SOME MAGNETIC PROPERTIES OF CHALCOGENIDE GLASSES As_2S_3 AND As_2Se_3 DOPED WITH Cr, Mn, AND Yb

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The article is concerned with the analysis of magnetic impurity influence on the properties of As_2S_3 and As_2Se_3 chalcogenide glasses. Measurements of magnetic susceptibility were performed in the 1-350 K temperature range and in the permanent magnetic fields up to 5 T. Amphoteric elements Mn and Cr, as well as rare-earth element Yb, were chosen as doping elements. Experimental data reveal different dependences of specific magnetic moment on temperature M = M(T) in the strong magnetic fields to 5 T and have some specific features which depend on dopant material and on composition of diamagnetic chalcogenide glass.

As_2S_3 and As_2Se_3 chalcogenide glasses with above-mentioned doping elements were synthesized by common melt-quenching technique in the laboratory of semiconductor physics of Kamianets-Podilsky National University (Ukraine), measurements of magnetic properties were carried out in the Wihuri Physical laboratory, University of Turku (Finland).

Pure chalcogenide glasses As_2S_3 and As_2Se_3 are diamagnetics. Measurements of specific magnetic moment M in a field of 5 T and the temperature range from 1 to 350 K give M values: for As_2S_3 $M_{mid} = -1.11\times10^{-6}$ A m^2/kg and for As_2Se_3 $M_{mid} = -6.7\times10^{-9}$ A m^2/kg. Differences in values of diamagnetic susceptibility of initial glasses apparently determine the peculiarities of M temperature dependence M = M(T) in weak magnetic fields (up to 100 Gs) at low temperatures $0<T<25$ K.

Introduction of impurities (Mn, Cr, Yb) with concentrations up to 8 wt % changes magnetic properties of investigated chalcogenide glasses. In the fields near 5 T the M(T) dependence is observed, which is the characteristic of paramagnetics and ferromagnetics in the paramagnetic range of temperature (Fig. 1).

This dependence is described without using the molecular field approximation by the expression

$$\chi_p = \frac{C}{T-\Theta} \tag{1}$$

where Θ is the paramagnetic Curie point, which may be different from Curie point and Neel point [1]. General magnetic susceptibility will be described by

$$\chi_p = \chi_0 + \frac{C}{T-\Theta} \tag{2}$$

Application of expression (2) to the description of the obtained experimental results for the As_2S_3 samples doped with 1 wt % of chromium gives the value Θ = 14.7 K. The constant C in expression (2) is proportional to the amount of admixture atoms (N), possessing intrinsic

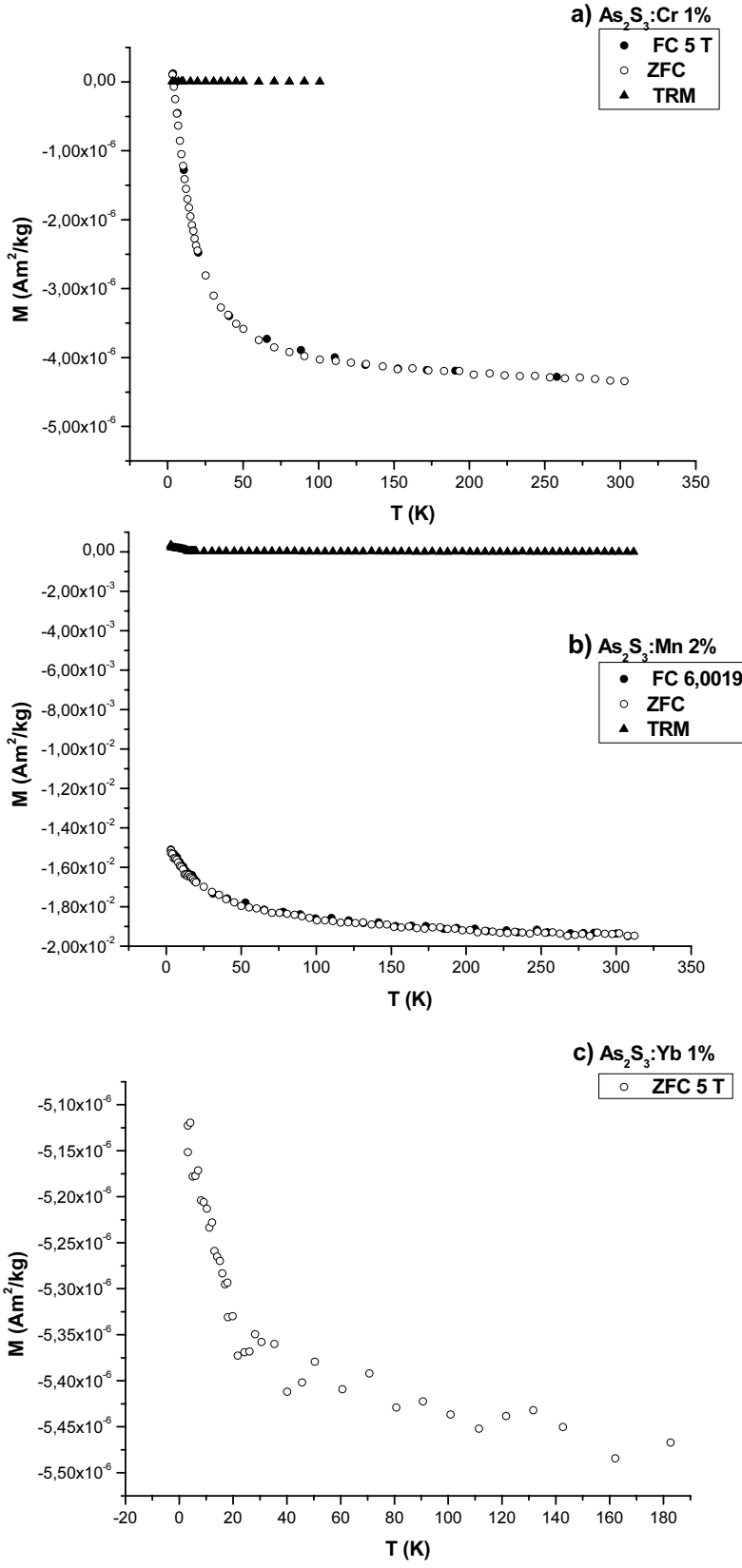


Fig. 1. Temperature dependence of mass magnetization in $As_2 S_3$ doped with: (a) 1 at % Cr (B = 5 T); (b) 2 at % Mn (B > 6 T); (c) 1 at % Yb (B = 5 T).

magnetic moment proportional to μ_B. Estimations of C using the obtained experimental results give $C \approx 0.059$ kg T/(A m^2 K). The slopes of $1/(\chi-\chi_0)$ dependences on temperature increase both with a change in the concentration of magnetic admixture and with the increase in magnetic-field. Comparison of three similar dependences which correspond to the introduction of different admixtures in identical concentrations reveals that the biggest slope is observed for As_2S_3 doped with Yb; the smallest, for the As_2S_3 samples doped with manganese.

Let us consider that the paramagnetic state corresponds to the chaotic distribution of intrinsic magnetic moments in a zero external magnetic field. We will also take into account that in amorphous structures characterized by the presence of short range order the most significant influence on the magnetic state is exerted by fluctuations of exchange interactions of magnetic moment and univalent anisotropy [2]. At present, there is no consistent theory of influence of amorphous structure on the degree of magnetic order [2]. According to [2], only three types of magnetic organization can exist in amorphous structures: (a) well-ordered ferromagnetic, (b) disordered ferromagnetic, and (c) spin glass (Fig. 2).

Measurements of magnetic properties (temperature dependence of the specific magnetic moment) were performed under the different con-

ditions of sample cooling. A sample was cooled in zero external magnetic field; then, the magnetic-field with specified magnitude was set. In the following, the magnetic-field was maintained constant during the sample heating. The interval of temperature variation was chosen in such a way that the maximal value of temperature exceeded the temperature of transition into the paramagnetic state. Hereinafter, such dependences are denoted as ZFC. Further, the sample was cooled in the magnetic field and M= M(T) was obtained, denoted as FC in figures. The third type of dependence was obtained by heating the sample without magnetic-field; it is denoted by TRM in figures (the residual magnetization).

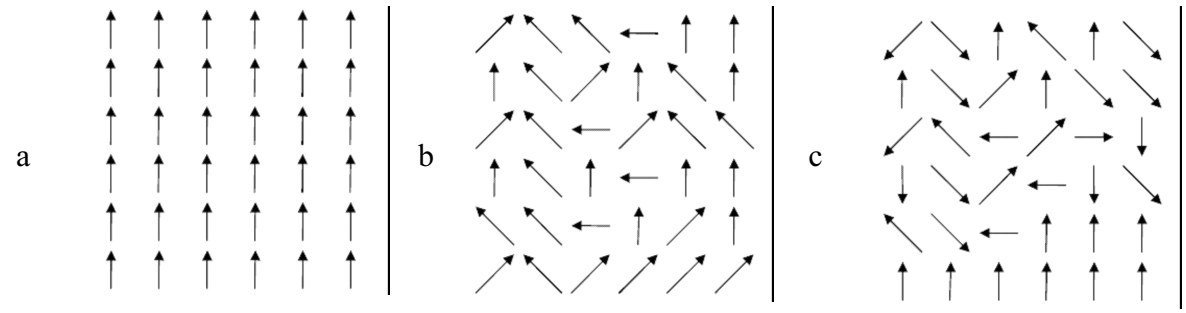


Fig. 2. Magnetic organization types in amorphous structures: a – well-ordered ferromagnetic; b – disordered ferromagnetic; c – spin glass.

The above-mentioned dependences are shown in Figs. 3a and 3b for the As_2S_3 sample doped with chromium.

In the magnetic fields higher than 500 Gs (Fig. 3b) peculiarities in M(T) dependences are not observed; ZFC and FC curves coincide. It can be seen (Fig. 3a, curve ZFC) that for the 80-Gs magnetic field in a temperature range below 25 K the increase of the specific magnetic moment is observed if the sample is cooled in magnetic field in comparison to the cooling without magnetic field. Figure 4 presents the M(T) temperature dependences for the bulk glasses As_2S_3 doped with 2 wt % of manganese. All curves show sharp growth of the dependence at 14.2 K. Even for the field B = 0.9969 T there is a small increase of M(T) in a region of 12–14 K. For a field of 6 T (Fig. 1) the M(T) dependence is described by the Curie-Weiss law (1), and for this case Θ is 34 K. Differences between the M(T) dependences for ZFC and FC curves remain up to the value of the external field B = 458 Gs, and this difference disappears in a field of 1970 Gs. This gives a possibility to consider that influence of the external field on the orientation of the intrinsic magnetic moments of the dopant atoms in the energy value exceeds the energy of their thermal movement.

At T = 5K the differences in the values of the specific magnetic moment for ZFC and FC branches depend on the magnitude of magnetic field (Table 1).

Table 1. Dependence of mass magnetization on the magnetic field.

	5 Gs	10 Gs	80 Gs	468 Gs	1970 Gs
FC, A m^2/kg	8×10^{-5}	10^{-4}	1.6×10^{-4}	1.6×10^{-4}	1.6×10^{-4}
ZFC, A m^2/kg	2×10^{-5}	2.5×10^{-5}	8×10^{-5}	1.4×10^{-4}	1.6×10^{-4}

Temperature dependences M(T) for the As_2S_3 samples doped with 5 wt % of manganese are presented in Fig. 5. Comparison of dependences shown in Figs. 4 and 5 reveals that an increase in the concentration of magnetic admixture influences the value of specific magnetic moment. Abrupt change in the M(T) dependence is increased in the value and occurs at somewhat bigger temperature than T = 14.7 K. The behavior of ZFC and FC dependences remains unchanged.

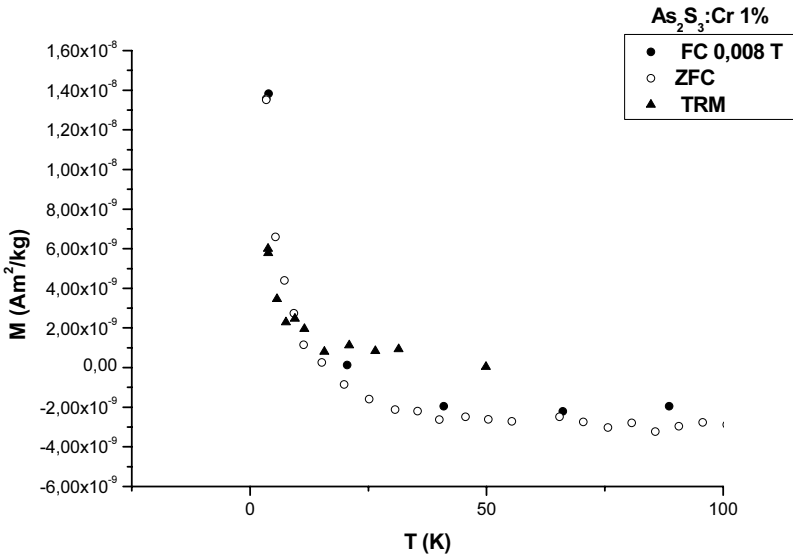


Fig. 3a. Temperature dependence of mass magnetization in As_2S_3 doped with 1% Cr (B=0.008 T).

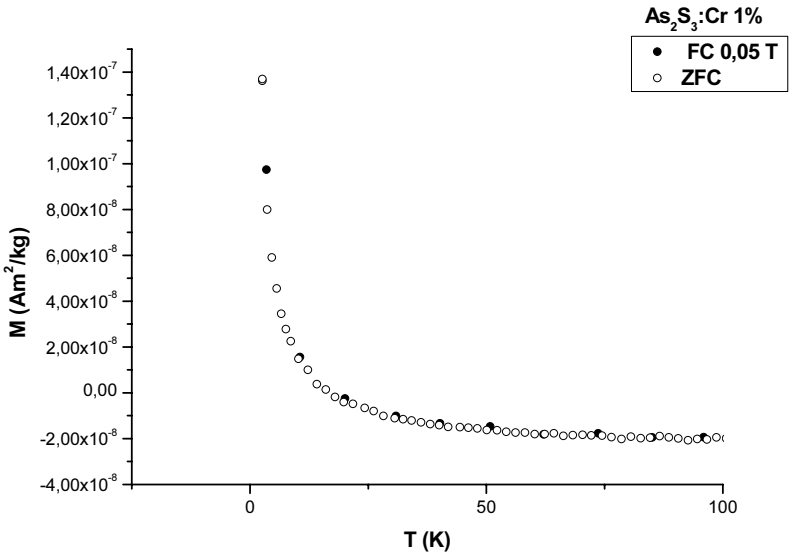


Fig. 3b. Temperature dependence of mass magnetization in As_2S_3 doped with 1% Cr (B=0.05 T).

The difference between M values for different sample cooling disappears at the value of external magnetic field B = 0.197 T.

At T = 5 K the differences in the values of specific magnetic moment for ZFC and FC branches depend on value of magnetic field (Table 2).

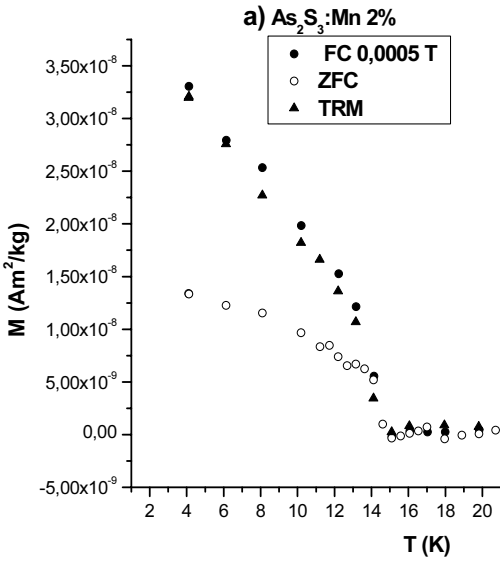
Absolute values of specific magnetic moment increase at least by an order of magnitude as compared to the data presented in Fig. 4. As the manganese concentration increases up to 8% the temperature of the M(T) abrupt change is shifted to the side of higher temperatures and equals 15.2 K.

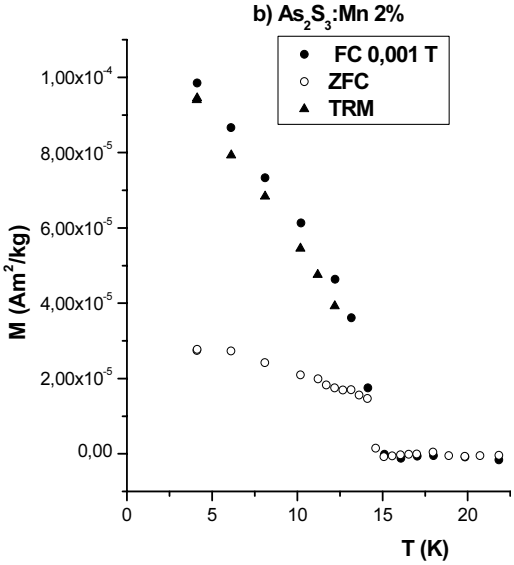
However, the value of specific magnetic moment hardly changes at all as compared to its value for samples with the manganese concentration 5%.

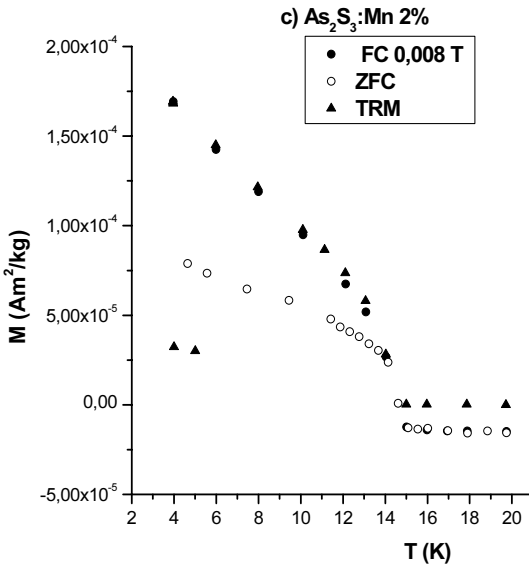
Temperature dependences M(T) for the As_2Se_3 sample doped with 5 wt % manganese are presented in Fig. 6. These dependences are similar to the ones shown in Fig. 5, where the manganese impurity was introduced into As_2S_3 chalcogenide glass. The sharp increase of M(T) is observed; we interpret it as a transition from the paramagnetic state into the ferromagnetic one at T = 14 K. The peculiarity of these dependences is that the difference between ZFC and FC curves is much greater (from 3 up to 7 times).

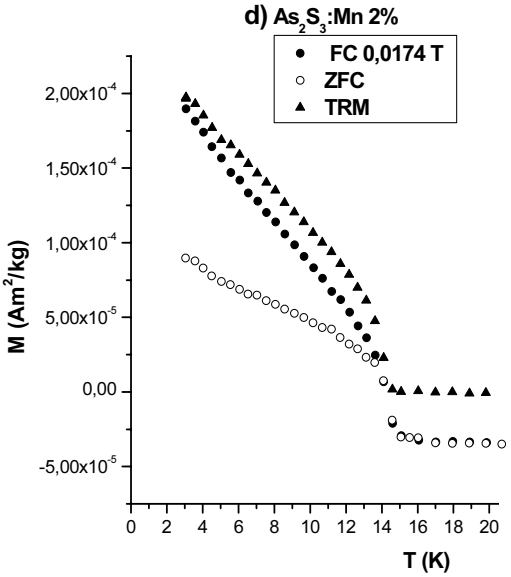
Table 2. Dependence of mass magnetization on the magnetic field.

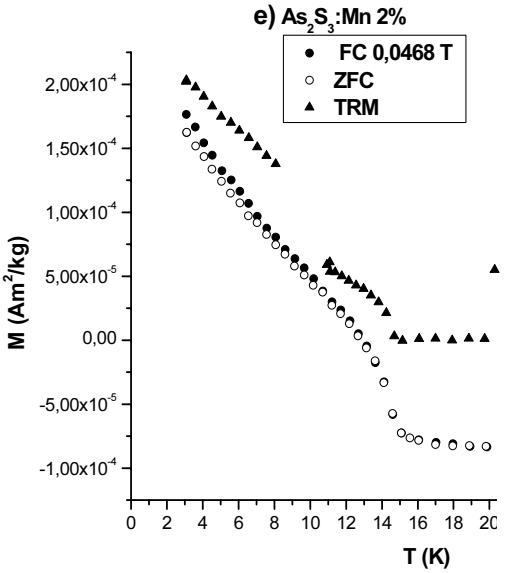
	FC, A m^2/kg	ZFC, A m^2/kg
5 Gs	3.8×10^{-4}	1.2×10^{-4}
10 Gs	5.8×10^{-4}	$1{,}5\times10^{-4}$
20 Gs	8.2×10^{-4}	2.2×10^{-4}
80 Gs	4.5×10^{-3}	6.27×10^{-4}
468 Gs	3.5×10^{-3}	2.7×10^{-3}
1970 Gs	4.7×10^{-3}	4.7×10^{-3}

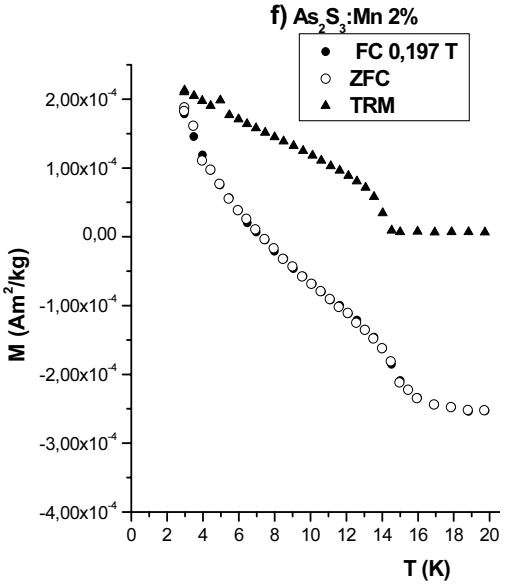

a) As2S3:Mn 2%
FC 0,0005 T
ZFC
TRM
M (Am2/kg)
T (K)

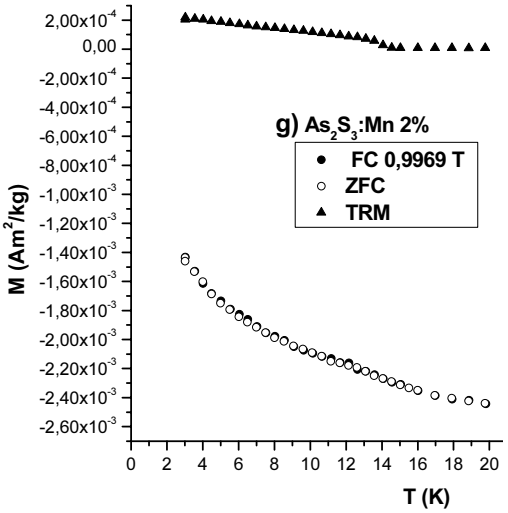

b) As2S3:Mn 2%
FC 0,001 T
ZFC
TRM
M (Am2/kg)
T (K)

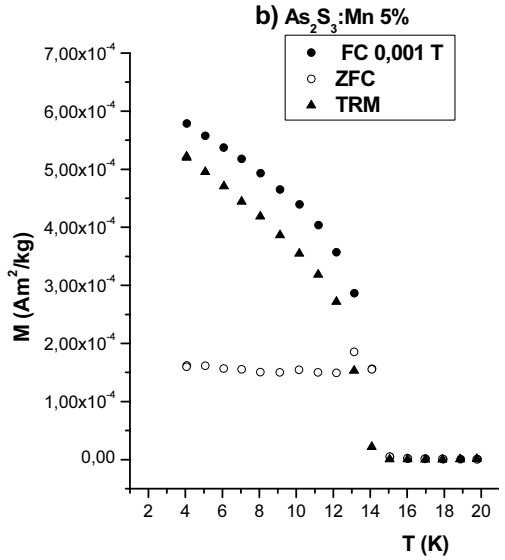

c) As2S3:Mn 2%
FC 0,008 T
ZFC
TRM
M (Am2/kg)
T (K)


d) As2S3:Mn 2%
FC 0,0174 T
ZFC
TRM
M (Am2/kg)
T (K)


e) As2S3:Mn 2%
FC 0,0468 T
ZFC
TRM
M (Am2/kg)
T (K)


f) As2S3:Mn 2%
FC 0,197 T
ZFC
TRM
M (Am2/kg)
T (K)





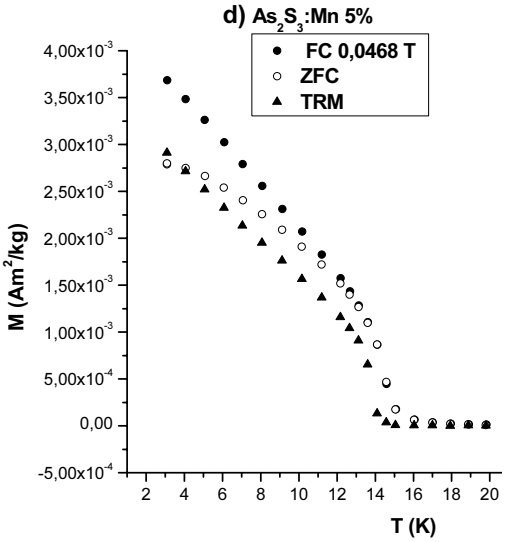
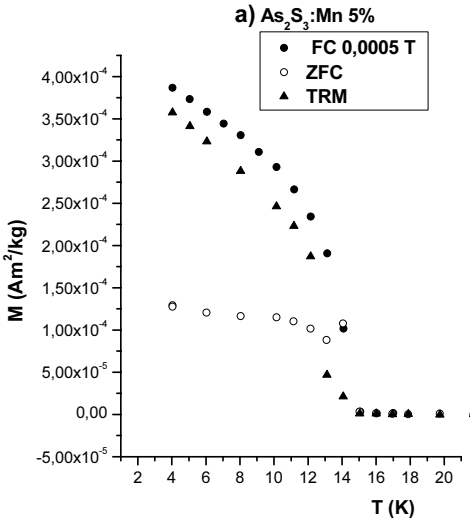
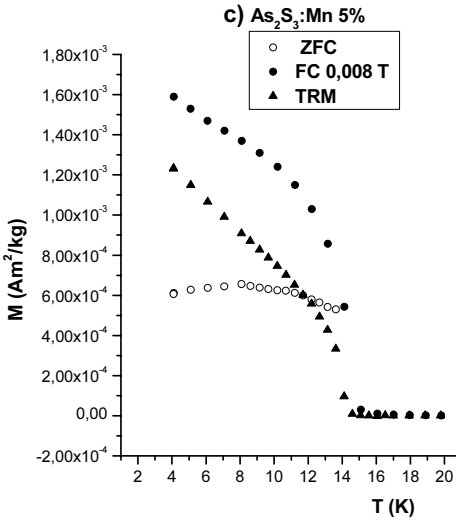
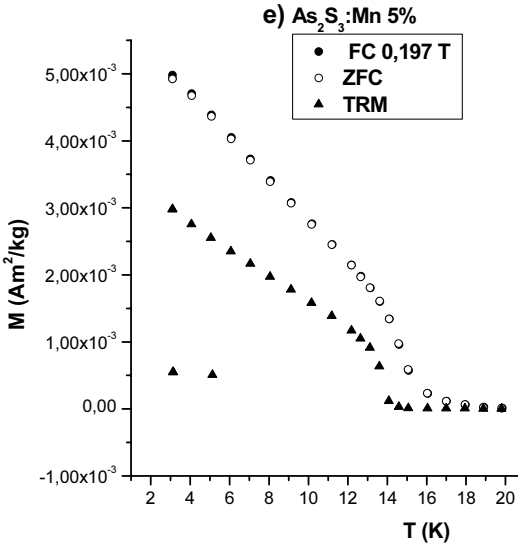


Fig. 5. Temperature dependence of specific magnetic moment in $As_2 S_3$ doped with: (a) 5% Mn (B = 5 Gs); (b) 5% Mn (B = 10 Gs); (c) 5% Mn (B = 80 Gs); (d) 5% Mn (B = 468 Gs); (e) 5% Mn (B = 0.197 T).

Fig. 4. Temperature dependence of mass magnetization in $As_2 S_3$ doped with: (a) 2% Mn (B = 5 Gs); (b) 2% Mn (B = 10 Gs); (c) 2% Mn (B = 80 Gs); (d) 2% Mn (B = 174 Gs); (e) 2% Mn (B = 468 Gs); (f) 2% Mn (B = 0.197 T); (f) 2% Mn (B = 0.9969 T).







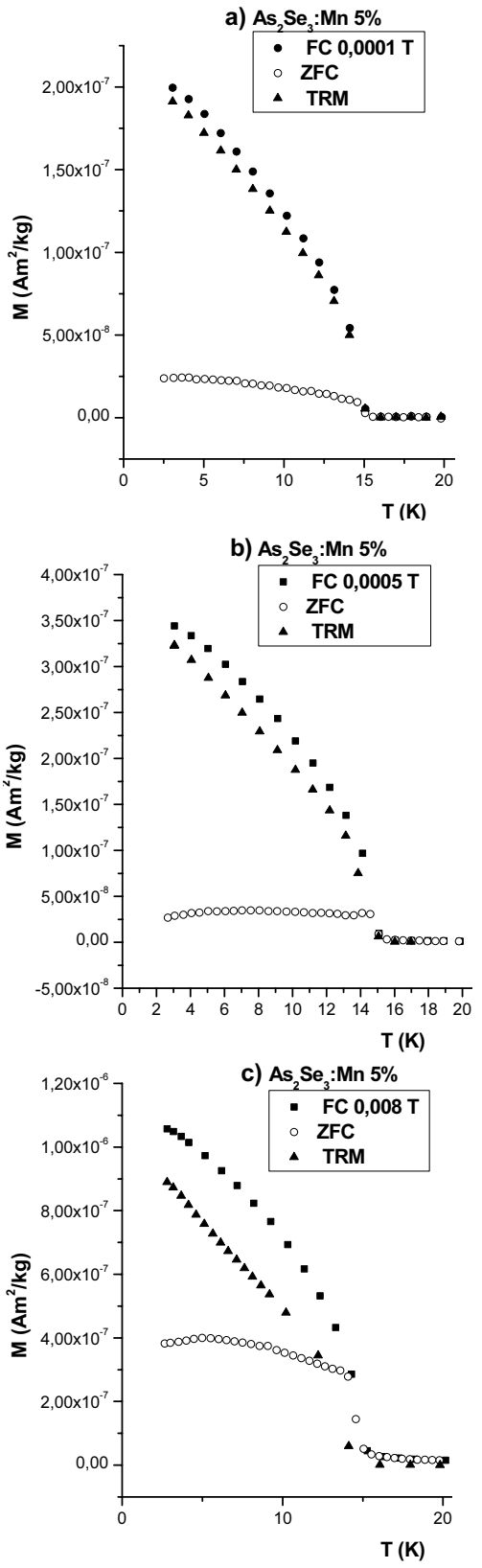


Fig. 6. Temperature dependence of mass magnetization in As_2Se_3 doped with: (a) 5% Mn (B = 1 Gs); (b) 5% Mn (B = 5 Gs); (c) 5% Mn (B = 80 Gs).

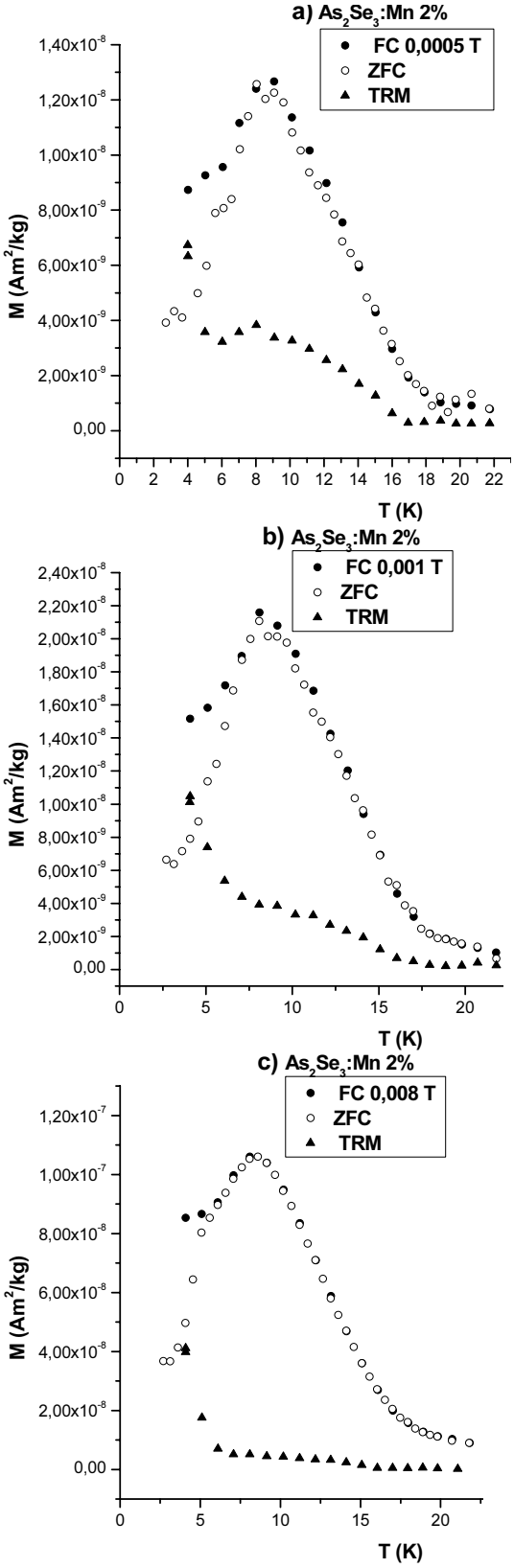


Fig. 7. Temperature dependence of mass magnetization in As_2Se_3 doped with: (a) 2% Mn (B = 5 Gs); (b) 2% Mn (B = 10 Gs); (c) 2% Mn (B = 80 Gs).

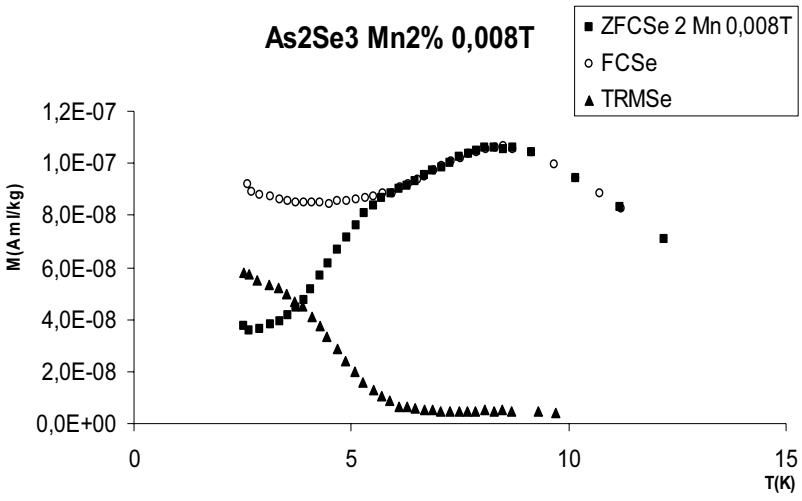


Fig. 7d. Temperature dependence of mass magnetization in As_2Se_3 doped with 2% Mn (B = 80 Gs).

The main difference between the results for selenium glasses and for sulphur glasses is that manganese admixture with a concentration of 2 wt % leads to absence of sharp change in magnetic properties at T = 14 K, and the values of the specific magnetic moment increase smoothly.

There is no difference between ZFC and FC dependences in the interval of temperatures where mass magnetization is growing smoothly. This difference appears only at the temperature near 7 K when M(T) decreases with the temperature.

Temperature dependences M(T) for the As_2Se_3 sample doped with 2 wt % of manganese are presented in Fig. 7 (a, b, c); the dependence (Fig. 7d) is plotted using greater number of the measured points. As it is seen from Fig. 7, temperatures of maximum mass magnetization (T_{max}) and temperature (T_1) at which difference between ZFC and FC curves appears depend on external magnetic field (Table 3).

As it is seen from the presented data, at the change in the admixture concentration in As_2 Se_3 the distribution of admixture magnetic moments varies. It is possible to consider that a magnetic order corresponding to ordered ferromagnetic (at the Mn concentration of 5%, Fig. 2a) changes to the one corresponding to the state of spin glass (Fig. 2c) at the Mn concentration of 2%.

These compounds were investigated in [3, 4].

Table 3. Temperature of maximum mass magnetization at magnetic field for As_2Se_3: Mn 2%.

B	T_{max}	T_1
5 Gs	9.2 K	7.64 K
10 Gs	8.5 K	7.1 K
80 Gs	8.3 K	6.14 K

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