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Magnetic Susceptibility and Local Structure of the Glasses $Ga_2S_3(As_2S_3, PbS)$–GeS_2–MnS

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A statistical model employing a mean-field approach is proposed to calculate the magnetic susceptibility of glasses containing paramagnetic transition metal cations. The model has been verified with experimental data taken on a series of glasses containing manganese(II), d^5, $S = 5/2$. © 2000 Academic Press

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INTRODUCTION

A knowledge of the second coordination sphere of the atoms forming a cation sublattice of glasses is important, not only for understanding the short-range magnetic interaction but also for understanding the medium-range interaction. A simple model of paramagnetic susceptibility of glasses which provide detailed information about composition of the second coordination sphere of transition metals was proposed (1, 2).

The useful glass-forming systems for such investigations are those based on chalcogenides, because the energy of indirect exchange interaction in covalent chalcogenide substances is large compared to partially ionic oxide substances. It is known from the investigations of M. Guittard *et al.* that high-quantity glasses based on Ga_2S_3 (3,4) can be produced where Mn and another transitional metal have been introduced. These authors have reported that Mn adopts a coordination number of 6 in glasses of MnS–Ga_2S_3–GeS_2 and have measured the temperature dependence of magnetic susceptibility of $0.4MnS$–$0.3Ga_2S_3$– $0.3GeS_2$ (3).

The aim of the present paper is the experimental verification of the model in obtaining information about the structure of the glasses $Ga_2S_3(As_2S_3$, PbS)–GeS_2–MnS.

MODEL

Let us first assume that the glass contains only one type of transition metal, B, with magnetic moment which does not depend on temperature and only one type of anion, A. In the second coordination sphere of B there exist z similar metal sites which are strongly exchange coupled with the central atom B. The other possibilities of exchange interactions can be neglected. g_i is the number of atoms $B(B_i)$ which have in the second coordination sphere i atoms B and $(Z\text{-}i)$ atoms of the diamagnetic metal (D). Within the mean field approach, the Weiss constant θ_i describing the behavior of the magnetic moment of B_i in magnetic field is a linear function of i. The real distribution of different structural units in the volume of glass can be described as a "spoiled" statistically uniform distribution. In other words, this is a distribution for which the probability (P) of finding two neighboring units having identical environment (containing a transition metal) differs by the segregation factor s from the probability for the case of the statistically uniform distribution. Therefore the magnetic susceptibility can be written as

$$\chi = C\left[\sum_{i=0}^{z}\frac{g_i}{T - i\cdot\theta_1}\right], \quad g_i = \gamma_i^z(b^*)^t\cdot(1-b^*)^{z-t}, \quad [1]$$

where C is the Curie constant; γ_i^z is the number of possible arrangements of i cations B and $(Z\text{-}i)$ cations D in Z positions. For the case of $Z = 6$, γ_i^z has the following values: $\gamma_0^6 = \gamma_6^6 = 1$; $\gamma_1^6 = \gamma_5^6 = 6$; $\gamma_2^6 = \gamma_4^6 = 15$; $\gamma_3^6 = 20$. The effective concentration of $B(b^*)$ is related to the segregation factor s and the real concentration of $B(b)$ by the relation

$$P = s\cdot\frac{b}{1-b} = \frac{b^*}{1-b^*}. \quad [2]$$

s is greater than unity if there is a tendency to association of structural units containing cation B, and it is less than unity if there is a tendency to the formation of complex structural units containing both B and D cations. When the concentration of B is equal to b^* and statistical uniform distribution takes place, the set of parameters $\{g_i\}$ is the same as for the glass under study, in which the concentration of B is equal

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to b and there exists a deviation from statistical uniform distribution.

Two approximations need additional discussions. As was mentioned above, θ_i is the linear function of i. The energy of the exchange interaction ($k\theta$) is smaller than that of any chemical bond. Consequently, the arrangement of electron density around B_i does not depend on the presence or absence of exchange interaction, or in other words, it does not depend on i.

Therefore, this equation is correct. However, it may be possible that the electronegativity of B differs from that of D. In this case, the replacement of a part of cations B in the second coordination sphere of the central cation B by cations D can lead to a redistribution of the electron density and the change of the energy of single exchange interaction of the central cation B. Thus, θ_i is not a linear function of i. For the glasses in the present study the electronegativity of B (Mn) is close to that of all D metals (Ge, Ga, Pb, or As), and so, we can use the above approach.

The energy of indirect exchange interaction decreases steeply with the increase of distance. This means that the exchange interactions with the other B cations, besides those Z cations which were considered above, can be neglected compared to $|\theta_1|$ and, so, $\theta_0 = 0$. However, if the exchange interaction is negative and the temperature of measurements is much smaller than $|\theta_1|$ the value of θ_0 is not negligible compared to the temperature of measurements and it is necessary to introduce $\theta_0 \neq 0$. However, it is not obvious that introduction of the additional free parameter is expedient. Let us try to describe the experimental data with $\theta_0 = 0$.

The model has two independent parameters, b^* and θ_1. According to the model, θ_1 is the same for all glasses with the same A, B, and Z. The aim of the work is to experimentally verify this result of the model. It is necessary for this purpose to investigate the sulfide glasses containing manganese with composition that differs from the GeS_2–Ga_2S_3–MnS (2).

EXPERIMENTAL

Chalcogenide glasses were synthesized in evacuated (to 10^{-3} mm Hg) sealed silica ampoules in a rocking furnaces. For the synthesis we used Ga, As, Pb, and Ge, in which the purity of the major element was greater than 99.999%. Sulfur (high-purity grade) was additionally distilled under vacuum. Arsenic was weighed immediately prior to evacuation of the ampoule for synthesis. We use two stages for the synthesis. The first is performed in the furnace with high gradient of temperature. The second was carried out upon continued rotation of the ampoule at the temperature of 1100°C for 5 h. The quenching was carried out in water from 800°C.

Magnetic measurements were carried out in the temperature range 4–300 K with an automated DSM 8 pendulum-type magnetometer equipped with a TBT continuous-flow cryostat and a DRUSCH electromagnet operating up to 1.5 T.

Data were collected as the difference between in zero and in field then corrected for the sample holder and the diamagnetism of the elements.

RESULTS AND DISCUSSION

The temperature dependence of the magnetic susceptibilities and the fits using equation (1) are presented in Fig. 1. These results are presented as the reciprocal magnetic susceptibility for more visual presentation of the magnetic properties of the glasses. The main part of the information about $\{g_i\}$ is contained in the low temperature region of the dependencies χ(T). That is why the temperature dependencies of the magnetic susceptibility are fitted, but not its reciprocal value.

The question about the expedience of the introduction of the free parameter was discussed above. It is supposed, in this paper, that θ_0 is equal to 0. The low temperature region of the dependencies of χ^{-1}(T) is presented in Fig. 2. It is clear, that this supposition does not lead to the strong deviations of the calculated dependence χ^{-1}(T) from experimental points.

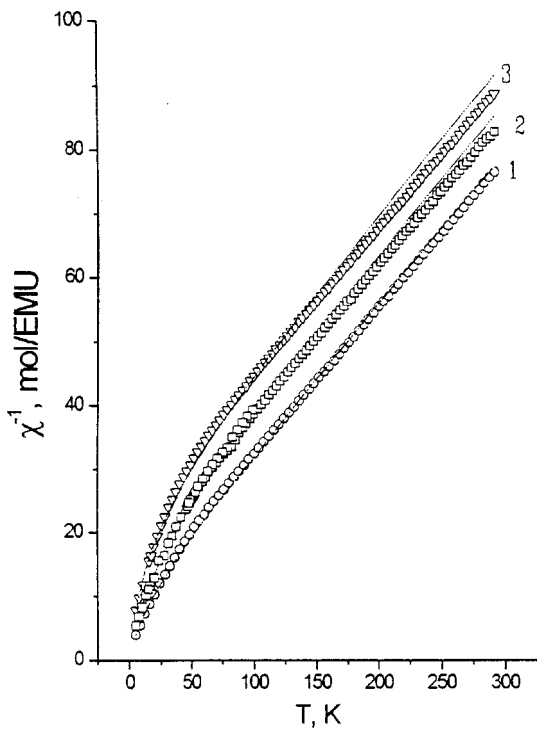

FIG. 1. Temperature dependence of the reciprocal molar paramagnetic susceptibility of the Mn containing glasses. Numbers correspond to those in Table 1. Points refer to experimental data. The results of the calculations are represented by lines.

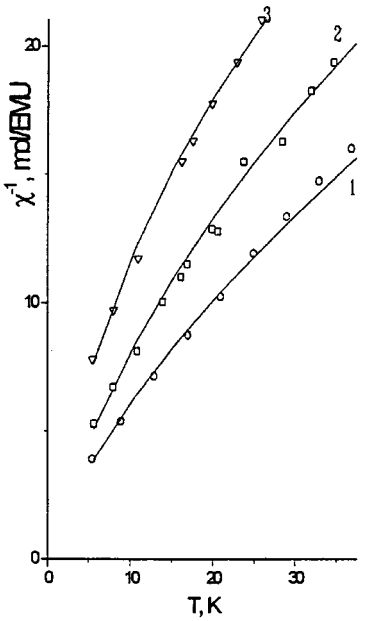

FIG. 2. Low temperature region of the temperature dependence of χ^{-1} in Fig. 1.

TABLE 1

N	Ga_2S_3	GeS_2	PbS	As_2S_3	MnS	*b*
1	0.110	0.734	0.073	—	0.083	0.075
2	0.073	0.728	—	0.109	0.090	0.076
3	0.071	0.710	—	0.107	0.112	0.095

The results of the calculation of the θ_1, b^*, and s are given in Table 2. According to the model the values of the θ_1 are approximately the same as those for glasses GeS_2–Ga_2S_3–MnS (–51 K) (2). The segregation factor s for glasses under consideration is larger than for glasses GeS_2–Ga_2S_3–MnS (for which it is equal to 1.5–2 (2)) but smaller than for glasses Ge–Sb–Se containing Fe ($s \approx 4$). The upper limits of the concentration of the transition metal in all the above-mentioned glasses are situated in reciprocal order. The enhanced values of the Weiss constants suggest that introduction of transition metals in chalcogenide glasses lead to the formation in the first instance of regions enriched with the structural units containing the metal and then by the formation of crystalline embryos (clustering). Consequently, the glass forming ability decreases. This is in

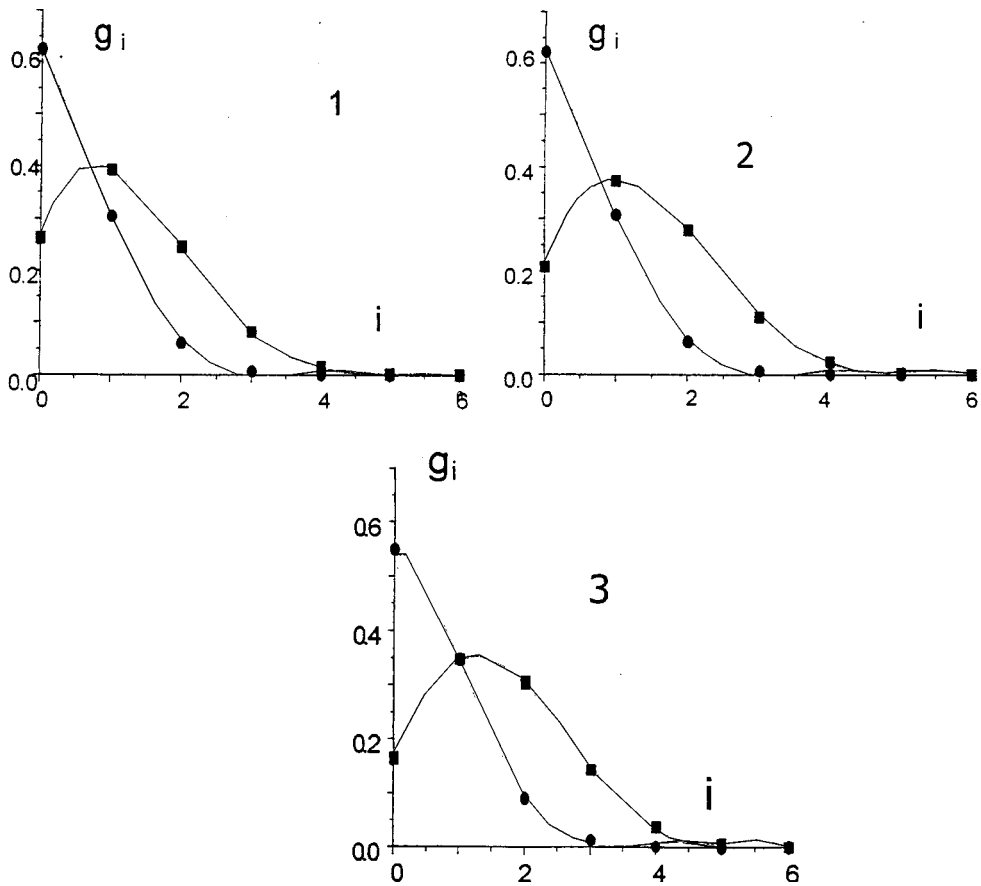

FIG. 3. The circles indicate the values of g_i for glasses with statistical uniform distribution. The squares indicate the values of g_i for real glasses. Numbers correspond to those in Table 1.

TABLE 2

N	$-\theta_1$ (K)	s	b^*	$(\sqrt{\overline{\delta^2}}/\bar{\chi})$ (%)
1	42	3.1	0.20	4.3
2	65	3.6	0.23	4.5
3	69	3.9	0.29	3.7

good agreement with the results of the investigation of the interaction of transition metals with chalcogenide glasses (5). Figure 3 shows the $\{g_i\}$ set which is calculated from magnetic susceptibility for investigated glasses with the $\{g_i\}$ set for the case of $s = 1$. From this graphic representation we observed a large deviation of the values calculated for the glasses under study and those expected theoretically. This deviation may again be a manifestation of the process of clustering of the paramagnetic ions in the glasses. Further work will be needed to validate these suggestions. Electron spin resonance may give the relaxation times which is dependent on the size of the clusters.

CONCLUSION

The model presented for the paramagnetic susceptibility of glasses describes the experimental data sufficiently well. The observed values of the Weiss constants may be due to the existence of clusters enriched in transition metal in chalcogenide glasses. This phenomenon is associated with decreasing glass forming ability of the alloys.

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