Percolation ferromagnetism and spin waves in Ge:Mn thin films

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We studied magnetic properties of thin Ge:Mn films obtained by implantation of Mn^+ ions into a single crystalline bulk germanium. In the net magnetic moment we were able to separate contributions originating from dispersed Mn^{2+} ions, ferromagnetic Mn_5Ge_3 precipitates, and regions of the germanium matrix enriched with diluted manganese—Mn_mGe_n alloys. In the subsystem of dispersed Mn^{2+} ions we observed a percolation transition into the ferromagnetic state at $T \leq 13$ K. Collective excitations, standing spin waves, were also detected below this temperature. The main parameters of the exchange interaction obtained from the analysis of the experimental spin-wave resonance data are consistent with results acquired from static magnetic measurements as well as with theoretical estimations for a percolation ferromagnet. Thus, we demonstrate that low-temperature magnetic properties of group IV magnetic semiconductor can be successfully explained within a magnetic polaron model.

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I. INTRODUCTION

During the last decade diluted magnetic semiconductors (DMS) have attracted a large experimental interest due to their vast potential for spintronics applications. In order to be useful for numerous industrial applications such materials should possess a large Curie temperature, T_c. Until recently the majority of studies were dedicated to magnetic semiconductors of group III–V, which are characterized by a relatively low Curie temperature hindering their practical implementation. Currently many experimental and theoretical studies are focused at group IV magnetically doped semiconductors. Doping of Ge by transition metals (mainly Mn) results in the ferromagnetic ordering.[1–3] Generally there are three transition temperatures of different origins occurring in $Ge_{1-x}Mn_x$.[1–3] Ferromagnetic ordering in the subsystem of dispersed Mn ions was observed at the lowest temperature $T_{C1} \leq 16$ K and explained by a percolation mechanism caused by overlapping of magnetic polarons.[2–4] The highest critical temperature $T_{C3} < 296$ K corresponds to a ferromagnetic transition in metallic Mn_5Ge_3 precipitates.[1,5] Besides, an intermediate transition temperature, $T_{C2}=50-150$ K, related to formation of local areas enriched in Mn can be observed in the $Ge_{1-x}Mn_x$ system.[1–3]

In this work we focused on low-temperature properties of Ge:Mn films. At present there is relatively little known about the nature of the percolation magnetism in this type of materials. The phenomenon was mainly investigated by means of dc magnetic measurements.[2,3] Ferromagnetic resonance, including spin-wave effects and spin dynamics, has not been previously studied in DMS materials in relation to the percolation mechanism of the ferromagnetic ordering.

In our earlier works we studied extensively electron spin resonance (ESR) phenomena associated with the absorption of the rf excitation in the Ge:Mn thin films ($x=2-8$ at. %).[6,7] In particular, we demonstrated that at low temperature ($T \leq 13$ K) the ferromagnetic resonance led to excitation of standing spin waves in the sample. However, the main mechanism of the low-temperature ferromagnetic ordering in Ge:Mn films was not determined at that point. Here we present a detailed study of the percolation mechanism of ferromagnetic ordering in Ge:Mn films and outline its main parameters obtained independently from static (superconducting quantum interference device (SQUID) magnetometry) and dynamic (ferromagnetic and spin-wave resonances) magnetic measurements.

II. EXPERIMENT

Ge:Mn thin films were prepared by implanting Mn^+ ions into single-crystal Ge(100) wafers (Fig. 1). Mn^+ ions were implanted with an energy of 100 keV at fluences of 1×10^{16}, 2×10^{16}, and 4×10^{16} at./cm^2 providing average volume concentrations of Mn of about $x=2$, 4, and 8 at. %, respectively, on top of the Ge substrate. These values correspond to the concentration of dispersed Mn^{2+} ions, $n_i=0.5\times10^{21}$, 1.2×10^{21}, and 1.6×10^{21} cm^{-3}, for $x=2$, 4, and 8 at. %, respectively. The projected depth range of Mn^{2+} ions is about 120 nm with the implant designed to yield a quasi-Gaussian profile. During the implantation, the samples were held at $T_{gr}=573$ K (unless otherwise stated). Additionally a few samples with the average volume concentration of about 2 at. % were grown at $T_{gr}=77$ and 513 K. Structural, electronic, and static magnetic properties of the samples have been extensively studied earlier by a number of experimental techniques, including transmission electron microscopy

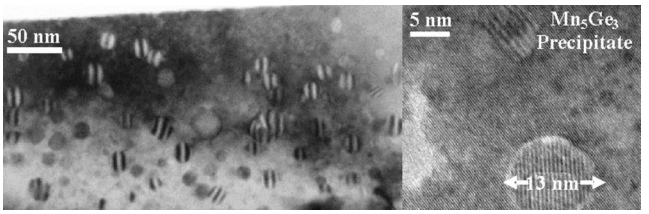

FIG. 1. Left panel: TEM image showing a cross section of the ion-implanted Ge:Mn film with the Mn concentration of 8%. Right panel: high-resolution closeup of a crystalline Mn_5Ge_3 nanocluster.

(TEM), x-ray diffraction, and x-ray photoelectron spectroscopy[8,9] and by means of *ab initio* calculations, see, e.g., Ref. 10. It was shown that the $Ge_{0.98}Mn_{0.02}$ film contains a small amount of amorphous semiconducting Mn-rich nanoclusters, Mn_mGe_n, with a mean diameter below 7.5 nm whereas $Ge_{0.96}Mn_{0.04}$ and $Ge_{0.92}Mn_{0.08}$ films contain metallic Mn_5Ge_3 crystalline clusters with a mean diameter of 9.5 and 13.1 nm, respectively.

Temperature dependence of the magnetization was measured using a SQUID magnetometer (MPMX 5XL, Quantum Design) at temperatures $T=2-350$ K and in the magnetic field $H=1$ kOe.

ESR measurements were carried out at 9.5 GHz with a modulation frequency of 100 kHz in the temperature range $T=4-300$ K using Bruker ESR-500 spectrometer and Oxford Instrument cryostat. The measured absorption signal was proportional to the first derivative of the microwave power, dP/dH. The sample was placed in a rectangular microwave resonator at the maximum of the rf magnetic field. Technical details of the experiment have been given elsewhere.[11]

III. RESULTS AND DISCUSSION

Figure 1 shows a TEM image of the Ge:Mn thin film, where Mn_5Ge_3 precipitates are clearly visible. However, the same films contain a large amount (up to 50%) of dispersed Mn^{2+} ions as measured by means of the x-ray photoelectron spectroscopy.[8,9] These two magnetic entities are characterized by significantly different Curie temperatures, where concentration-dependent $T_{C1}=5-13$ K is attributed to diluted Mn^{2+} ions and $T_{C3}\approx 292$ K corresponds to the ferromagnetic transition in metallic Mn_5Ge_3 precipitates. Additionally, the intermediate transition temperature, $T_{C2}=60$ K, observed only in the film with $x=4\%$ is related to formation of the diluted Ge_mMn_n alloy [see Fig. 2(a) and Ref. 6]. Here we focus at the subsystem of dispersed Mn^{2+} ions and discuss its magnetic properties.

The *lowest* critical temperature, $T_{C1}\leq 13$ K, was defined as a minimum of the dm/dT derivative [Fig. 2(a)]. Generally, T_{C1} may correspond to a percolation transition into the ferromagnetic state where all diluted Mn^{2+} ions are involved into ferromagnetic exchange.[2,3] The percolation model is based on an assumption that indirect exchange between magnetic centers (Mn^{2+} ions) is carried out by localized charge carriers (holes in the case of Ge:Mn).[12] The exchange interaction between localized holes and magnetic ions leads to formation of magnetic polarons. Magnetic polaron is a quasiparticle consisting of a localized and polarized hole and a number of surrounding magnetic ions. While direct exchange between localized holes is antiferromagnetic, indirect exchange between magnetic polarons can be ferromagnetic assuming a relatively large concentration of the magnetic impurity. At high temperature, there is no correlation between individual polarons, their spins are oriented arbitrarily and the net magnetic moment obeys the Curie law for paramagnets. However, as temperature decreases, the radius of a polaron increases and individual polarons spread up. At a certain temperature (known as a percolation temperature) the wave functions of neighboring polarons begin to overlap involving magnetic ions belonging to different polarons. The interaction leads to correlation between spins of the individual magnetic ions and appearance of the net magnetic moment. When such correlated cluster of magnetic polarons spreads through the whole sample, the ferromagnetic ordering is complete.

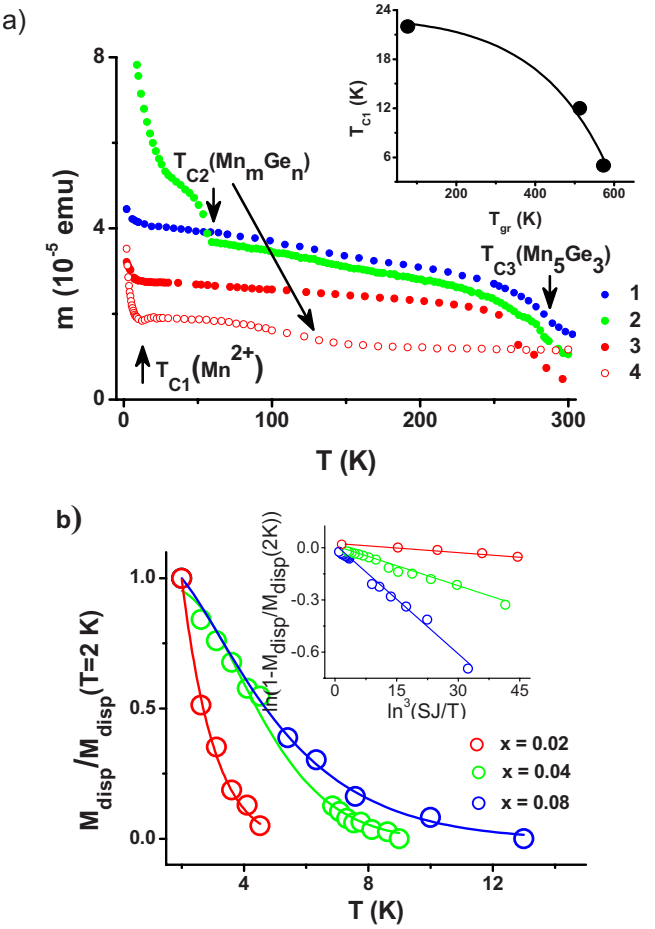

FIG. 2. (Color online) (a) Temperature dependencies of the magnetic moment in Ge:Mn thin films, measured during field cooling in the field, $H=1$ kOe: $1-x=8\%$, $T_{gr}=573$ K; $2-x=4\%$, $T_{gr}=573$ K; $3-x=2\%$, $T_{gr}=573$ K; $4-x=2\%$, $T_{gr}=513$ K. Transition temperatures are marked by arrows. The field was applied perpendicular to the film plane. The inset shows dependence of the Curie temperature in the system of dispersed Mn^{2+} ions, T_{C1}, on the implantation temperatures, T_{gr}, in Ge:Mn thin films with the Mn concentration of $x=2$ at. %. (b) Normalized temperature dependencies of the magnetic moment in the subsystem of dispersed Mn^{2+} ions. The inset shows the same data in the logarithmic coordinates as described in the text. Solid lines are approximations by the Eq. (1).

A. Static magnetic measurements

In all Ge:Mn films studied here by means of SQUID magnetometry, the magnetic moment decreases gradually with temperature (in contrast to a Bloch-type M vs T curve) in the low-temperature range, $T_{C1}\leq 13$ K [Fig. 2(a)]. As it was shown previously, this type of the temperature dependence is characteristic for the percolation ferromagnetic ordering.[12,13]

At $T_{C1} < 13$ K, there are three "active" magnetic subsystems: dispersed Mn^{2+} ions, Mn_mGe_n clusters, and Mn_5Ge_3 precipitates. Magnetic contributions of these subsystems can be separated and Fig. 2(b) shows the temperature dependence of the normalized partial magnetic moment related only to the subsystem of dispersed Mn^{2+} ions, M_{disp}. This contribution was extracted using the following routine. We assume that at high temperatures $M_{disp}=0$. The high-temperature part ($T > T_{C1}$) of the $M(T)$ dependence was extrapolated into the low-temperature region and subtracted from the total magnetic moment. Further we approximated the experimental $M_{disp}(T)$ dependence for the subsystem of diluted Mn^{2+} ions using the expression obtained within the percolation model:[13]

$$M(T) = M(0)\left[1 - \exp\left(-L^3 n_h \ln^3 \frac{SJ}{T}\right)\right], \quad (1)$$

where $M(0)$ is the magnetic moment at $T \to 0$ K, n_h is the concentration of localized holes, L is their localization radius, T is the temperature, $S=5/2$ is the spin of a Mn^{2+} ion, and J is the exchange integral for neighboring Mn^{2+} ions. In our case $M_{disp}(T)$ and $M(0) \equiv M_{disp}(2\ \text{K})$ are experimental values while $L^3 n_h$ and J are variable fitting parameters. A close correlation between the experimental dependence, $M_{disp}(T)$, and the fit obtained using the Eq. (1), see Fig. 2(b), indicates a percolation nature of the ferromagnetism in the Ge:Mn thin films. For static magnetic measurements, the value of the exchange integral determined from the Eq. (1) is $J \sim 60 \pm 10$ K. The parameter $L^3 n_h \sim 0.01400 \pm 0.00083$ also obtained from the fit is significantly less than unity which also points out at the percolation mechanism. The normalized temperature dependencies of the magnetic moment, $\ln[1 - \frac{M_{disp}(T)}{M_{disp}(2\ \text{K})}]$ vs $\ln^3(\frac{SJ}{T})$, are shown in the inset in Fig. 2(b). The good linearity of the experimental data in these coordinates indicates the appropriateness of the chosen model, see Eq. (1).

B. Dynamic magnetic measurements

The existence of a long-range magnetic order in Ge:Mn thin films at $T_{C1} \leq 13$ K is a necessary condition for excitation of a spin-wave resonance there [Fig. 3(a)]. In the case of the spin-wave resonance excited in the perpendicular geometry and Gaussian distribution of the magnetization through the film thickness, the dependence of the resonant field, H_{res}, on the spin-wave mode number k can be described as

$$H_{res} = H_0 - \frac{D_{ex}\left[\frac{3\pi}{2}\left(k + \frac{1}{4}\right)\right]^{2/3}}{d^2}, \quad (2)$$

where D_{ex} is the exchange constant and d is the film thickness.[14] Figure 3(b) shows the experimental dependencies, H_{res} vs $k^{2/3}$, and their fit by the Eq. (2). The figure demonstrates that the theoretical model describes the experimental results with a sufficient accuracy, proving the presence of the spin-wave resonance in all studied Ge:Mn films. The values of the exchange constant D_{ex} defined from the Eq. (2) are 2.1×10^{-8}, 3.3×10^{-8}, and 3.7×10^{-8} Oe cm^2 in

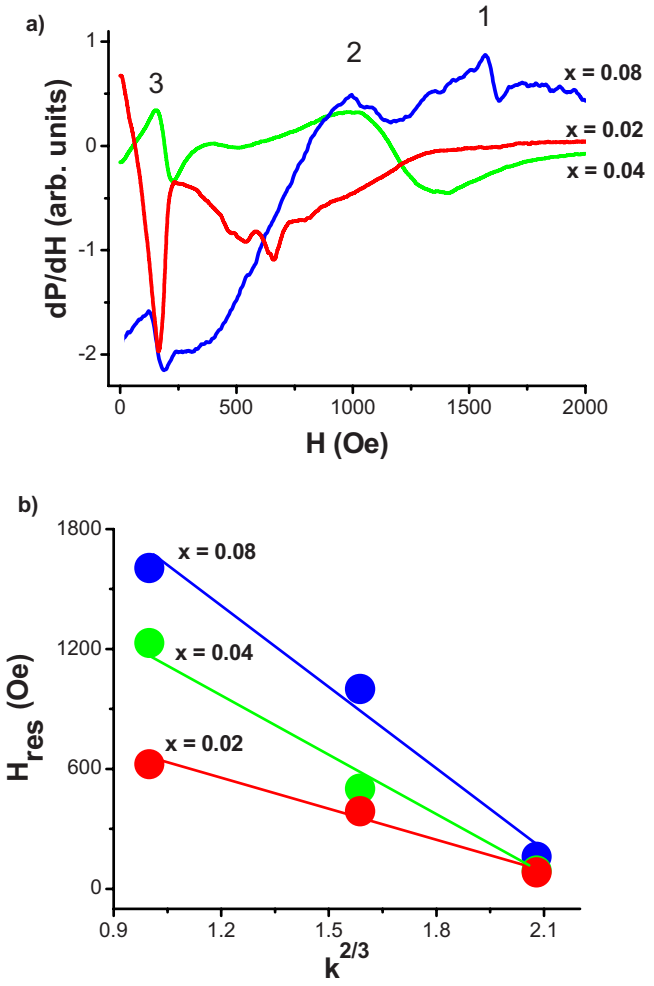

FIG. 3. (Color online) (a) ESR spectra of the spin-wave state in Ge:Mn thin films with Mn concentration of $x=2$, 4, and 8 at. % at $T=4$ K. The dc magnetic field is perpendicular to the film plane. (b) Dependencies of the resonant field on the wave number $k^{2/3}$ at $T=4$ K. Solid lines are approximations by the Eq. (2).

Ge:Mn films with the Mn concentration of $x=2$, 4, and 8 at. %, respectively. In the case of dynamic magnetic measurements the value of the exchange integral, $J \sim 66 \pm 14$ K, was calculated using the following expression:[15]

$$J = \frac{D_{ex} g \mu_B}{2 S r_S^2}, \quad (3)$$

where $g=2$ is the g factor of a Mn^{2+} ion, μ_B is the Bohr magneton, r_s is the averaged distance between Mn^{2+} ions, $r_s=11.8$, 9.8, and 8.3 Å in Ge:Mn films with the Mn concentration of 2, 4, and 8 at. %, respectively. The obtained values of D_{ex} and J are in good agreement with the results reported earlier for similar systems.[12,16] It is noteworthy that the value of the exchange integral obtained from ESR measurements is very close to its magnitude calculated from the independent dc magnetization measurements using a percolation model (see above).

The lowest Curie temperature, T_{C1}, as determined from magnetization measurements increases linearly with the con-

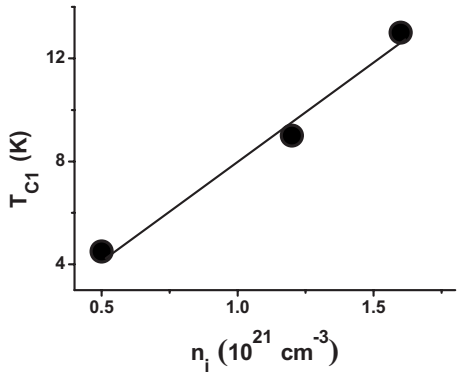

FIG. 4. Dependence of the lowest Curie temperature, T_{C1}, on the concentration of dispersed Mn^{2+} ions, n_i, in Ge:Mn thin films. Solid lines are approximations by the Eq. (4).

centration of dispersed Mn^{2+} ions, n_i, see Fig. 4. In the frame of the percolation model, the Curie temperature is defined as

$$T_C = sSJ(L^3 n_h)^{1/3} \sqrt{\frac{n_i}{n_h}} \exp\left[-\frac{0.86}{(L^3 n_h)^{1/3}} \right], \qquad (4)$$

where $s=1/2$ is the spin of the localized hole, $S=5/2$ is the spin of the Mn^{2+} ion, J is the exchange integral as defined above from ESR measurements [Eq. (3)], n_i is the concentration of dispersed Mn^{2+} ions known from structural measurements, n_h is the concentration of the localized holes, and L is their localization radius.[12] Here, we assume that n_h is proportional to n_i for all concentrations of magnetic ions in the considered temperature range. Thus, the variable parameters in Eq. (4) are L and n_h whereas all other parameters are either known or measured directly. Although the exact nature of localization is usually not considered within the scope of the percolation model, it can originate, for example, in the Coulomb interaction between the charge carriers and impurity ions or excitons (in this case $L=a_B$, where a_B is the Bohr radius of charge carriers) or Anderson mechanism of localization. We fitted the experimental dependence, T_{C1} vs n_i, using Eq. (4). Figure 4 shows a good correlation between the experimental results and theoretical assumptions. From the fit we obtain parameters $n_h/n_i \sim 0.4 \pm 0.1$ and $L \sim 4.7 \pm 1.3$ Å, whose values are consistent with previous literature results.[12] It is noteworthy, that L is significantly smaller than the Bohr radius of holes, $a_B \sim 75$ Å, and electrons, $a_B \sim 45$ Å, in germanium, which demonstrates a strong degree of localization. Thus, the lowest experimental Curie temperature, T_{C1}, as measured in a static regime by means of SQUID magnetometry is satisfactory described by the percolation model where all experimental parameters were obtained from independent (ESR and structural) measurements.

As the implantation temperature decreases, migration of Mn ions caused by thermoactivated diffusive processes becomes less and lees favorable. Eventually, at low enough growth temperature the cluster formation can be completely suppressed. This results in a significantly increased amount of dispersed Mn^{2+} ions, n_i, and, therefore, raise of T_{C1} [see Eq. (4)]. The experimental evidence of this is presented in Fig. 2(a), where the temperature dependencies of the magnetic moment are compared for Ge:Mn films with the same averaged concentration of Mn, $x=2$ at. % but implanted at different growth temperatures. We demonstrate that the decrease in the implantation temperature, T_{gr}, and the corresponding increase in the number of dispersed Mn^{2+} ions at the same nominal concentration of Mn leads to a significant raise of T_{C1} which is related to the ferromagnetic percolation transition in the films [Fig. 2(a) inset]. The result is in good agreement with the model described above and proves the validity of the percolation mechanism in the explanation of the magnetic effects occurring in the Ge:Mn system at low temperatures.

IV. CONCLUSIONS

Low-temperature magnetic properties of thin Ge:Mn films obtained by implantation of Mn^+ ions into a single crystalline bulk germanium have been studied by means of SQUID magnetometry and magnetic resonances. The reported experimental results can be explained within the bound magnetic polaron model. In particular, the lowest critical temperature, T_{C1}, corresponds to a ferromagnetic percolation transition in a system of dispersed Mn^{2+} ions. From the analysis of the spin-wave resonance phenomenon in the low-temperature regime, $T<T_{C1}$, we defined main parameters of the exchange interaction which are in good agreement with approximations obtained from static magnetic measurements. Thus, we demonstrate that magnetic properties of diluted Mn ions in Ge:Mn films can be successfully explained by a magnetic polaron model.

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