Research articles

The magnetic state in the binary Dy$_x$Ge$_{1-x}$ ($x \leq 0.02$) alloy semiconductor

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**Abstract**

Diluted bulk magnetic alloy semiconductors Dy$_x$Ge$_{1-x}$ ($x \leq 0.02$) were prepared by a two-step fabrication procedure and studied experimentally by XRD, EDX and magnetic methods. The polycrystalline materials had the ccp (cubic closed-packed) structure of the host Germanium up to $\sim$2 at.% of Dysprosium. They exhibited different low-temperature and high-temperature behaviors. Low-field dc magnetic susceptibility data showed sharp peaks and irreversibility between zero-field cooled and field-cooled states for $x < 0.02$. A stable antiferromagnetic phase with temperature of the antiferromagnetic to paramagnetic transition $T_N = 25$ K was observed at $x = 2$ at.% of Dysprosium. The solubility range of the binary Dy$_x$Ge$_{1-x}$ alloy system is limited to $\sim$2 at.% due to the large atomic radius of the solute. The low-temperature magnetic phase is characterized as spin-glass below 2 at.%. The magnetic relaxation and non-linear susceptibility $\chi_{nl}$ of Dy$_{0.02}$Ge$_{0.98}$ were analyzed, and the spin-glass phase was defined with the critical exponents of the phase transition $\beta = 0.52 \pm 0.10$, $\gamma = 2.85 \pm 0.10$ and $\delta = 6.49 \pm 0.02$. From the Curie-Weiss behavior of the susceptibility at high temperatures, we determined an average effective Dy-Dy exchange constant $J_1 = -6.90$ K and effective magnetic moment per Dy ion $\mu_{eff} = 10.08$ $\mu_B$. The rare-earth Dy atoms behave as isolated in Ge matrix at high-temperatures.

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**1. Introduction**

The nature and stability of the magnetic phase in dilute magnetic semiconductors (DMS) has been studied theoretically [1–5] to validate the room temperature (RT) ferromagnetism (FM) in semiconductors (SCs), and experimentally [6–10] to utilize additionally the spin of the SC carriers in combined, magnetic-memory and logic devices.

The FM phase is fragile and dependent on the ratio ($n_c/n_i$) in magnetically doped SCs; $n_c$ and $n_i$ are the carrier and dopant concentrations, respectively [1–2]. The carrier concentration and the Fermi wave number ($k_F$) are related, $k_F \propto n_c^{1/3}$, and the dopant concentration determines the mean spacing ($l_x$) between the magnetic ions, $l_x \approx n_i^{-1/3}$. For a FM ordering, $l_x$ should be $< 1/k_F$, thus $l_x < 1$; then the indirect, carrier mediated Ruderman-Kittel-Kasuya-Yosida interaction (RKKY) is not disrupted by the direct antiferromagnetic (AFM) coupling [2,5]. The magnetic interaction may become random and the magnetic behavior spin-glass-like when short-range AFM coupled magnetic ions set in the RKKY wave upon increasing of the $n_i$ [2,5]. This becomes especially relevant in degenerate, magnetically-doped SCs for which $k_F$ increases and $l_x$ becomes commensurate with $1/k_F$.

The carrier and dopant concentrations, $n_c$ and $n_i$, are changed simultaneously in doping of a SC, and conditions for clustering and strong damping of the RKKY may occur. The strong damping is exhibited as glassiness of the material, i.e. slow dynamics and frustration. The latter arise in SCs or metallic disordered systems [6,11], as well as in phase-separated systems [12–15] pertinent for the magnetic memory effects [15].

The onset of clustering is defined by a temperature $T_a$ above the phase transition ($T_{ph}$) where sizable magnetic clusters begin to form [2,4]. It is related to the $T_{ph}$ as $T^a = \exp(\alpha l_x^\gamma)T_{ph}$ and increases when the length scale ($l$) of the magnetic interaction integral decreases relatively to the separation distance $l_x$, i.e. $\frac{1}{l} \gg 1$ ($\alpha$ is a dimensionless factor) [2,5].

In search of RT FM semiconductors, Germanium (Ge) has been doped with various 3d transition magnetic metals as Mn [7], Cr [8], Fe [8,16]. The binary phase diagrams of Mg$_x$Ge$_{1-x}$ (M = Cr, Mn, Co, Fe) [17] contain a range of the solute ($0 < x < 0.30$) with insufficiently explored physical properties such as solubility of the constituents, magnetic and optical properties. Having covalent radii slightly larger than the covalent radius of Ge ($122$ pm, $1$ pm = $10^{-10}$ m), it is relatively easy to incorporate 3d magnetic ions into...
the host lattice by various fabrication techniques [7–8,16,18]. FM properties are reported for single crystalline Mn$_{0.90}$Ge$_{0.99}$ (Curie temperature $T_C = 285$ K [7]), Cr$_{0.01}$Ge$_{0.99}$ ($T_C = 126$ K [8]), Fe$_{0.05}$Ge$_{0.95}$ ($T_C = 233$ K [8]), and in a number of low-dimensional Ge-based material [16,18]. The FM interaction in these SCs is mediated through the primary carriers achieved in doping – holes in Mn$_{0.90}$Ge$_{0.99}$ [7], Cr$_{0.01}$Ge$_{0.99}$ [8] and electrons in Fe$_{0.05}$Ge$_{0.95}$ [8]. Specifics and details on obtaining the majority of the carriers in the doped SCs remains an open question in many works [7–8,16,18].

Germanium is a small bandgap SC (0.66 eV at RT) with high mobilities of the carriers as compared to other SCs [19] – 0.39 m$^2$/Vs for the electrons and 0.18 m$^2$/Vs for the holes. These attributes are utilized in near-infrared (IR) detecting devices [20]. Dopant ions and shifts the detecting range to the mid- and far-IR wavelengths. The small gap, however, facilitates the occurrence of SC degeneracy and fragility of the FM state; e.g. 1 at.% of incorporated magnetic atoms results in $n_c \approx 7 \times 10^{18}$ carriers/cm$^3$ and degeneracy [19]. Magnetically, Ge is a diamagnetic material with temperature-dependent susceptibility, which increases upon cooling down to LHe (liquid Helium) temperatures by $\approx 5\%$ in intrinsic Ge and by up to $10\%$ in doped materials [21].

Dysprosium (Dy) is a rare-earth (4f) magnetic metal with deep-embedded magnetic moment in the 4f-shell and atomic radius 1.22 Å. It has a complex, temperature-dependent magnetic structure: FM below 85 K, AFM from 85 K to 178 K and paramagnetic (PM) above 178 K with PM susceptibility $\chi_{PM} \approx 9 \times 10^{-4}$ m$^3$/kg [22,23]. Hosted in a diamagnetic metallic copper (Cu) [15,24], the intermetallic DyCu compound exhibited a variety of magnetic structures and field-induced phases, but no magnetic relaxation and memory effect [15].

The binary phase diagram of Dy–Ge [17] specifies a range of $0 < x < 0.26$ (26 at.% of Dy) in which the properties of the composite material Dy$_x$Ge$_{1-x}$ are not explored and the role of the Dy magnetic ions in the Ge matrix is described insufficiently.

We investigate in this work the correlated magnetic behavior and the magnetic phase in the very-diluted alloy semiconductor Dy$_x$Ge$_{1-x}$ ($x \leq 0.02$). We also study the solubility of Dy in Ge in these concentration limits under the applied fabrication conditions.

2. Experimental

The starting materials, Ge 99.99% and Dy 99.999% (Sigma Aldrich), were weighted in related amounts in an air protected atmosphere and arc-melted to prepare the ingots of the semiconductor alloys. They were subsequently heat-treated for homogenization at the temperature of 900 °C for 20 h in flowing argon (Ar) at the rate of 20 sccm (standard cubic centimeters per minute) maintaining atmospheric pressure in the chamber.

The crystalline structure of the alloys was studied by XRD measurements made at RT on a Rigaku Ultima diffractometer applying the powder diffraction technique using CuK$_\alpha$ radiation. The homogeneously magnetic crystalline state was additionally confirmed by thermoremanent magnetization measurements (TRM) made from 4.2 K to RT. This technique is applied to reveal alien magnetic phases, which may show up as cusps at their phase transition temperatures [25,26].

The elemental composition in the SC alloys was determined by using energy dispersive X-ray spectroscopy (EDX) and compared with the nominal composition. We used for the EDX measurements a scanning electron microscope (SEM) JSM – 5600 equipped with an EDX spectrometer.

The magnetic state of the alloy was studied by low-field dc magnetization measurements using a Quantum Design Magnetic Property Measurement System 3 (QD MPMS 3). The materials were characterized initially by the zero field-cooled (M$_{ZFC}$, field-cooled (M$_{FC}$) and TRM magnetization measurements. The M$_{ZFC}$ measurements were made after cooling a sample down to LHe in zero magnetic field, applying a probing linear magnetic field (H) chosen from the M$_{ZFC}$ vs. H dependence and recording the data-points in H upon warming to RT. The M$_{FC}$ measurements were made applying the same H and temperature step in cooling down to LHe. The TRM data were recorded in zero-field upon warming at the temperatures of the ZFC/FC measurements.

The nature and stability of the magnetic phase below the temperature of the maximum $T_C$ in M$_{ZFC}$($T$) were investigated by time-dependent magnetization measurements M($t$, T, H) using the FC protocol for a reliable, strong, noise-free magnetic signal. The material was cooled down in a field of $H = 240$ kA/m (3000 Oe) to a temperature $T = 0.6 T_C$ [11] and aged at these T and H for a waiting time $t_w = 20$ min. The magnetic field was reduced to zero after the ageing procedure and the time dependence of the magnetization M$_{FC}$($T$, $T = const$, $H = 0$) was recorded for a period of $\approx 3$ h.

The magnetic phase below $T_C$ was also investigated by studying the non-linear susceptibility of the materials ($\chi_{nl}$), which was obtained utilizing M vs. H isotherms [27–29]. We applied multiple FC measurements to determine the points in the H–T plane [27,28]. In each M$_{FC}$ vs. T cycle, the specimen was cooled down from RT to a temperature $T = 3 T_C$, at which the magnetic interactions in the material are assumed negligible. A constant field in the range of 5–5000 Oe was applied at the $T \approx 3 T_C$ and a plot M$_{FC}$($T$, $H = const.$, $\Delta T = const.$) was recorded upon cooling down to LHe. The temperature of the specimen was subsequently cycled back to $3 T_C$ in the last measuring field, and a M$_{FC}$($T$, $H = const.$, $\Delta T = const.$) plot was recorded in the next field of interest [27,28].

The non-linear susceptibility is derived from the M$_{FC}$ vs. H isotherms and its behavior around a possible phase transition temperature is analyzed [27–29] in terms of divergence of the $\chi_{nl}$ [30] and characteristic scaling parameters [31,32].

3. Results and discussion

3.1. Crystalline structure of the Dy$_x$Ge$_{1-x}$ alloys

The powder diffraction patterns revealed that the investigated alloys had the diamond structure of the parent Ge up to 2 at.% of Dy. The lattice parameters increased linearly with Dy concentration in this range as shown in Fig. 1. The data are displayed with 1% error bars. The two samples of Dy$_{0.01}$Ge$_{0.99}$ presented with two points at $x = 1$ at.% in Fig. 1 are obtained with different brands of the starting materials (Sigma Aldrich and Alfa Aesar) using different fabrication equipment. The solid line in Fig. 1 is the linear least-square fitting of the data with intercept on the vertical axis equal to the lattice parameter of pure Ge, 5.66 ± 0.04 Å and a slope of 0.02 ± 0.04 Å/at.%. Many SC solid solutions may reach high values of the solute (x) preserving the crystalline structure of the solvent [6]. Their lattice parameters are linearly dependent on the concentration (x), and obey Vegard’s law [33a,b] $a = a_0 x (1 - x) + a_0'$ x, where $a_0$ and $a_0'$ are the lattice constants of the primary elements, Ge and Dy, respectively, for this work.

Vegard’s law is applied successfully in all Mn-doped II – VI semiconductors, regardless that the primary elements may have very different crystalline structures [6]. Theoretical work [34] proves validity of Vegard’s law when the difference in the lattice parameters of the two components forming the solid solution is up to 5%. Deviations from Vegard’s law within ±5% variations of the lattice parameters are calculated in Ref. [34].

Germanium has a cubic close-packed (ccp) crystalline structure with lattice parameter $a = 5.6575$ Å, cell volume $181.32$ Å$^3$ and atomic radius $r = 122$ pm.
Dysprosium has a hexagonal close-packed (hcp) crystalline structure with lattice parameters \( a = b = 3.5930 \, \text{Å} \), \( c = 5.6537 \, \text{Å} \), cell volume 185.99 Å\(^3\), i.e. only 2.6% larger than the cell volume of Ge, and considerably larger atomic radius \( r = 228 \, \text{pm} \). With these parameters of the starting materials and in the applied production conditions, our X-ray results confirmed that a solid solution with the parent structure could exist up to 2 at.% of Dy only. Above 2 at.% of Dy, the hcc crystalline structure sets in the solid solution (details are marked in the inset of Fig. 1). The materials above 2 at.% of Dy remain magnetically homogeneous, antiferromagnetic, with one and the same temperature of the AFM – PM transition ~25 K, which is in support of the assumption that the solubility of the constituents above 2 at.% of Dy is limited.

The scattering of the results in Fig. 1 is less than 1% (\%1). This is in agreement with the conclusions in Ref. [34] for the possible deviations from Vegard’s law when the lattice parameter of the second element is ~5% larger (see Fig. 2 of Ref. [34], case 2 therein).

3.2. Magnetic characterization of \( \text{Dy}_x\text{Ge}_{1-x} \)

3.2.1. General magnetic characterization of \( \text{Dy}_x\text{Ge}_{1-x} \)

We present in Fig. 2 the dc low-field magnetic behavior of two materials, \( \text{Dy}_{0.01}\text{Ge}_{0.99} \) and \( \text{Dy}_{0.02}\text{Ge}_{0.98} \). Both samples exhibit a low-temperature magnetic phase and a high-temperature paramagnetic phase.

In Fig. 2(a) are shown the temperature dependences of the ZFC and FC mass susceptibilities, \( \chi_{\text{ZFC}}(T) \) and \( \chi_{\text{FC}}(T) \) of \( \text{Dy}_{0.01}\text{Ge}_{0.99} \), \( \chi = \frac{M}{H} \). M ≡ mass magnetization, and in Fig. 2(b) are displayed the \( \chi_{\text{ZFC}}(T) \) and \( \chi_{\text{FC}}(T) \) of \( \text{Dy}_{0.02}\text{Ge}_{0.98} \). Both materials are measured in 100 Oe magnetic field, which is in the linear range of M(H) at temperatures above the maxima of the \( \chi_{\text{ZFC}}(T) \) plots.

While \( \text{Dy}_{0.02}\text{Ge}_{0.98} \) exhibits antiferromagnetic behavior, \( \text{Dy}_{0.01}\text{Ge}_{0.99} \) has a bifurcation of the \( \chi_{\text{ZFC}} \) and \( \chi_{\text{FC}} \) plots below the temperature \( T \approx 20 \, \text{K} \) with a peak at \( T_\text{f} \approx 10 \, \text{K} \). The inset of Fig. 2(a) displays details of the susceptibility below 30 K for \( \text{Dy}_{0.01}\text{Ge}_{0.99} \).

Bifurcation of the dc \( \chi_{\text{ZFC}}(T) \) and \( \chi_{\text{FC}}(T) \) plots with a peak in them is one of the indications for a possible spin-glass phase below a phase transition temperature, \( T_\text{f} \). Other characteristics of the spin-glass phase are the time development of the magnetization and the nonlinear dc susceptibility, the last being one of the most informative and conclusive.

The inflection points of the \( \chi_{\text{ZFC/FC}}(T) \) plots on the high-temperature side are 20 K for \( \text{Dy}_{0.01}\text{Ge}_{0.99} \) and 34 K for \( \text{Dy}_{0.02}\text{Ge}_{0.98} \). Some authors define these as the transition temperatures to the paramagnetic phase [25,35,36].

To investigate the time evolution of the phase in \( \text{Dy}_{0.01}\text{Ge}_{0.99} \), we aged \( \text{Dy}_{0.01}\text{Ge}_{0.99} \) at 7 K in 3000 Oe for 20 min and recorded the \( M_{\text{ZFC}}(t, T = 7 \, \text{K}, H = 0 \, \text{Oe}) \) for ~3 h after reducing the magnetic field to zero. The result – normalized magnetization vs. time is presented in Fig. 2(c).

If the magnetic state is spin-glass-like, it will exhibit time-dependent \( M(t) \) with a specific shape of the graph, an inflection point in it, and a maximum in the relaxation rate \( S \equiv \text{d}M/\text{d}t(\text{int}) \) at the waiting time \( t \approx t_\text{d} \) [11,25,37]. If the magnetic state is stable FM or AF, or the measurement is made above a transition temperature in the paramagnetic state, the magnetic relaxation is thermal and there are no significant, above 0.1% changes in the values of the magnetization.

The time evolution of \( M(t) \) can be analyzed on the basis of various models for slow dynamics in magnetic systems. A Kohlrausch-Williams-Watt (KWW) stretched exponential law \((\sim \exp(-t/\tau)^\beta)\) is often applied to describe the relaxation of the magnetization below \( T_{\text{N}} \) for spin-glasses [15,25,38]. The time \( \tau \) in the KWW expression is a multiple of the waiting time \( t_\text{d} \). The shape parameter \( \beta \) is related to the number of the intermediate states through which the system evolves toward equilibrium [38], \( n, \) as \( \beta = 1 – n \). The percolation model puts restrictions on the possible values of the stretching exponent between 1/3 and 1, 1/3 \( \leq \beta \leq 1 \) [39]. It approaches 1 when the number of the intermediate states \( n \) diminishes [38].

In contrast, a power law \((\sim t^{-\alpha})\) describes the thermal relaxation for most materials, including the spin-glasses above the phase transition temperature [15,25].

We utilized both expressions to fit the data and found that the best fitting at 7 K for the magnetic relaxation, with less than 3% standard deviation, is obtained with the KWW model. This fitting is shown with the solid line in Fig. 2(c). It is in support of a spin-glass nature of the phase in \( \text{Dy}_{0.01}\text{Ge}_{0.99} \) below 10 K.

We obtained for the characteristic time \( \tau = 7000 \pm 40 \), which is approximately four times the waiting time \((\approx 4t_\text{d})\), and for the shape parameter \( \beta = 0.422 \pm 0.003 \). These values are in agreement with values for spin-glass materials [15,25,37,39] (see i.e. Refs 35 and 36 in Ref. 15, Refs 18 and 19 in Ref. 25).

The magnetic relaxation speed \( S(\text{int}) \) at 7 K is presented in the inset of Fig. 2(c). It has the characteristic peak for the spin-glasses at the total waiting time \( t_\text{d} \approx 21 \, \text{min} \) [11,25,37].

3.2.2. The paramagnetic phase in \( \text{Dy}_x\text{Ge}_{1-x} \)

The high-temperature plots of the \( \chi_{\text{ZFC/FC}}(T) \) susceptibilities are utilized to obtain the Curie-Weiss parameter \((\theta)\) and the Curie constant \((C)\) of a material. The paramagnetic susceptibility of diluted magnetic alloys can be described by the Curie-Weiss law, \( \chi(T) = \frac{C}{T - \theta} \) (+ is used for AFM materials, – for FM, \( x \) is the concentration of Dy in \( \text{Dy}_x\text{Ge}_{1-x} \)) [6.40–42]. At low fields and at high temperatures the approximation \( \frac{C}{T} \ll 1 \) holds, and though a modified Brillouin function is applied to describe the magnetization for arbitrary concentrations and temperatures, \( M \) is still linear with respect to the magnetic field, and the magnetic susceptibility \( \chi(T) \equiv M(T)/H \) displays at high temperatures Curie-Weiss behavior [6.40–42].

Experimentally the Curie-Weiss temperatures \( (\theta(x)) \) are determined from the intercepts of the inverse susceptibility with the temperature-axis, \( \frac{1}{\theta} = \frac{1}{T} \frac{d\chi}{dT} = 0 \). The Curie constants \( C(x) \) are estimated from the slopes of the graphs \( \chi(T) = \frac{C(x)}{T} \). To exclude persisting coupling interactions, the susceptibility data are considered well above the temperatures of the maximum \( T_N \) and
bifurcation. We used in this work data above \( T / C 21 \)\(^5\). The diamagnetic contribution of the Ge matrix is subtracted to account for the pure PM phase with the magnetic interactions in it [6,40–42].

The Curie – Weiss temperatures in the molecular field model are presented as [6,43]

\[
h(x) = \frac{2}{3} J \left( \frac{1}{2} J + 1 \right) \sum_{p} J_{pz} \frac{1}{k_B} \]

The parameter \( J_p \) in Eq. (1) is the exchange integral between the \( p \)th neighbors, \( z_p \) is the number of the magnetic atoms in the \( p \)th coordination sphere, \( J \) is the quantum mechanical angular momentum, \( k_B \) is the Boltzmann constant.

In the nearest-neighbor approximation \( \sum_{p} J_{pz} \frac{1}{k_B} = J_1 z \), thus

\[
h(x) = \frac{2}{3} J \left( \frac{1}{2} J + 1 \right) \frac{1}{k_B} \]

The effective exchange constant \( J_1 \) can be calculated from the experimental value \( \Theta(x) \) as

\[
J_1 = \frac{3}{2} \frac{\Theta_0}{J(1 + 1/2)}
\]

after estimating \( \Theta_0 \) by \( \Theta(x)/x_{\text{nominal}} \) (or more precisely as \( \Theta(x)/x_{\text{magn}} \), where \( x_{\text{magn}} \) is the concentration determined from magnetic measurements). For Ge diamond structure \( z = 12 \) and \( J = 15/2 \) [43].

The Curie constant per mole is related to the effective magnetic moment in the PM material \( \mu_{\text{eff}} \) through the equation [29,40–43]

\[
C_{\text{mol}}(x) = \mu_0 \left( \frac{g \mu_B}{2} \right)^2 \frac{1}{3k_B} \frac{1}{N_a} x = \mu_0 \mu_{\text{eff}}^2 \frac{1}{3k_B} N_a x = C_{\text{mol}}^0 x
\]

where \( \mu_{\text{eff}}^2 = \left( \frac{g \mu_B}{2} \right)^2 (J + 1) \) is the square of the quantum mechanical magnetic moment, \( N_a \) is Avogadro’s number, and \( \mu_0 \) and \( \mu_B \) are the permeability of free space and Bohr magneton, respectively. The molar Curie constant for the hypothetical material with \( x = 1 \) is

\[
C_{\text{mol}}^0 = \frac{\mu_0^2 \mu_B^2 N_a}{3k_B}.
\]

We determine \( C_{\text{mol}}(x) \) from experimental values of the mass Curie constant \( C(x) \); \( \mu_{\text{eff}} \) is calculated subsequently from the estimated \( C_{\text{mol}}^0 \). The molar magnetic susceptibility equals \( \chi_{\text{mol}} = \chi_{\text{magn}} A_{\text{DyGe1-x}} \), where \( A_{\text{DyGe1-x}} \) is the molar mass of the created compound material.

In Fig. 3 we demonstrate the validity of the linear dependences \( \Theta(x) = \Theta_0 x \) and \( C(x) = C_0 x \) for \( x \) up to 2 at.%. The solid lines give a good representation of the data to the linear law (with adjusted \( R \)-squared \( \geq 0.98 \)).

We determined with Eqs. (1) and (2) the dopant concentration \( x_{\text{magn}} \) in the solid solution, the nearest neighbor interaction integral \( J_1 \) and the effective magnetic moment \( \mu_{\text{eff}} \) of the Dy atom in the crystalline lattice.

In Fig. 2(d) are presented the temperature dependences of the inverse susceptibilities \( 1/x \) for two of the studied materials – \( \text{Dy0.01Ge0.99} \) and \( \text{Dy0.02Ge0.98} \). The list of all investigated materials with their estimated parameters is displayed in Table 1: in column 1 is the nominal atomic concentration of Dy, in columns 2 and 3 are the Curie-Weiss temperatures and the Curie constants, in column 4 is the dopant concentration determined from magnetic measurements, in column 5 is the interaction integral, in column 6 is the estimated effective magnetic moment of a Dy atom in the Ge host, and in column 7 are the standardless EDX quantification results.

The Curie-Weiss temperatures are negative, gradually increasing in magnitude with increasing Dy as the antiferromagnetic
from the EDX measurements $x_{EDX}$ for four Dy$^x$Ge$_{1-x}$ alloys. Regarding the large difference of the atomic sizes in Dy$^x$-mediation of the magnetic cation interaction by the intervening distortion of the tetrahedral bond geometry and its effect on the Curie-Weiss temperatures, Curie constants, estimated concentrations from magnetic measurements $x_{magn}$, interaction integral $J_1$, effective magnetic moment $\mu_{eff}$ and the results from the EDX measurements $x_{EDX}$ for four Dy$^x$Ge$_{1-x}$ ($x \leq 0.02$) semiconductor alloys.

Table 1
Curie-Weiss temperatures, Curie constants, estimated concentrations from magnetic measurements $x_{magn}$, interaction integral $J_1$, effective magnetic moment $\mu_{eff}$ and the results from the EDX measurements $x_{EDX}$ for four Dy$^x$Ge$_{1-x}$ ($x \leq 0.02$) semiconductor alloys.

<table>
<thead>
<tr>
<th>$x_{nominal}$</th>
<th>$\Theta(x)$ [K]</th>
<th>$C(x) \cdot 10^5$ [m^3/K/kg]</th>
<th>$x_{magn}$</th>
<th>$J_1$ [K]</th>
<th>$\mu_{eff}$ [\mu_B]</th>
<th>$x_{EDX}$</th>
</tr>
</thead>
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<tr>
<td>0.006</td>
<td>$-22.05 \pm 0.50$</td>
<td>1.05 $\pm 0.02$</td>
<td>0.0052</td>
<td>$-7.18$</td>
<td>9.39</td>
<td>0.0055 $\pm 0.002$</td>
</tr>
<tr>
<td>0.01</td>
<td>$-35.60 \pm 0.50$</td>
<td>1.64 $\pm 0.02$</td>
<td>0.0115</td>
<td>$-6.85$</td>
<td>9.92</td>
<td>0.010 $\pm 0.003$</td>
</tr>
<tr>
<td>0.016</td>
<td>$-55.65 \pm 0.70$</td>
<td>3.20 $\pm 0.02$</td>
<td>0.0152</td>
<td>$-6.86$</td>
<td>10.57</td>
<td>0.015 $\pm 0.002$</td>
</tr>
<tr>
<td>0.02</td>
<td>$-69.18 \pm 0.70$</td>
<td>3.99 $\pm 0.02$</td>
<td>0.0203</td>
<td>$-6.68$</td>
<td>10.45</td>
<td>0.020 $\pm 0.002$</td>
</tr>
<tr>
<td>Average</td>
<td>$-6.89 \pm 0.03$</td>
<td>10.08 $\pm 0.20$</td>
<td></td>
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</table>

Figure 3. Curie-Weiss temperatures and Curie constants for Dy$^x$Ge$_{1-x}$ alloys with $x \leq 0.02$. The solid lines are the best fits of the data to linear regression.

3.2.2. Static scaling of spin freezing in Dy$_{0.01}$Ge$_{0.99}$

To investigate for spin-glassiness, we performed scaling analysis [27–31] of the disordered magnetic state in Dy$_{0.01}$Ge$_{0.99}$. In this method the total non-linear susceptibility $\chi_{nl}$ is derived and analyzed near the phase transition temperature, $T_{ph}$, the critical exponents of the phase are evaluated, and the material is classified according to the range of the exponents and the physical model [27–31].

It is known from experiments that the behavior of basic magnetic parameters is expressed near the phase transition temperature $T_{ph}$ with critical exponents. E.g. the magnetic susceptibility is described as $\chi \propto (T - T_{ph})^{-\upsilon}$ at the temperatures above the phase transition $T > T_{ph}$, the magnetization as $M \propto (T_{ph} - T)^\beta$ at $T < T_{ph}$, and as $M \propto (H)^\gamma$ at $T = T_{ph}$ (see e.g. Ref. 43, page 119, the table therein for the physical models).

The magnetization is a function of the odd powers of the field $[27,43,45]$, $M(T,H) = \chi_1(T)H - \chi_2(T)H^3 - \chi_4(T)H^5 - \ldots$, where the multipliers $\chi_1(T)$ and $\chi_i(T)$ are the linear and the non-linear susceptibility terms, respectively, dependent only on the temperature ($i = 2, 4, 6 \ldots$). Thus, the non-linear susceptibility, defined as $\chi_{nl}(T,H) = \chi_1(T) - M(T,H)/H$, is a function of the even powers of the field, $\chi_{nl}(T,H) = H^2 [\chi_2(T) - \chi_4(T)H^2 + \ldots]$ [27,45, the references therein].

The scaling analysis is compatible with experimentally established laws and theoretical findings. The parameters utilized in it are the reduced temperature deviation $t \equiv (T/T_{ph} - 1)$, the phase transition exponent $\delta$, the ordering parameter $\beta$ and the susceptibility exponent $\gamma$. Only two of the critical exponents are independent [27,45,46a,b], the others are either calculated through hyperscaling relations or established using a second scaling function, complementary to the first.

The estimated magnetic moments per Dy ion displayed in Table 1 are comparable with the theoretical estimations for isolated Dy atom, $\mu_{iso} = 10.63 \mu_B$ [43] and experimentally measured values of isolated Dy. $\mu_{iso} = 9.94 \mu_B$ [44]. Our result is in support that the rare earth atoms with strongly localized 4f electrons behave at paramagnetic temperatures as isolated magnetic entities.

The trends for the development of $J_1$ in A$^x$B$^{1-x}$ magnetic semiconductors [6] are explained by Spalec et al. [42] on the basis of the distortion of the tetrahedral bond geometry and its effect on the mediation of the magnetic cation interaction by the intervening anion. Regarding the large difference of the atomic sizes in Dy$^x$Ge$_{1-x}$, we have reason to assume that the distortion of the bond geometry is one reason for the small values of the exchange integral.

The isolated Dy$^{3+}$ ions have $S = 5/2$, $L = 5$ and $J = 15/2$ in the ground state [43]. We take $z = 12$ as the number of the nearest neighbors when Dy atoms are incorporated randomly in the Ge diamond crystalline lattice. This results in an average value $J_1 = -6.89$ K for the exchange integral – a value overall lower than the one for the Zn$_{1-x}$Mn$^2+$Se semiconductor $J_1 \approx -13.5$ K [40] and close to the values of the narrow-bandgap Cd$_{1-x}$Mn$^2+$Se, $-7.9$ K [6] and Telluride semiconductors: $J_1 \approx -6.9$ K for Cd$_{1-x}$Mn$_x$Te and $J_1 \approx -7.2$ K for Hg$_{1-x}$Mn$_x$Te [42].

The estimated magnetic moments per Dy ion displayed in Table 1 are comparable with the theoretical estimations for isolated Dy atom, $\mu_{iso} = 10.63 \mu_B$ [43] and experimentally measured values of isolated Dy. $\mu_{iso} = 9.94 \mu_B$ [44]. Our result is in support that the rare earth atoms with strongly localized 4f electrons behave at paramagnetic temperatures as isolated magnetic entities.
Values of the critical exponents for FM materials are grouped into a few universal classes, such as the mean field model (MF) with $\beta = 0.5$, $\gamma = 1.0$, $\delta = 3.0$, the 3D Heisenberg model (3DH) with $\beta = 0.365$, $\gamma = 1.386$, $\delta = 4.80$, the 3D Ising (3DI) model with $\beta = 0.325$, $\gamma = 1.241$, $\delta = 4.82$ [47].

The cited critical exponents for AFM materials are scarce, not thoroughly investigated and classified. Works report of unusually low values of $\beta$ ($\beta = 0.06$) instead of the usual $\beta = 0.328 \pm 0.002$ [48].

For spin-glasses $\delta$, $\gamma$ and $\beta$ are overall higher, which reflects the shape of the measured magnetization and susceptibility curves: $3.0 < \delta < 6.9$, $2.3 < \gamma < 3.8$, $0.500 \leq \delta < 1.4$ [27–29,45,49].

Some authors [27–29,31] utilize for the analysis the function

$$\chi_{nl}(T = \text{const.}, H) = f_1(y) \text{ with limiting conditions: for } y \to 0 \ f_1(y) \to \text{constant}, \text{ and for } y \to \infty \ f_1(y) \to y^{-\gamma}. \ \Phi \text{ in } f_1(y) \text{ is another critical exponent discussed below.}$$

With this scaling function the fields $H$ are varied from low to high, and universal scaling is made for temperatures $T > T_f$. The scaling yields values for $T_{ph}$, $\delta$, and $\Phi$. The asymptotic behavior of the function $f_1(y)$ encapsulates simple physical cases [31]: for $y \to 0$, the non-linear susceptibility approaches $\chi_{nl} \propto H^{2\delta}$ which is consistent with the experimental law $M \propto (H)^{1/2}$ and the theoretical requirement that the non-linearity susceptibility depends on the even powers of the field. When $y \to \infty$, the non-linear susceptibility approaches $\chi_{nl} \propto H^{2\delta}$, consistent with the experimental law $\chi \propto (T - T_{ph})^{-\gamma}$ and the even power-dependence of the $\chi_{nl}$ on the field. The limiting requirement yields a relation between the critical exponents $\gamma = \Phi(1 - 1/6)$ [27,28].

Other authors [45,49] utilize the function

$$\chi_{nl}(T = \text{const.}, H) = f_2(z) \text{ with the limiting conditions, for } z \to 0 \ f_2(z) \to z, \text{ and for } z \to \infty \ f_2(z) \to z^{1/\nu}.$$  
In this method the temperatures are varied from low to high, and universal scaling is made for all applied fields. The scaling yields values for the $T_{ph}$, $\delta$ and $\gamma$. The asymptotes of the function $f_2(z)$ also describe plausible physical cases: for $z \to 0$, $\chi_{nl}$ approaches $\chi_{nl} \propto (T - T_{ph})^{-\delta}$, consistent with experimental $\chi \propto (T - T_{ph})^{-\gamma}$ and theoretical $\chi_{nl} \propto H^{2\delta}$. The condition $z \to \infty$ yields another hyper-scaling relation between the exponents. Indeed, when $z \to \infty$ $\chi_{nl} \to |T_{ph} - 1|^{\nu} |H|^{1/\nu - 1} \to H^{2\delta}$.  

Then $\delta = \nu - 1$ should equal $\beta$, which yields $\beta = \frac{\nu - 1}{\nu} = \frac{2}{3}$ [27,28] and Widom scaling relation $\delta = 1 + \frac{\nu - 1}{4}$ [47, the references therein].

Both scaling functions $f_1(\frac{H}{H_{0.01}})$ and $f_2(\frac{H}{H_{0.01}})$ are complementary [46], their choice is preferential and determined from the conditions, under which the experiments are carried out.

We obtained the temperature and field dependences of the non-linear susceptibility $\chi_{nl}(T, H)$ from the measured magnetization vs. field isotherms $M(T = \text{const.}, H)$. The linear susceptibility for each temperature $\chi(T = \text{const.}, H)$ was estimated from extrapolating of the total susceptibility-data as the field approaches zero, $\chi(T = \text{const.}, H)$ [27–29]. The field dependences of the non-linear susceptibility were calculated as $\chi_{nl}(T = \text{const.}, H) = \chi(T = \text{const.}) - \chi(T = \text{const.}, H)$.

In Fig. 4(a) and (b) are displayed the temperature and field dependences of the total non-linear susceptibility $\chi_{nl}(T, H)$ of Dy$_{0.01}$Ge$_{0.99}$ (Fig. 4(a)) exhibits growth of $\chi_{nl}$ of more than two orders of magnitude upon cooling from $T = 3T_c$ down to $T \approx T_c$. Peaks in the $\chi_{nl}(T, H = \text{const.})$ plots are observed around the temperature of 10 K. Unlike the total susceptibility which is usually suppressed at applying high fields, the non-linear susceptibility increases in magnitude with increasing fields, as seen in Fig. 4(a).

The field-dependences of $\chi_{nl}(T = \text{const.}, H)$, displayed in Fig. 4(b), exhibit a low field-range of linear dependences on $H^2$ up to $\approx 500$ Oe, and fields, at which $\chi_{nl}(T = \text{const.}, H)$ reach saturation. The latter is consistent with the general behavior of the Brillouin function at high fields and low temperatures. The non-linear susceptibility drops sharply at various, consistently increasing temperatures above the $T_c$ as seen in Fig. 4(b). The first non-linear susceptibility term $\chi_{nl}(T)$ is predominant in the linear range. It is estimated from fitting of the data at fields up to 500 Oe to a function $F = \chi_{nl} - H^2$. Its intensive growth of three orders of magnitude upon cooling to $T_c$, as our calculations show, indicates a spin-glass nature of the material [29–31].

In Fig. 5(a) and (b) is presented the static scaling of the $\chi_{nl}$ using the functions $f_1$ and $f_2$, respectively.

The scaling according to the function $f_1$, shown in Fig. 5(a) yields values for the $T_{ph} = 10.30 \pm 0.10$ K, $\Phi = 3.31 \pm 0.10$ and $\delta = 6.49 \pm 0.02$. Calculating $\beta$ and $\gamma$ from these results yields for $\beta = 0.51$ and for $\gamma = 2.80$. These critical exponents are in accordance with cited values for spin-glasses as evidenced by Table 2 and Refs. [27–29,45,49].

The limiting values of the function $f_1$, shown with the lines in Fig. 5(a), tend to a constant when $y \to 0$, and to the slope of the collapsed curves $\approx 1.70$ when $y \to \infty$. The calculated value of $\gamma$ from the slope $= [2\gamma/\Phi]$ equals 2.83, in good agreement with $\gamma = 2.80$ obtained from the estimation using $\gamma = \Phi(1 - 1/6)$ [27,28].

The scaling according to the function $f_2(z)$ is presented in Fig. 5(b). It yields values for the $T_{ph} = 10.20 \pm 0.10$ K, $\delta = 0.52 \pm 0.10$ and $\gamma = 2.85 \pm 0.10$. The asymptotes of $f_2(z)$ are shown with the lines in Fig. 5(b); when $z \to 0$, $f_2$ consistently decreases, when $z \to \infty$, $f_2$ tends to the slope of the collapsed curves $\approx 0.16$. The slope is equal to $\delta = \frac{1}{2\nu} = \frac{6.25}{4}$.  

The scaling using the functions $f_1$ and $f_2$ yielded close results for the $T_{ph}$ and the critical exponents. The difference of $1\%$ in the values of the transition temperature we explain with the error in the fitting procedure and error in determining the precise values of the magnetic fields.

The static experiments are well described in terms of a phase transition at a final critical temperature, $T_{ph} \approx 10.20 \pm 0.10$ K. In semiconductor spin-glasses the critical behavior might change along the concentration line. Once the magnetic percolation limit is reached for a given crystalline structure, the system can undergo long-range FM or AFM order with definite $T_c$ or $T_{ph}$. At the concentration level of $x = 0.01$ studied in this part, the appearance of Dy$_{x}$Ge$_{1-x}$ alloy semiconductors show a transition from SG to AFM order at $x = 0.02$. This fact suggests that randomness in the distribution of Dy ions within the crystal lattice of Dy$_{x}$Ge$_{1-x}$ may be a key feature of the SG state. Additional evidence of the intrinsic Dy disorder comes from the fact that the values of the critical exponents ($\beta = 0.52 \pm 0.10$, $\gamma = 2.85 \pm 0.10$, $\delta = 6.49 \pm 0.02$) fall within those reported for the site-disordered DMS [29,45,49] and doped intermetallic spin glasses [27,28], as demonstrated in Table 2.

It is seen in Table 2 that the value of $\beta$ for Dy$_{0.01}$Ge$_{0.99}$ is on the low side of the reported, and the value of $\delta$ is on the high side. Close values for $\beta$ and $\delta$ are seen in Table 2 for the La$_{2}$As$_{0.95}$Si$_{0.05}$Cu$_{1-x}$Ni$_{x}$O$_{4}$ system, which undergoes transitions from a superconducting material to a spin-glass, and subsequently to a disordered antiferromagnetic insulator upon increasing the concentration of Ni [49,52]. Unusually low values of $\beta$ were reported in Ref. [48] for the antiferromagnetic phase transition of azurite.
Fig. 5. Static scaling using functions $f_1$ and $f_2$. (a) The data collapse in Fig. 5(a) is made for temperatures $1.2 T_{ph} \leq T \leq 1.7 T_{ph}$ for fields varying from 5 Oe to 4000 Oe. (b) The collapse in Fig. 5(b) is obtained at the indicated fields for temperatures from 6 K to 65 K. The lines in Fig. 5(a) and (b) represent the asymptotic limits of the experimental data.

Table 2
Critical exponents for intermetallic, semiconducting and insulating disordered spin-glasses.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>Tendency upon doping</th>
<th>References/Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho$<em>5$Co$</em>{50}$Al$_{45}$ Intermetallic SG</td>
<td>0.512</td>
<td>2.784</td>
<td>6.4</td>
<td>SG $\rightarrow$ FM</td>
<td>[27] 3DH</td>
</tr>
<tr>
<td>Gd$<em>5$Co$</em>{50}$Al$_{45}$ Intermetallic SG</td>
<td>0.61</td>
<td>2.4</td>
<td>4.9</td>
<td>SG $\rightarrow$ FM</td>
<td>[28] 3DH</td>
</tr>
<tr>
<td>Zn$_{1-x}$Mn$_x$In$_2$Se$_4$ SC SG</td>
<td>1.09</td>
<td>3.28</td>
<td>4</td>
<td>SG $\rightarrow$ FM</td>
<td>[29,50] Quasi-2D</td>
</tr>
<tr>
<td>Zn$_{1-x}$Mn$_x$In$_2$Te$_4$ SC SG</td>
<td>0.9</td>
<td>3.6</td>
<td>5</td>
<td>Disorder persists</td>
<td>[45,50] 3DH</td>
</tr>
<tr>
<td>(Ga,Mn)As SC SG</td>
<td>0.4</td>
<td>1.1–1.3</td>
<td>3–4.783</td>
<td>Disorder persists</td>
<td>[51] 3DH</td>
</tr>
<tr>
<td>La$<em>{1.85}$Sr$</em>{0.15}$Cu$_1$–Ni$_x$O$_4$ SC SG</td>
<td>0.55–0.75</td>
<td>3.2–3.8</td>
<td>6.06–6.82</td>
<td>Superconductor $\rightarrow$ SG $\rightarrow$ AFM insulator</td>
<td>[49,52] 3DH–3DH</td>
</tr>
<tr>
<td>AlMnSi (15% Mn) amorphous insulating SG</td>
<td>1.4</td>
<td>3.1</td>
<td>3.21</td>
<td>SG</td>
<td>[53] 3DH</td>
</tr>
<tr>
<td>CsNiFe$_2$ disordered insulator</td>
<td>1.2</td>
<td>3</td>
<td>3.5</td>
<td>SG</td>
<td>[54] 3DH Insulator</td>
</tr>
<tr>
<td>Dy$<em>{50}$Ge$</em>{30}$ Sc SG</td>
<td>0.52</td>
<td>2.85</td>
<td>6.49</td>
<td>SG $\rightarrow$ AFM</td>
<td>Present study</td>
</tr>
</tbody>
</table>
(Cu3(CO3)2(OH)2). Thus, Dy0.01Ge1−x system may be unique in the trend to study the gradual development of the critical exponents upon doping toward the AFM state.

4. Conclusions

We aimed at creating a continuous substitutional Dy0.01Ge1−x solid solution with atoms of the magnetic element Dysprosium randomly distributed at the atomic sites of the parent Germanium, and with crystalline structure of the host. Our X-ray results proved that this is possible up to 2 at.% of Dy. A stable antiferromagnetic phase with a transition temperature to the paramagnetic phase at TN = 25 K is exhibited in Dy0.02Ge0.98. Moreover, our results show that this transition temperature and the magnetic properties of the alloys do not change significantly upon further doping, which is in support of the assumption that the solubility limit is reached in Dy0.01Ge1−x, and solubility saturation is possibly achieved between 2 and 3 at.% of Dy. As seen in the inset of Fig. 1, at 3 at.% of Dysprosium, the material has different crystalline structure.

Solubility of two elements in a binary alloy system depends on a number of factors such as the relative sizes of the atoms, the temperature and pressure at which the material is created. It is well known that elements with larger particles are less soluble. With atomic radii of 122 pm and 228 pm for the solvent and solute, respectively, a solubility limit of 2 at.% is achieved at 900 °C heat-treatment for 20 h in atmospheric pressure for the Dy0.01Ge1−x alloy system. These fabrication conditions leave a small room for experimenting and optimizing the solubility ranges.

Magnetically, these semiconductor alloys display different low-temperature and high-temperature phases. The low-temperature magnetic phase gradually develops from a dilute spin-glass-like into antiferromagnetic at 2 at.% of Dy as proved experimentally and modelled in Fig. 6.

Particularly for the Dy0.01Ge0.99 alloy semiconductor, the spin-glass state is characterized with an ordering exponent β = 0.52, susceptibility exponent γ = 2.85 and phase transition exponent δ = 6.49, which are within cited parameters for spin-glasses. A tendency of a low value of β and a high value of δ, observed with our material, is outlined for two-dimensional Ising materials (2dI) [43, Table 6.2 therein], in which the magnetic spins occupy a two-dimensional (2d) lattice in the process of coupling, and the dimensionality of the magnetically coupled spins (D) is one (1). The large size of Dy atoms facilitates formation of magnetic clusters already at 1 at.% of Dy, and this concentration can be named conditionally moderate for the Dy0.01Ge1−x system. Our results for the critical exponents are between the values of the corresponding parameters for two-dimensional Ising and three-dimensional Ising models [43]. At this point, they are incomplete in terms of dimensionality of the spins and their occupation in the Ge lattice, future low-energy neutron scattering experiments are in scope. Overall, Dy0.01Ge1−x system seems incisive for the development of the critical exponents towards an antiferromagnetic stable phase.

From the high-temperature magnetic measurements, we obtained an average value of the nearest neighbor exchange integral in the mean-field approximation J1 = −6.90 K, in alliance with J1 for other narrow-band semiconductors. For the effective magnetic moment per Dy ion, the estimations yielded μeff = 10.08 μB, in support that rare-earth Dy atoms behave as isolated in Ge matrix at high-temperatures.

As low doped, PM at RT semiconductors, these materials exhibit increased conductivity (three times, unpublished preliminary data) and high mobility of the carriers, which promotes their application in MESFETs (metal-semiconductor field-effect transistors) in microelectronics.

References

[12] Several phase transitions at different temperatures may occur in one and the same material, e.g. magnetic, electronic and structural. The coexisting states can lead to phase separation – breaking of the material into fractions of different phases with different physical properties. This is an intrinsic property of many DMSs and diluted magnetic oxides [13, 14].