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Non-linear magnetic susceptibility of some vanadate glasses

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The first measurements of the anomalous variation of d.c. magnetic susceptibility of the $(50 - x)P_2O_5$–xM–$50V_2O_5$ ($M = Bi_2O_3$ and Sb_2O_3, and $x = 0$ to 40 mol % M) oxide glasses around 20 to 30 mol % M are reported here. Similar anomalous behaviour was also observed in the electrical and other physical properties of the glasses (reported in the previous paper). Like electrical and dielectric properties, this anomaly in the magnetic properties was also found to be mostly associated with the anomalous variation of the V^{4+}/V^{5+} ratio (around 20 to 30 mol % M) with the concentration of M. From the temperature (80 to 300 K)-dependent magnetic susceptibility data the V^{4+} ion concentrations have also been calculated, which agree quite well with those obtained from chemical analysis, and the small discrepancy is attributed to the presence of V^{3+} and/or V^{2+} ions in the glass.

1. Introduction

Semiconducting oxide glasses containing transition metal ions (TMI) such as vanadium, copper, iron, etc., are of great interest because of their uses as memory switching devices [1–3], cathode materials in batteries [4], etc. The electrical transport properties of the glasses containing TMI have been more extensively studied [5–12] compared to their magnetic properties [13–19]. However, a magnetic study also seems to be very interesting to elucidate the conduction mechanism of these oxide glasses. Friebele *et al.* [16] reported the magnetic properties of the vanadium phosphate glasses over the composition range 60 to 90 mol % V_2O_5. From the magnetic susceptibility and the electron spin resonance (ESR) study, they observed the existence of nearest neighbour antiferromagnetic (AFM) coupling between V^{4+} ions. Nicula *et al.* [19] studied magnetic properties of V_2O_5–As_2O_3 glasses and observed very weak antiferromagnetic interaction between the V^{4+} ions randomly distributed in the glass matrix. From nuclear magnetic resonance (NMR) studies, Lynch *et al.* [17] obtained the values of the hyperfine constants which are characteristic features of isolated V^{4+} ions in the V_2O_5–P_2O_5 glasses. Magnetic properties of some other binary TM oxide glasses as measured by several authors [15–19], however, indicated a different behaviour of the oxide glasses.

A few studies of the structural and magnetic properties of the oxide glasses containing iron ions have also been reported [20–23]. Iron ions in these glasses are considered to form clusters which exhibit superparamagnetic behaviour, and below the freezing temperature, individual spins are frozen in random directions because of antiferromagnetic interactions between nearby ions. The freezing temperatures of the iron-containing glass differ largely, depending on glass compositions [22, 23], and this difference in freezing temperature is considered to originate from the change in the local structure of iron ions (due to their compositional dependencies).

In the previous paper [24] we have reported the non-linear behaviour of the concentration-dependent electrical and other properties of the $(50 - x)P_2O_5$–xM–$50V_2O_5$ ($M = Bi_2O_3$, Sb_2O_3 and GeO_2; $x = 0$ to 40 mol % M) glasses. In the present article we have tried to explore the origin of the non-linear behaviour of the electrical properties of the vanadate glasses in the region 20 to 30 mol % M (see [24]) from the study of the concentration and temperature dependencies of the d.c. magnetic susceptibility of these glasses. An attempt has also been made to calculate the values of V^{4+} ions in these glasses from the magnetic susceptibility data and to compare them with those obtained chemically (see [24]).

In the present paper the abbreviations VPB, VPA, VPG and VP are used for the $(50 - x)P_2O_5$–xBi_2O_3–$50V_2O_5$, $(50 - x)P_2O_5$–xSb_2O_3–$50V_2O_5$, $(50 - x)P_2O_5$–$xGeO_2$–$50V_2O_5$, and $50P_2O_5$–$50V_2O_5$ glasses, respectively. The preparation techniques for all these glasses have already been discussed [24].

2. Experimental results

2.1. Magnetic susceptibility

The d.c. magnetic susceptibility, χ, in the temperature range 80 to 300 K was measured by a Curie-type balance [25]. The measured susceptibility of all the samples (VPB and VPA glasses at all concentrations) were calibrated against the standard sample $Hg[Co(CNS)_4]$. To treat the bulk magnetic susceptibility data, corrections due to atomic diamagnetic contributions from O^{2-}, V^{5+}, V^{4+}, Bi^{3+} and Sb^{3+} were first made [26]. No magnetic field-dependence

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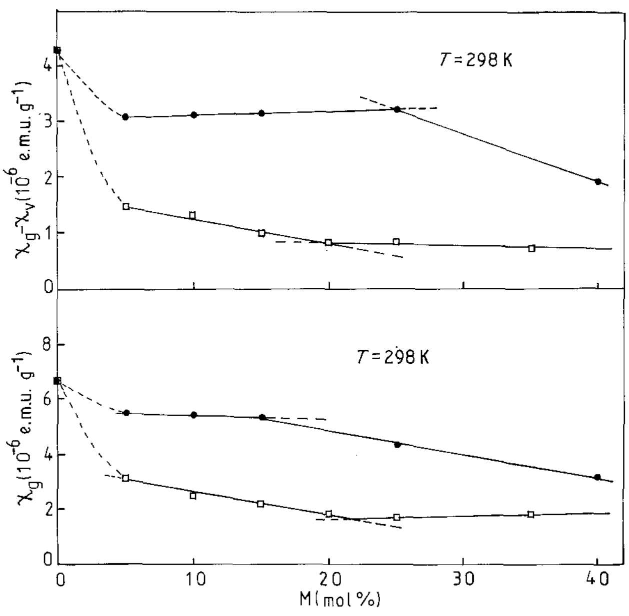

Figure 1 Concentration dependence of specific susceptibility (χ_g) and ($\chi_g - \chi_v$) (χ_v = temperature-independent paramagnetic susceptibility) of (●) VPA and (□) VPB glasses.

susceptibility was observed and all the glasses were found to be paramagnetic with specific susceptibility (χ_g) of the order of 10^{-6} e.m.u. g^{-1} in the measured temperature range (80 to 300 K). Because VPG and VPA glasses behave in a similar manner in all their physical and chemical properties, elaborate magnetic properties of the VPB and VPA glasses for different concentrations only are measured and discussed in this paper, with little reference to the magnetic property of the VPG glass when required.

The variation of χ_g with concentration, x, for the VPB and VPA glasses is shown in Fig. 1. Although the concentration of V_2O_5 is kept constant (50 mol %) in the above glasses, reduction of the P_2O_5 concentration with increase of Bi_2O_3 or Sb_2O_3 gives rise to a decrease of χ_g. Here also a small change in the slope of the $\chi_g - x$ curve around 20 to 25 mol % Bi_2O_3 or Sb_2O_3 is observed. It is also seen from Fig. 1 that the values of χ_g for the VPA and VPB glasses are always lower than those of the VP glass. The values of χ_g as a function of temperature are shown in Figs 2 and 3 indicating the Curie–Weiss nature of the curves, particularly in the high-temperature region.

The deviation from the straight line in the low-temperature region (below 200 K) can be explained by the "effective field model" of an amorphous antiferromagnet proposed by Simpson [27] where a fraction of the paramagnetic ions would be coupled antiferromagnetically while the rest would remain as magnetically isolated paramagnetic ions. However, the characteristic low-temperature behaviour suggested from this model lies well below the temperature range of our investigations.

The observed deviation from the Curie–Weiss-like behaviour strongly suggests the presence of temperature-independent paramagnetic susceptibility (χ_v) together with the paramagnetic Curie term. The specific susceptibility data (after diamagnetic corrections) of the samples can most appropriately be fitted with an equation of the form

$$\chi_g = \chi_v + C/(T - \theta) \qquad (1)$$

where C is the Curie constant and θ is the Curie temperature. χ_v is the temperature-independent Van Vleck paramagnetic term which arises from the contributions of different covalent bonds. Although the bonding electrons of the V–O bonds are drawn away from the vanadium by phosphorus [13], increasing the effective ionic character, there still exists an appreciable percentage of covalency in the bonds which is effected by the presence of (M).

The values of χ_v for all the glasses of VPB and VPA groups have been estimated from the χ_g^{-1}–T curves (Figs 2 and 3) and are shown in Table I. For the VPB glasses, as observed from Table I, the values of χ_v increase slowly, showing a maximum around 20 mol % Bi_2O_3, but for the VPA glasses a corresponding maximum is not observed.

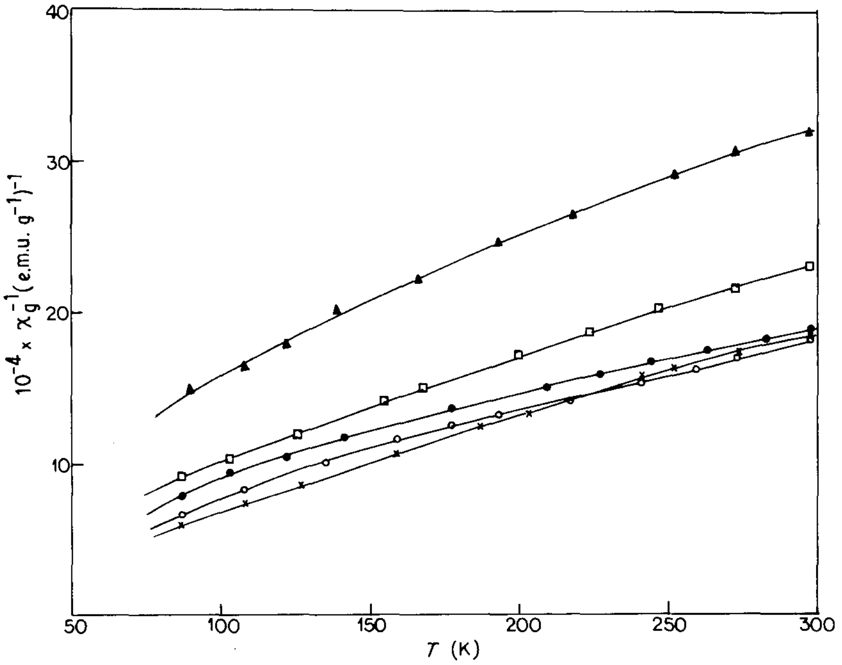

Figure 2 Thermal variation of inverse susceptibility (χ_g^{-1}) of the VPA glasses; (○) 5 mol %, (×) 10 mol %, (●) 15 mol %, (□) 25 mol %, (▲) 40 mol % Sb_2O_3.

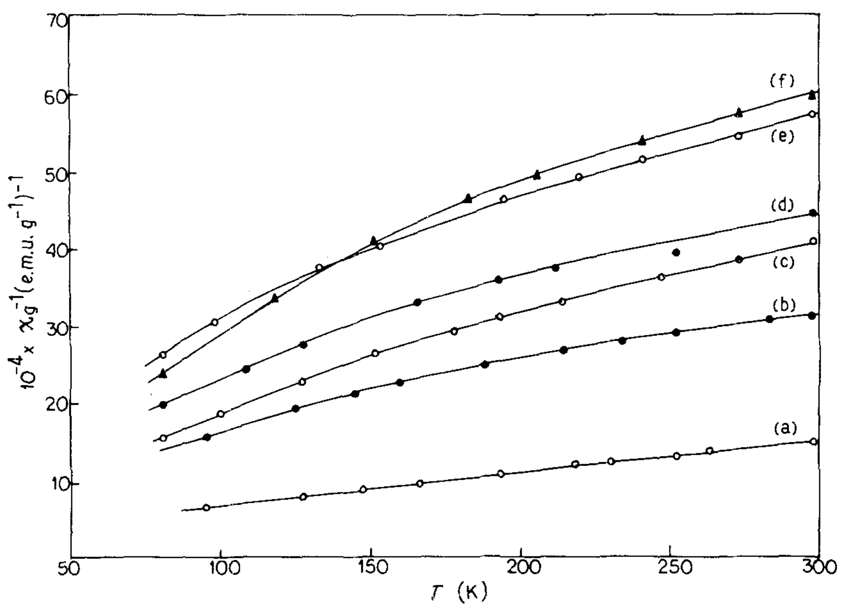

Figure 3 Thermal variation of inverse susceptibility (χ_g^{-1}) of the VPB glasses; (a) 0 mol %, (b) 5 mol %, (c) 10 mol %, (d) 15 mol %, (e) 25 mol %, (f) 35 mol % Bi_2O_3.

The $(\chi_g - \chi_v)^{-1}$–T curves (Fig. 4) obey Curie–Weiss behaviour. The values of the Curie constant (C) and Curie temperature (θ) have been determined from Fig. 4 and are also shown in Table I. The Curie constant $C = N\mu_B^2\mu_e^2/3k_B$ where N, μ_B, and μ_e are, respectively, the number of vanadium ions, the Bohr magneton, and the effective moment of the vanadium ions $\approx 1.73\,\mu_B$, is a direct measure of the concentration of paramagnetic V^{4+} ions in the glasses. This is true if it is assumed that (i) no V^{3+} or V^{2+} ions are present, and (ii) complete quenching of orbital angular momentum giving $\mu_e = 1.73\,\mu_B$ (with spin $s = 1/2$ and $g = 2$). An estimate of the V^{4+} ion concentrations was made from the C values mentioned above (Equation 1) and also compared with those obtained chemically (Table I). The V^{4+} ion concentrations thus obtained from the VPA glass agree fairly well with those obtained chemically (see Table I). The variations of V^{4+} ion concentration (obtained chemically and from magnetic susceptibility data) with mol % Bi_2O_3 and Sb_2O_3 are shown in Fig. 5. The concentration of V^{4+} ions slowly increases with the addition of Sb_2O_3, reaches a maximum for about 25 mol % Sb_2O_3 and then decreases again. This behaviour agrees with the result obtained from the chemical analysis of V^{4+} ions and also reflected in the electrical conductivity data (see [24]). The little discrepancy in the V^{4+} values obtained chemically and from the magnetic data (Fig. 5) for the VPA glass may be due to various causes. Among these, the contributions to the magnetic susceptibility from the V^{2+} and V^{3+} ions which are expected to be present in the glasses [15] would be very important. Moreover, the wet chemistry determination of V^{4+} ions has the inherent uncertainty that in the solution two V^{4+} ions may be formed from the combination of V^{3+} and V^{5+} ions (or a transition from $V^{5+} \rightarrow V^{4+} + e^-$ might also occur).

However, from Table I and also from Fig. 5, a larger discrepancy in the V^{4+} ion concentration for the VPB glass, especially for higher concentrations of Bi_2O_3, may be noticed. In the VPB glasses no maximum could be found in the V^{4+} concentration as determined from the chemical analysis. On the other hand, the V^{4+} concentration gradually decreases as the P_2O_5 concentration is gradually reduced by Bi_2O_3 oxide, which is in contrast to the variation of V^{4+} ions obtained from the chemical analysis (see Table I and also [24]).

It was observed (from Fig. 3 of [24] that the variation of V^{5+}/V^{4+} ratio with concentration, x, is almost the same for the VPA and VPG glasses, while that for the VPB glass is quite different. This discrepancy between the two glass systems, might also be

TABLE I Some parameters obtained from magnetic susceptibility data for the VPB and VPA glasses

Glass compositions	χ_v (10^{-6} e.m.u. g^{-1})	θ(K)	C (10^{-4} cm g sec)	Conc. V^{4+} (10^{21} cm^{-3})
$50V_2O_5$–$50P_2O_5$	2.31	16	11.85	6.12 (3.90)[a]
$50V_2O_5$–$45P_2O_5$–$5Bi_2O_3$	1.71	5	4.31	2.59 (3.65)
$50V_2O_5$–$40P_2O_5$–$10Bi_2O_3$	1.12	10	3.87	2.35 (3.40)
$50V_2O_5$–$35P_2O_5$–$15Bi_2O_3$	1.31	16	2.65	1.61 (3.30)
$50V_2O_5$–$25P_2O_5$–$25Bi_2O_3$	0.90	−3	2.48	1.56 (4.32)
$50V_2O_5$–$15P_2O_5$–$35Bi_2O_3$	1.01	25	1.80	1.16 (3.60)
$50V_2O_5$–$45P_2O_5$–$5Sb_2O_3$	2.40	17	8.90	5.04 (4.60)
$50V_2O_5$–$40P_2O_5$–$10Sb_2O_3$	2.25	35	8.80	5.01 (4.85)
$50V_2O_5$–$35P_2O_5$–$15Sb_2O_5$	2.15	−7	9.59	5.48 (5.20)
$50V_2O_5$–$25P_2O_5$–$25Sb_2O_3$	1.13	−14	9.97	5.77 (5.49)
$50V_2O_5$–$10P_2O_5$–$40Sb_2O_3$	1.16	−27	6.41	3.82 (4.60)

[a] The values within parentheses are obtained from chemical analysis (see [24]).

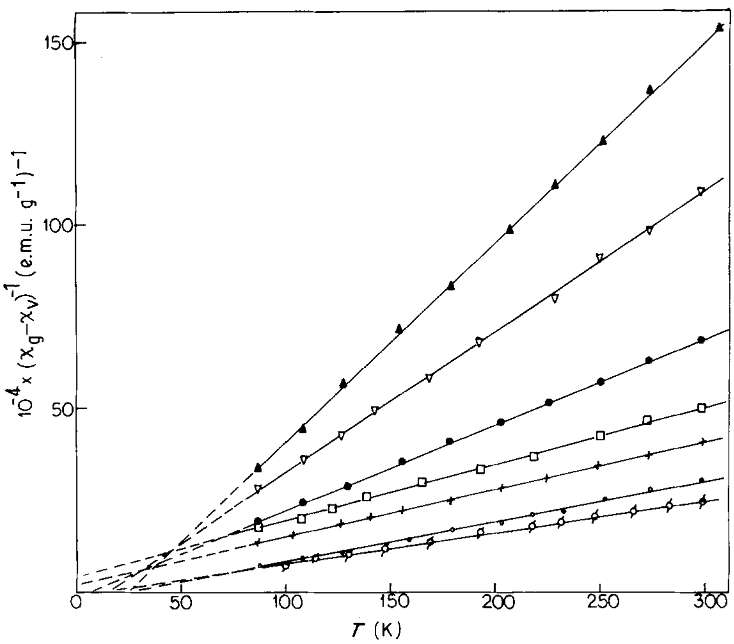

Figure 4 Thermal variations of $(\chi_g - \chi_v)^{-1}$ of the VP, VPB, and VPA glasses for different concentrations of Bi_2O_3 and Sb_2O_3. Bi_2O_3: (●) 5 mol %, (▽) 15 mol %, (▲) 25 mol %; Sb_2O_3; (○) 10 mol %, (×) 25 mol %, (□) 40 mol %; (ϕ) $50V_2O_5$–$50P_2O_5$.

due to the different amount of V^{2+} and/or V^{3+} states present in these glasses. As discussed above, these V^{3+} ions might combine with V^{5+} ions to be detected as two V^{4+} ions ($V^{3+} + V^{5+} \rightarrow 2V^{4+}$). From Table I it can also be noticed that the V^{4+} concentration as calculated from the chemical analysis for the VPB glasses, is about twice as large as that calculated from the magnetic data. This is, however, not the case with the VPA glass, where V^{4+} obtained using chemical analysis is almost equal to the value of V^{4+} obtained from the magnetic susceptibility data (Fig. 5). This difference is the behaviour of the VPB glasses from that of the VPA glasses might also be associated to some extent with the difference in the percentage ionization power [29] of the M oxides or the difference in the behaviour of the network-forming oxides (covalency, etc.).

A close look at the values of Curie temperature (θ) in Table I indicates the absence of antiferromagnetic (AFM) interaction among the V^{4+} ions in the glasses of our investigation. Friebele *et al.* [16] observed strong AFM coupling between the V^{4+} ions in the vanadium-rich phase of the phase-separated V_2O_5–P_2O_5 glasses. The glass systems of the present investigations, as mentioned earlier, did not show any phase separation or inhomogeneity as observed from SEM and X-ray diffraction studies [28].

Lynch *et al.* [17] observed from NMR and ESR studies the values of hyperfine constants which are characteristics of isolated V^{4+} ions in the vanadium phosphate glass. Some of the samples of VPA glasses (Table I) have, however, shown negative Curie temperature, indicating AFM coupling between V^{4+} ions. However, the values of (θ) are very small in these cases,

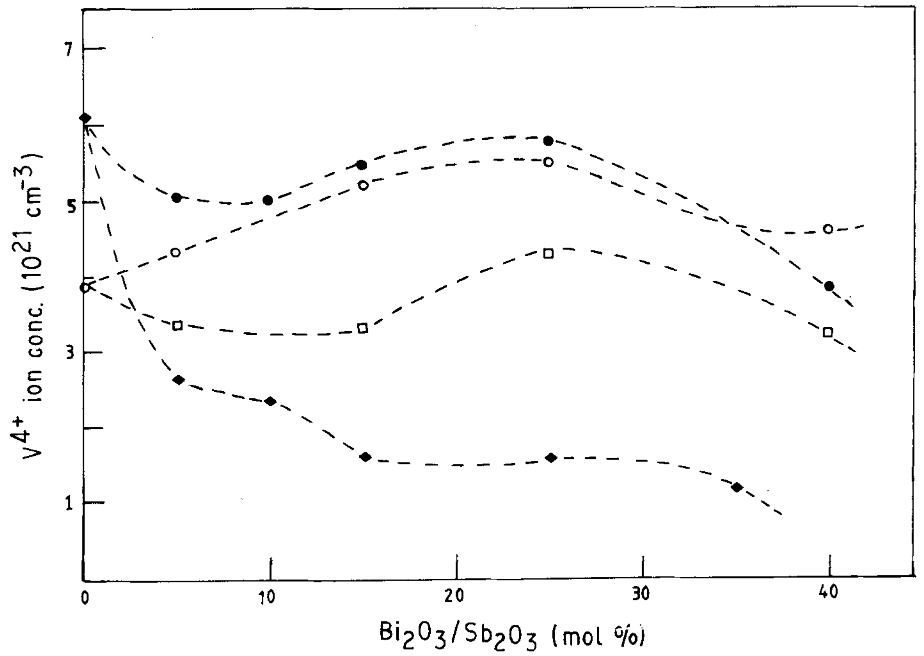

Figure 5 Variation of V^{4+} ion concentration obtained from chemical analysis (●), (■) and magnetic susceptibility data (○, □) for the (■, □) VPB glasses with concentrations of Sb_2O_3 and Bi_2O_3, respectively.

which indicate very weak antiferromagnetic interaction. No AFM Neel temperature for these glasses could be detected.

It is reasonable to conclude at this point that the magnetically isolated V^{4+} ions are randomly distributed in the glass matrix and they do not form clusters. However, in some specimens of VPA glass, a small fraction of V^{4+} ions might be coupled antiferromagnetically while the major fraction of V^{4+} ions remains as magnetically isolated paramagnetic ions, as proposed earlier by Simpson [27] in his theoretical model. The above possibility is reasonable for the VPA glasses showing a larger concentration of V^{4+} ions (Table I) which reduce the average V^{4+}–V^{4+} distance, favouring antiferromagnetic coupling.

3. Conclusion

Magnetic susceptibility, χ, of the vanadate glasses V_2O_5–P_2O_5–M with various concentrations of M (Bi_2O_3, and Sb_2O_3) have been studied. It appears that although the temperature- and concentration-dependent susceptibility data show a similar anomaly at almost the same concentration at which the electrical conductivity and other properties showed some anomaly [24] no one-to-one correspondence between the overall magnetic and electrical properties of these glasses was found. There might be various causes of this discrepancy. The possibility of the coexistence of the magnetic V^{3+} and V^{2+} ions [29, 30] and their contributions (which could not be accounted for) in the electrical and magnetic properties might be important for this discrepancy.

It is also believed that the microstructure and structural modifications produced by increasing the Bi_2O_3, Sb_2O_3, etc., oxides in the V_2O_5–P_2O_5 glasses play an important role in the electrical and magnetic properties of the vanadate glasses.

Finally, it should also be pointed out that like EPR and chemical analysis, magnetic susceptibility data might also provide very useful information about the transition metal ion concentrations in the transition metal oxide glasses.

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