of non-coupled ions at the critical concentration in these glasses is bigger, the intensity at this critical concentration is naturally larger.

Finally at very low concentrations, *i.e.* up to about 5 mol%, a small absorption signal centered at $g = 4.3$ was seen in both the glass systems; we attribute this to the small amount of iron that might have entered the glass melt in the form of impurities.

3.3 Magnetic susceptibility measurements

The temperature variation of the reciprocal of the susceptibility for the Cu-Te two system is given in Figure 6; the behaviour of the data on the Cu-Te-B system is identical. The diamagnetic corrections were not necessary because their values are about hundred times lower than experimental values. The functional dependence of χ^{-1} on T, the Curie-Weiss behaviour, shows an antiferromagnetic interaction in the glasses for $x > 20$ mol%. These observations are in agreement with EPR results. Values of the temperature θ_p of the Curie-Weiss relation, molar Curie constant C_M and magnetic moment μ_eff were determined and are shown in Table 3.

In both the glass systems, thermal variation of the reciprocal susceptibilities, χ^{-1}, follows a Curie law ($\theta_p = 0$ K) for molar concentration of less than 20% of CuO. Up to this concentration the copper ions are predominantly isolated, but EPR data indicates that in the concentration range $3 \le x \le 20$ a clustering tendency is not excluded. When $x > 20$ mol%, the local correlations between magnetic ions are dominant and their density is sufficiently high thus forcing them to be coupled. The values of θ_p increase in absolute magnitude with the increase of the CuO content. This suggests that magnetic interactions increase with CuO concentration. A comparison of θ_p values for the two systems shows that the effective magnetic interaction between copper ions is stronger in the binary system.

Values of the magnetic moment μ_eff given in Table 3 were calculated using the following relation:

$$\mu_\mathrm{eff} = 2.828 \left(\frac{C_\mathrm{M}}{x} \right)^{\frac{1}{2}}. \qquad (1)$$

The value of the numerical prefactor implies the assumption that all the copper ions introduced in the batch contribute with the magnetic moment of the bivalent state in the glass being measured. The values obtained are lower than the magnetic moment of the free ion ($\mu_{\mathrm{Cu}^{2+}} = 1.73\mu_\mathrm{B}$) indicating the presence of antiferromagnetic interaction. It should be pointed out though that the presence of monovalent copper ions *could* also contribute towards this decrease in the effective moment. This would certainly be the case if the glasses were melted in the reducing conditions; however, our glasses were melted in the normal atmosphere.

4 Conclusions

In the xCuO·(1−x)TeO$_2$ and xCuO·(1−x)[75TeO$_2$·25B$_2$O$_3$] systems, homogenous glasses were obtained in a wide compositional range ($0.1 \le x \le 50$ mol%). X-ray diffraction and density measurements indicate that for low concentrations of CuO the copper ions are accommodated in the tellurite or Boro-tellurite network without straining the network. However for larger concentrations we see a shortening of the Te-O bond accompanied by an increase in the density; this increase is above that would be expected from simple linear mixing. We interpret this in the following way. At higher concentrations a sort of demixing occurs and in the glass there are regions occupied predominantly by CuO in an amorphous form. The density of CuO is larger than that of TeO_2 and we suppose that these CuO regions are bordered by a buffer layer. It is reasonable to further suppose that the density of the buffer layer has an intermediate value and the length of the Te-O bond in the layer is smaller than the rest of the tellurite network. Existence of this layer is then responsible for a density larger than that expected from simple proportionality arguments. A comparison of the data of the two glass systems reveals that this anomalous increase in the density due to intermediate layer is bigger in the boro-tellurite glasses. We propose that this is due to the fact that for the same concentration of the CuO, the CuO rich regions in the Boro glass are smaller but more numerous. A simple calculation shows that this adequately explains the difference in the density trends of the two glass systems. We will see below that our magnetic measurements can also be consistently explained within this model.

Results of the EPR and magnetic measurements indicate the following scenario. Up to 1 mol% concentration, the Cu^{2+} ions are isolated in predominantly axially distorted octahedral environment and at this low density the interaction between them is dipolar. For concentrations in the range $3 \leq x \leq 20$ mol%, EPR results indicate a clustering tendency of the copper ions though the ions maintain the axially distorted symmetry of the ligand field around them. At higher concentrations, *i.e.* for $x > 20$ mol%, copper ions interact mostly through a negative superexchange interaction leading to antiferromagnetic coupling between the magnetic moments of the neighboring ions. We also think that in this concentration range negligibly few ions have the original symmetry of the neighborhood of the isolated ion. However, since the regions in which we have mostly coupled copper ions are bigger at this high concentration, the *effective* magnetic interaction is stronger. This is indicated by larger values of θ_p as well as lower values of the effective magnetic moment associated with a single ion; it is worth remembering that the interaction is antiferromagnetic. We also observe that for the *same* concentration the glasses in the Boro system have lower values of θ_p and higher of μ_{eff}. This is in agreement with our model according to which CuO regions in Boro system are smaller.

Finally, we would like to make some comments about the possibility of existence of monovalent copper ion. X-ray diffraction data as well as the density data do not distinguish between the two types of copper ion. EPR data also cannot say anything definite on this issue. And since we have not performed optical absorption measurements, the only data presented here which can distinguish between the two states is the magnetic susceptibility data. We must admit that the difference between the measured value of the effective magnetic moment ($\sim$1.3) and the theoretical value of the free ion (1.73) even for the low concentration of 20% could have a contribution of the non-magnetic monovalent ion. Additionally, it is possible that due to the volatile nature of the oxides involved the concentration of the Cu ions in the glasses measured is not the same as in the batch used to make the glass. Since we did not undertake accurate chemical measurements of the concentration of the Cu ions in the final glass we cannot rule out the contribution of this factor. Thus, only the accurate determination of the final composition coupled with optical absorption measurements on thin sections of the glass samples can allow more definitive statements on the existence of monovalent Cu ions in the glass. However, it can be safely asserted that so far as the role of B_2O_3 is concerned, it does not introduce additional monovalent ions; this is different than what was observed earlier in ternary tellurite glasses [14–17]. Nonetheless our model of CuO rich regions with a buffer layer consistently explains the difference between the measured properties of the glasses in the two systems.

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