Synthesis and magnetic properties of solid solutions of a diluted magnetic semiconductor $(Zn_{1-x}Fe_x)_3As_2$

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Abstract. The magnetic properties of the new semimagnetic semiconductor $(Zn_{1-x}Fe_x)_3As_2$ with $x < 0.04$ have been investigated over a wide temperature range. Single crystals of ZFA were grown using the modified Bridgeman technique. The results of X-ray analyses and the magnetometry data show that the border of solid solutions in this system lay near $x = 0.015$. Further increasing of x leads to the growing of the second phase, which was identified as Fe_2As. A notable feature of our magnetometry results is the spin-glass-type freezing of magnetic moments in the temperature range of 10 - 50 K. The value of the freezing temperature decreases when the magnetic field increases and in 2 kOe magnetic field the effect is no longer observable. It is likely that the observed freezing phenomena are due to the cluster nature of magnetic properties of ZFA. The thermoremanent magnetization measurements give evidence for two types of clusters in the magnetic system of ZFA.

1. Introduction

Compounds of the type $(A_{1-x}B_x)_3As_2$ with A = Zn, Cd and B = Mn form a class of II_3V_2 diluted magnetic semiconductors (DMS) [1]. In DMSs, a part of cations is replaced by a transition metal or rare earth elements with partially filled d- and f-shells, respectively. The transition metal or rare earth ions are randomly distributed in the host lattice. As a result, two types of interactions take place in the DMS crystal: (i) the sp-d (sp-f) exchange interaction between the band carriers and localized magnetic moments of these ions and (ii) the d-d (f-f) interaction between the ions themselves. One of the types of practical application of a DMS is its use as an injector for the spin polarized current of charge carriers in heterostructures [2]. Solid solution $(Zn_{1-x}Fe_x)_3As_2$ ($x \leq 0.015$) (ZFA) is a new diluted magnetic semiconductor of the A_2B_5 group. ZFA is isomorphic to pure Zn_3As which has the width of the band gap $E_g \approx 1$ eV and tetragonal crystal structure (space group $I41cd$) [3].

2. Experimental results and discussion

$(Zn_{1-x}Fe_x)_3As_2$ (ZFA) was synthesized from stoichiometric melts of Zn_3As_2 and Fe in the range of $0.005 < x < 0.04$ by using the modified Bridgeman method (slow cooling in the presence of a temperature gradient). They are isomorphic to pure Zn_3As_2 ($x = 0.0$), which at room temperature has a tetragonal structure with the space group $I4_1cd$ (the so called α-phase of Cd_3As_2) [4]. The crystal were growing in carbon-coated quartz ampoules with a conical bottom, inserted in sealed quartz ampoules under a vacuum of 10^4 Torr. Large monocrystalline ingots were obtained by using a cooling speed of 2°C/h and a temperature gradient of l-2°C/cm. Powder X-ray investigations showed that the obtained crystals were homogenous up to $x = 0.015$. However, the diffractograms of the samples with $x > 0.02$

revealed growth of the second phase, identified as Fe_2As. The dc magnetic measurements were made a with SQUID magnetomiter in the range 4-120 K using magnetic fields up to 2 kOe. A notable feature of our magnetometry results is a spin-glass-type freezing of magnetic moments in the temperature range 10-50 K.

The investigations of the magnetic properties of ZFA were performed using the samples with $0.005 < x < 0.04$. Figure 1 present the temperature dependencies of the magnetic susceptibility χ of ZFA with $x = 0.01$ in a number of magnetic fields. It is seen from curves 1-3 that the magnetic susceptibility of the specimen, cooled in zero magnetic field χ_{ZFC} starts to grow in the field when increasing the temperature, exhibit a broad maximum and then decreases. Cooling the specimen in the field (FC case) leads to growing the χ_{FC} with the following saturation at temperatures just below the χ_{ZFC} maxima. The appearance of a maximum in the ZFC susceptibility curves suggests that freezing of magnetic moments in the sample takes place. The difference between χ_{ZFC} (T) and χ_{FC} (T) curves becomes smaller and finally disappears together with the shifting to lower temperatures and smearing out of the χ_{ZFC} maxima, which defines the freezing temperature, T_f, when increasing of the magnetic field from 50 Oe to 2 kOe. Such influence of the magnetic field on the freezing phenomenon is the most characteristic feature of spin glasses [5].

The same behaviour, in general, with a change in temperature and applied magnetic field is exhibited by ZFA with $x = 0.005$, as can be seen in Figure 2. Half as much decreasing of the concentration of magnetic impurity decreased about one order of magnitude the value of χ and slightly shifted the position of χ_{ZFC} (T) maxima to the lower temperatures in comparison with $x = 0.01$ sample. The saturation of χ_{ZFC} (T) takes place at lower temperatures, than in the previous case, and, moreover, it starts to increase after the saturation when cooling at 500 Oe and 2 kOe. A further increase in the of Fe concentration up to $x = 0.015$ leads to an increase in χ to about 1.5 times in comparison with $x = 0.01$ together with the appearance of a high-temperature "shoulder" near the maximum on the χ_{ZFC} (T) curves in magnetic fields up to 50 Oe (see Figure 3). The behaviour of χ_{FC} (T) appeared to be new at $T < 12$ K when cooling at 5 Oe in comparison with the previous samples: in this region of temperatures χ_{FC} (T) slightly decreases instead of saturation ($x = 0.01$ case) or instead of growth (case $x = 0.005$). A feature on the corresponding ZFC curve (Figure 3) at the same temperatures should be noted.

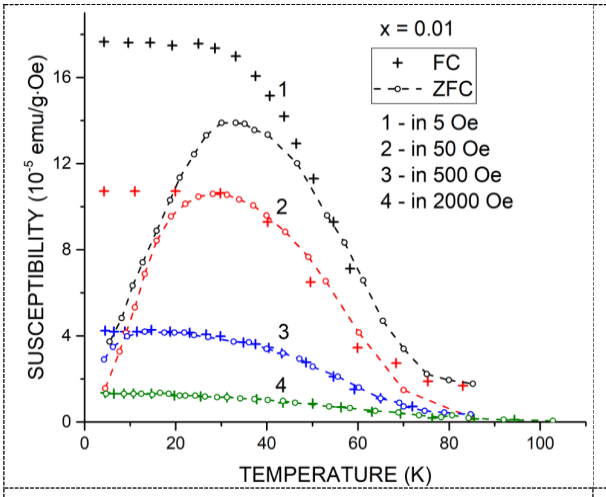

Figure 1. Temperature dependence of the magnetic susceptibility of a ZFA ($x = 0.01$) single crystal.

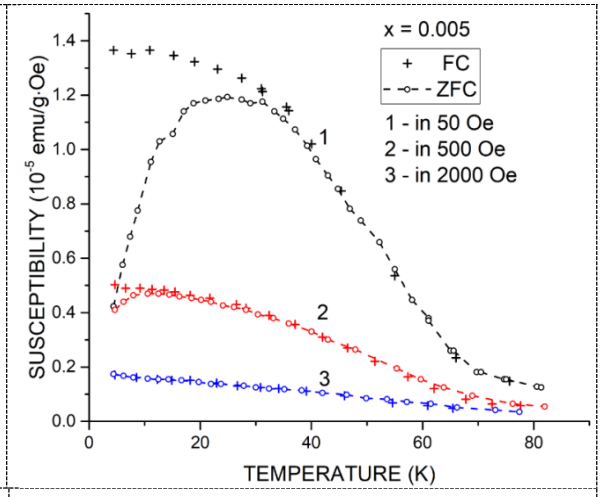

Figure 2. Temperature dependence of the magnetic susceptibility of a ZFA ($x = 0.005$) single crystal.

The same feature is seen at 5 Oe magnetic field in Figure 4, where the results for the sample with, $x = 0.02$, are presented. This sample exhibits a decrease in χ and a broadening of the χ_{ZFC} maximum in

comparison with the other samples. Full saturation of the susceptibility when cooling was achieved only at 50 Oe applied field. In higher fields growing of χ during cooling in the field was observed. This fact becomes understandable, taking into account the data for specimen with x = 0.04, which are presented in Figure 5. For this composition no maxima exists on the χ (T) dependencies and only the difference between ZFC and FC curves appears below the certain temperature in small magnetic fields. The χ_{ZFC} dependencies are practically similar for all magnetic fields applied and show the existence of the strong antiferromagnetic interactions in this material, as it can be seen in Figure 6, where the temperature dependencies of the inverted ZFC susceptibility of this sample are presented. The estimation of the Curie temperature gave the magnetic field dependent negative values of -94 K and 89 K for 5 and 50 Oe correspondingly (where the freezing phenomena were observed) and - 90 K for higher fields, where the ZFC and FC temperature dependencies are similar.

The prominent feature of spin glasses is a certain dependence of T_f on the magnetic field and the concentration of magnetic impurity [4].

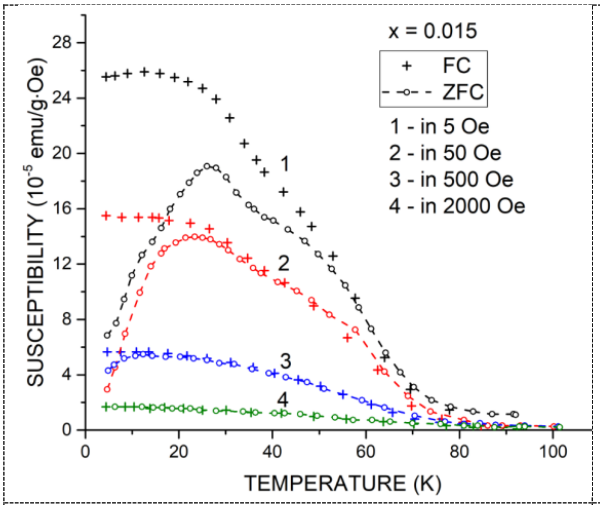

Figure 3. Temperature dependence of the magnetic susceptibility of a ZFA (x = 0.015) single crystal.

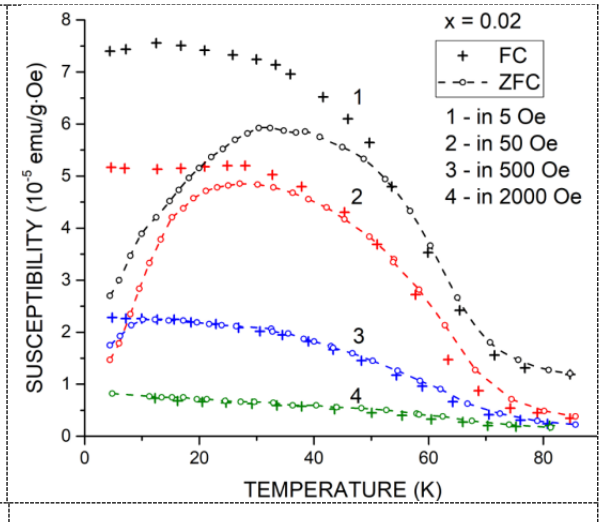

Figure 4. Temperature dependence of the magnetic susceptibility of a ZFA (x = 0.005) single crystal.

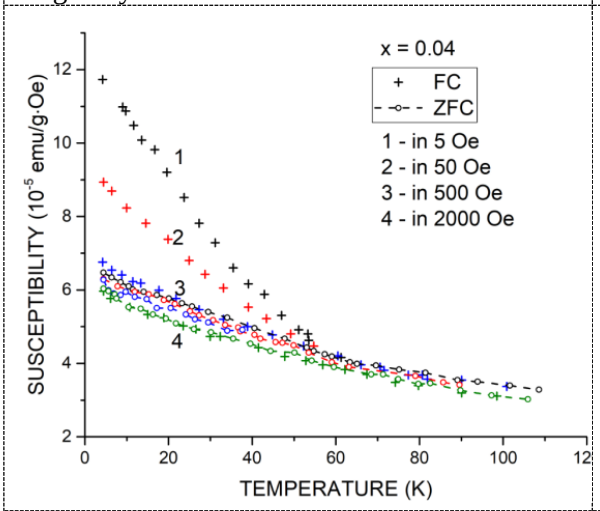

Figure 5. Temperature dependence of the magnetic susceptibility of a ZFA (x = 0.04) single crystal.

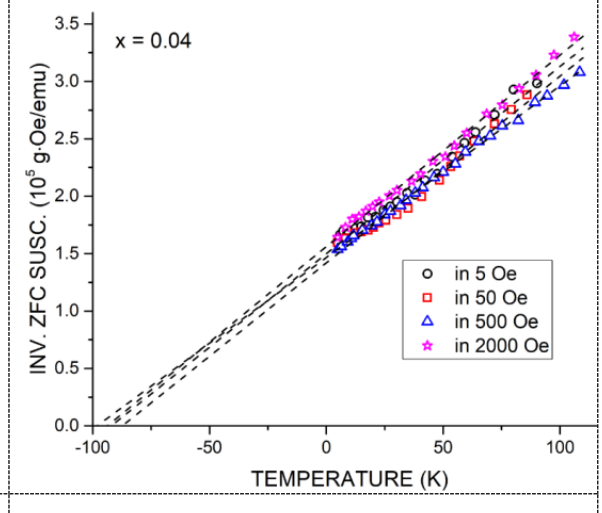

Figure 6. Temperature dependence of the magnetic inverted ZFC susceptibility (x = 0.04) single crystal.

We found that the value of the saturated M_{FC} increases as x change from 0.005 to 0.015 in all applied magnetic fields, but then at x > 0.02 starts to decrease. Moreover, the magnetic field dependence of M_{FC} undergoes a change in it's behaviour at x = 0.04: $M_{FC}(H)$ becomes linear up to 2 kOe instead of an approximately logarithmic dependence in the other samples. This change in the behaviour correlates well with the temperature dependencies of χ in ZFA, showing a considerable influence of antiferromagnetism on the magnetic properties of the specimen with x = 0.04. Magnetic systems exhibiting the freezing phenomena in a field should possess magnetic remanent properties after the field is removed of a field. Two types of remanency are distinguished: thermoremanent magnetization (TRM), which is observed in zero field after cooling the sample in the field, and isothermal remanent magnetization (IRM), which is the effect of field a cycling. All of TRM at 4.2 K just after removing of the field exhibit saturating behaviour, and the full value of TRM was achieved after 500 Oe already.

The value of TRM practically does not changes when increasing the field from 500 Oe to 2 kOe, what means that at 500 Oe all magnetic moments in the system are already orientated and frozen. Another type of remanency isothermal remanent magnetic moment of the specimens with x = 0.005 and x = 0.01, was also studied versus the magnetic field at 30 K as well as the magnetization in the field. The magnetic field dependencies of the specific magnetization M and IRM for x = 0.005 and x = 0.01 at 30 K (near the value of T_f for these specimens) were investigated. The saturation character of M vs. H and IRM vs. H is obvious for x = 0.01, and for x = 0.005 the saturation was achieved in lower fields. The values of the field after which M (IRM) are practically constant are about 500 Oe (1000 Oe) for x = 0.005 and 2.5 kOe (500 Oe) for x = 0.01, correspondingly.

3. Conclusion

One of the most characteristic properties of ZFA is that its magnetic behaviour depends strongly on the history of the sample (see Figure 1-5). This fact suggests the existence of a spin-glass-type freezing of magnetic moments in this material. The same can be concluded from the saturation of IRM vs. H and the small hysteresis. Also the increasing of the ZFC magnetization with temperature and the existence of a maximum in the temperature dependence of the ZFC susceptibility are spin-glass properties. Increasing of the applied magnetic field shifts this maximum to lower temperatures.

The two very different slopes of TRM vs. T (one of which depends on the magnetic field previously applied) in our data indicate the existence of two types of magnetic clusters in ZFA. The same is suggested by the wideness of the ZFC susceptibility maxima in ZFA and even "splitting" in the sample with x = 0.015. Nonstatistical distribution of iron in ZFA cannot be ruled out. In this case the probability of the formation of clusters with strong internal interactions and relatively big magnetic moments grows as well as the existence of the second phase. The changing of the concentration of iron in ZFA allow to observe the transition from the system, containing clusters, mixed with the lost spins (x = 0.005) through the intermediate state (x = 0.01) to the clusters of several types with complex internal interactions (x = 0.015) and even to the appearance of the second phase (x > 0.015).

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