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Crystal Structure and Magnetic Properties of $Mn_{1-x}Gd_xSe$ Solid Solutions

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The synthesis of polycrystalline $Mn_{1-x}Gd_xSe$ solid solutions is carried out by solid state reaction method followed by quenching from the temperature of 1370 K. The X-ray diffraction studies realized at 300 K revealed that the structure of the single phase samples in the $0 < x < 0.15$ concentration range is identified on base a face centered cubic crystal cell of $Fm3m$ space group. The heating of the solid solutions to 900 K does not affect on the magnetic susceptibility as the dependences is identical to the measurements in the "heating-cooling" regime. Comparing the research results of magnetic properties of the $Mn_{1-x}Gd_xSe$ solid solutions with those of $Mn_{1-x}Gd_xS$ solid solutions, we can conclude that substitution of manganese ions by gadolinium in manganese selenide lead to more changes in the basic magnetic characteristics than in manganese sulfide.

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1. Introduction

The priority areas of condensed matter physics and solid-state electronics are energy-saving technologies and alternative energy sources. Therefore, the increased interest is attached to magnetic semiconductors capable of operating over a wide temperature range. In this regard, it is interesting to synthesize the solid solutions with cationic substitution in the system $Mn_{1-x}Gd_xSe$ and to study its magnetic properties depending on the chemical composition, temperature and magnetic field. Monoselenide manganese is an antiferromagnetic and p-type semiconductor [1]. It was assumed that the substitution of manganese cations with Gd ferromagnetic metal in solid solutions can create the conditions for the demonstration of the ferromagnetic properties. While maintaining the semiconducting properties of the main matrix MnSe there is possibility for the transition from the antiferromagnetic p-type semiconductor to a ferromagnetic semiconductor with n-type conductivity. The aim of this work is the synthesis of solid solutions in quasi-sectional MnSe–GdSe and study the peculiarities of their crystal structure and magnetic properties of solid solutions depending on composition and temperature.

2. Synthesis of solid solutions $Mn_{1-x}Gd_xSe$ and methods of the experiment

Samples of $Mn_{1-x}Gd_xSe$ solid solutions were synthesized by solid state reactions. Manganese and gadolinium monoselenides were synthesized using initial powders of the chemical elements: electrolytic manganese metal (99.6%); Aldrich chemistry gadolinium (–40 mesh, 99% metals basis); elemental selenium (puriss. spec. 17-4). $Mn_{1-x}Gd_xSe$ solid solutions of compositions $x = 0.05$, 0.1, 0.15, and 0.5 were synthesized on the basis of the basic MnSe and GdSe compounds. Synthesis was done in the conditions of 10^{-2} Pa vacuum. Primary synthesis products were thoroughly grinding to obtain powders. Then pellets were formed under pressure for homogenizing annealing at 1370 K. After a two-hour exposure fusion the products were tempered in cold water. At the final step the grayish-silver homogeneous solid ingots were obtained. XRD analysis of the synthesized $Mn_{1-x}Gd_xSe$ solid solutions was made in the Cu K_α radiation by points mode: step scan angle was equal to $\Delta 2\theta = 0.03$ degree, while set of information time at the point of reference was equal to $\Delta\tau$ =3 s. The specific magnetic susceptibility temperature dependence was studied with ponderomotive method in the magnetic field with induction $B = 0.86$ T and in temperature range of $\approx 80 \le T \le 950$ K [2–4]. Measurement magnetic susceptibility error of the sample of known weight is $\Delta\chi = \pm 10^{-11}$ m^3 kg^{-1}. Measurement error of specific magnetization referred to the weight of the sample is measured $\Delta\sigma = \pm 0.005$ A m^2 kg^{-1}.

3. Experimental results

Compounds MnSe, GdSe and $Mn_{0.95}Gd_{0.05}Se$, $Mn_{0.9}Gd_{0.1}Se$, $Mn_{0.85}Gd_{0.15}Se$ solid solutions were synthesized. The X-ray reflexes of based on MnSe solid solutions are indicated on the basis of the cubic cell of the space group $Fm3m$. According to the results of radiographic studies, the values of the unit cell parameter of $Mn_{1-x}Gd_xSe$ solid solutions was determined. Dependence $a = f(x)$ is shown in Fig. 1.

The measurement results of the temperature dependence of magnetic susceptibility $10^{-2}/\chi = f(T)$ of the $Mn_{0.95}Gd_{0.05}Se$, $Mn_{0.9}Gd_{0.1}Se$, $Mn_{0.85}Gd_{0.15}Se$

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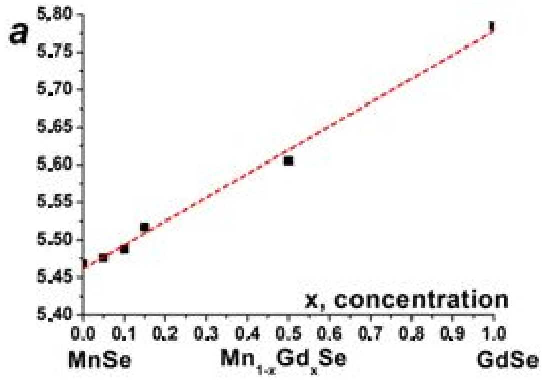

Fig. 1. The concentration dependence of the unit cell parameter of $Mn_{1-x}Gd_xSe$ solid solutions.

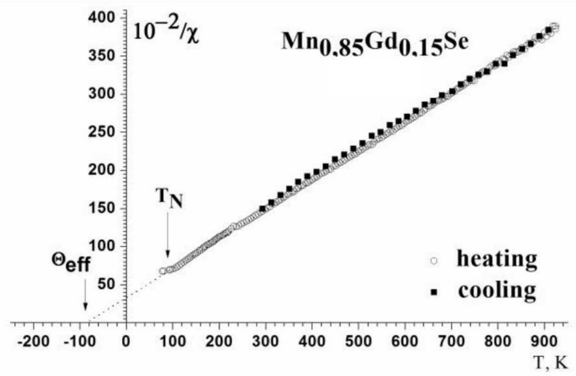

Fig. 4. The temperature dependence of the magnetic susceptibility of $Mn_{0.85}Gd_{0.15}Se$ solid solutions.

solid solutions and GdSe compound are shown in Figs. 2–5.

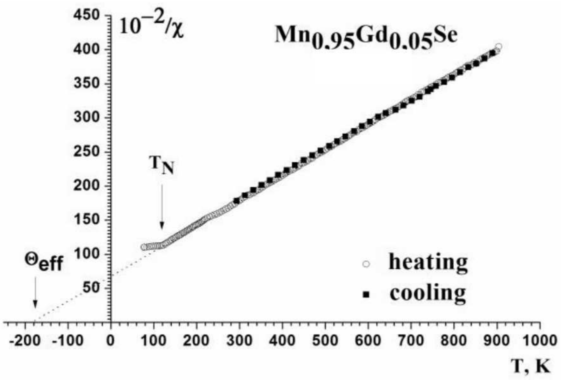

Fig. 2. The temperature dependence of the magnetic susceptibility of $Mn_{0.95}Gd_{0.05}Se$ solid solutions.

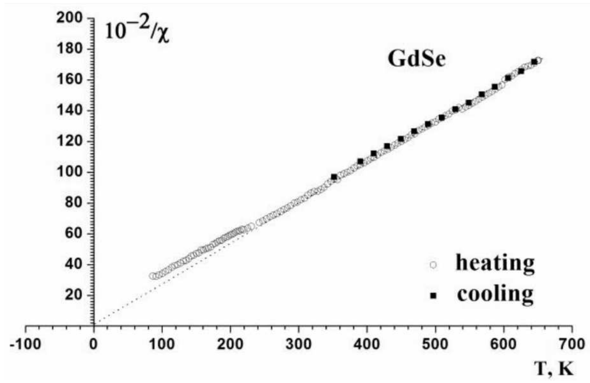

Fig. 5. The temperature dependence of the magnetic susceptibility of GdSe compound.

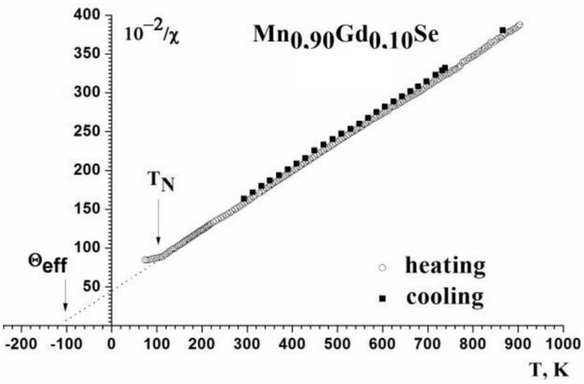

Fig. 3. The temperature dependence of the magnetic susceptibility of $Mn_{0.9}Gd_{0.1}Se$ solid solutions.

The anomaly in 230 K region is associated with possible changes in the spin state of magnetically active atoms.

The temperature dependence of a reversible magnetic susceptibility give the possibility to control the implementation of the Curie–Weiss law, so as to determine antiferromagnetic ordering by negative value of Weiss temperature.

With increasing gadolinium content from $x = 0.05$ to $x = 0.15$ the Néel temperature of solid solutions decreases from $T_N = 12$ K for $Mn_{0.95}Gd_{0.05}Se$ to $T_N \approx 90$ K for $Mn_{0.85}Gd_{0.15}Se$. It is noted that heating of the solid solution to 900 K temperature does not lead to irreversible changes in the magnetic susceptibility because the dependence of $10^{-2}/\chi = f(T)$ measurements in the "heating-cooling" mode is identical. Identified feature has practical importance.

Magnetic susceptibility value of solid solutions increases with increase of gadolinium content. Increase in gadolinium content in the solid solutions leads to a decrease of the Néel temperature from $T_N \approx 135$ K for MnSe [5] to $T_N \approx 90$ K for $Mn_{0.85}Gd_{0.15}Se$ composition. The Néel temperature is determined by the minimum of the temperature dependence of inverse magnetic susceptibility.

The paramagnetic Curie–Weiss temperature also reduces from $\theta_{\text{eff}} \approx |-180|$ K for $Mn_{0.95}Gd_{0.05}Se$ to $\theta_{\text{eff}} \approx |-80|$ K for $Mn_{0.85}Gd_{0.15}Se$ composition. Stochastic distribution of ions in the lattice leads to a destroying of the exchange interaction as the neighboring ions are magnetically active ions with different number of unpaired electrons. The magnetic sublattices with the same amount of manganese will have a destroying of the exchange interaction, and the energy of the magnetic coupling greatly weakened, that leads to the disappearance of the magnetic ordering and a decrease in the Curie–Weiss temperature.

Using tangents α angle of inclination to the x axis of the straight part of the temperature $10^{-2}/\chi = f(T)$ dependence was determined the magnetic moment value of the solid solutions (Table) using the relationship (1). Increase of gadolinium content in solid solution leads to an increase in the magnetic moment.

TABLE

Magnetic moments of $Mn_{1-x}Gd_xSe$ solid solutions.

Composition	p, magnetic moment
MnSe	5.93 μ_B
$Mn_{0.95}Gd_{0.05}Se$	6.17 μ_B
$Mn_{0.90}Gd_{0.1}Se$	6.21 μ_B
$Mn_{0.85}Gd_{0.15}Se$	6.29 μ_B

In Table are given the values of the resulting magnetic moments created by magnetically active ions of the $Mn_{1-x}Gd_xSe$ solid solutions, which were calculated according to the Curie–Weiss law (1):

$$\chi = \frac{C}{T - T_C}. \quad (1)$$

If make a comparison of results of magnetic properties measurements which were carried out in this work with results of work [6], we can see that substitution of manganese ions by gadolinium ions in manganese selenide leads to more significant changes of the magnetic characteristics, than in a $Mn_{1-x}Gd_xS$ system. For example, the Néel temperature for $Mn_{0.9}Gd_{0.1}Se$ composition is equal to ≈100 K, and for $Mn_{0.9}Gd_{0.1}S$ composition ≈120 K. This is due to the size factor of the anions.

4. Conclusions

The solid solutions of $Mn_{1-x}Gd_xSe$ ($0 \le x \le 0.5$) system were synthesized. Based on the dependence of the cubic unit cell parameter a of the crystal from concentration $a = f(x)$ one can assume with some error that the continuous solid solution in this system at the used synthesis mode exist at the range of concentrations ($0 \le x \le 0.5$). The magnetic susceptibility temperature dependence of the $Mn_{0.95}Gd_{0.05}Se$, $Mn_{0.9}Gd_{0.1}Se$, $Mn_{0.85}Gd_{0.15}Se$ solid solutions and GdSe compounds was studied. It was determined that:

a) with gadolinium content increase of the Néel temperature of solid solutions decreases from $T_N = 135$ K for $Mn_{0.95}Gd_{0.05}Se$ to $T_N \approx 100$ K for $Mn_{0.85}Gd_{0.15}Se$;

b) magnetic susceptibility value of solid solutions increases with gadolinium content increase;

c) the dependence $10^{-2}/\chi = f(T)$ is identical for measurements in the "heating-cooling" mode in the temperature range 80–900 K;

d) the magnetic moment of the solid solutions increases with ferromagnetic Gd concentration increase.

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