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Magnetic and thermophysical properties of $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ solid solutions

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Abstract

The structural, magnetic, and thermophysical properties of cation-substituted sulfides $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ ($0.04 \leq X \leq 0.25$) with the NaCl-type face-centered cubic lattice have been investigated. The range of existence of long-range antiferromagnetic order has been established. The anomalies observed in the temperature dependence of the specific heat correspond to the temperatures of the magnetic phase transition. The anomaly in the specific heat caused by electron transitions between the 4f levels and d band states has been observed. It has been found that the coefficient of thermal expansion decreases with increasing concentration of substituents in the magnetically ordered region and remains nearly invariable in the paramagnetic phase.

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, much attention has been focused on the physical properties of compounds with rare-earth elements (Gd, Sm, Ho, etc). The interest in these compounds is due to their possible application in microelectronics, radio engineering, and spintronics. According to the results reported in [1, 2], gadolinium-substituted manganese sulfides form $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ solid solutions with the NaCl-type face-centered cubic (fcc) crystal lattice that are characterized by semiconductor type conductivity. In these solid solutions, both concentration ($X_C = 0.3$) and temperature ($T_C = 450$ K) metal-insulator phase transitions occur. Cation substitution in these solid solutions changes the hole conductivity typical of manganese monosulfide to electron conductivity. The ability of Gd isotopes to absorb neutrons can be used in the aerospace industry. As is known [3–6], manganese monosulfide α -MnS is an antiferromagnet ($T_N = 150$ K) with the NaCl-type fcc lattice. In its magnetic structure, magnetic moments of manganese ions are ferromagnetically ordered in the (111) plane and antiferromagnetically ordered between the

planes [7]. The calculation of the α -MnS band structure by the electron density functional method revealed that the upper Hubbard t_{2g} and e_g bands are partially occupied due to p–d hybridization of sulfur and manganese ions [8]. The electrons lying below the Fermi level in the t_{2g} and e_g bands give rise to hole conductivity, which is confirmed by the thermopower and Hall effect measurements [9].

GdS sulfide is an antiferromagnetic metal with a Néel temperature $T_N = 45$ K [10–12]. The electronic structure of GdS was determined in [13]. The electron configuration of gadolinium ions is $4f^75d^1$. Two electrons pass to a sulfur ion and one electron passes to the conduction band. The f shell of a gadolinium ion is half-occupied and electrons are localized close to the nucleus. The high energy levels of the f states are located near the bottom of the conduction band in the vicinity of the chemical potential. The band states are formed by s–d hybridization of electrons on manganese and gadolinium cations. Most of the electrons on manganese ions are in the localized state and coupled by the exchange interaction; the rest of electrons form the conduction band with ferromagnetic ordering of spins. As a result of competition between the

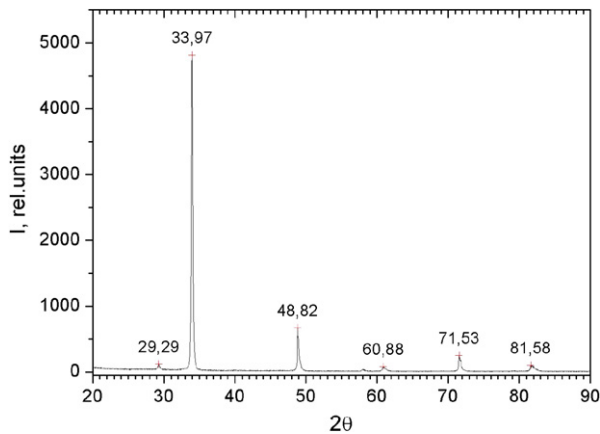


Figure 1. X-ray diffraction patterns of a $\text{Gd}_{0.1}\text{Mn}_{0.9}\text{S}$ sample measured at $T = 300$ K.

exchange interactions, the type of a magnetic order can change with concentration.

The aim of this study was to establish the region of existence of long-range magnetic order and find the correlation of the magnetic, structural, and thermophysical characteristics of the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ crystals upon isostructural cation substitution of gadolinium for manganese.

2. Experimental and discussion

Synthesis of the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ solid solutions was described in detail in [14, 15]. Phase composition and the crystal structure of the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ samples were determined with a DRON-3 x-ray diffractometer in $\text{CuK}\alpha$ -radiation at 300 K. The magnetic properties were investigated on a superconducting quantum interference device magnetometer at temperatures of 4.2–300 K in magnetic fields of up to 500 Oe. Thermal expansion was measured with a DIL-402 C dilatometer (Netzsch) in the temperature range 100–350 K in the dynamic mode with a heating rate of 5 K min^{-1} . Specific heat was measured by an ac calorimetric method [16]. The samples with characteristic sizes of about $3 \times 2 \times 0.4$ mm^3 were heated by light pulses with a modulation frequency $f = 2$ Hz. The resulting periodic oscillations of the sample's temperature were measured using a chromel–constantan thermocouple with a wire diameter of 0.025 mm. To improve the heat contact, the thermocouple joint attached to the sample was flattened to 5 μm . In the region of the phase transitions, the temperature varied at a rate of no higher than 0.05 K min^{-1} .

According to the data of the x-ray analysis, the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ ($0.04 \leq X \leq 0.25$) samples have the NaCl-type fcc lattice typical of α -MnS. Figure 1 shows typical x-ray diffraction patterns of a sample with concentration $X = 0.1$.

As the concentration of cation substitution X is increased, the lattice parameter a grows from 0.522 nm for α -MnS to 0.532 nm for $\text{Gd}_{0.3}\text{Mn}_{0.7}\text{S}$, since the ionic radius of the substituent exceeds that of the substituted element ($r_{\text{Mn}} = 0.83$ Å and $r_{\text{Gd}} = 0.94$ Å).

Figure 2 shows temperature dependences of magnetization for $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ with $X = 0.15$ and 0.25 measured

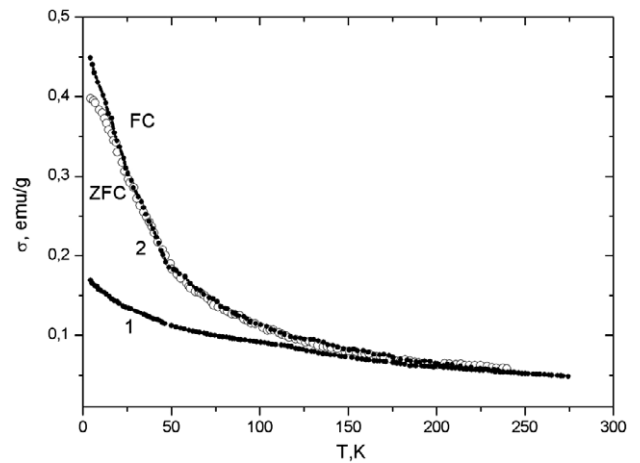


Figure 2. Temperature dependences of magnetization for the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ compound with (1) $X = 0.15$ and (2) $X = 0.25$. FC is cooling in the field $H = 500$ Oe; ZFC is cooling in zero magnetic field.

in a magnetic field of 500 Oe. The dependence $\sigma(T)$ for these samples is qualitatively different from $\sigma(T)$ for manganese monosulfide. For the sample with $X = 0.25$, in the low-temperature region ($T < T_N$), the dependence of magnetization on the conditions of cooling of the sample in zero magnetic field (ZFC) and in the field $H = 500$ Oe (FC) are observed (figure 2); i.e. the magnetic moment induced in the sample by an external magnetic field depends on the prehistory of the sample. In the sample with the same composition, the FC magnetization exceeds the ZFC magnetization. This is apparently related to the formation of a noncollinear spin structure and freezing of the transverse spin component in the field at low temperatures due to the competition between ferro- and antiferromagnetic interactions at some critical gadolinium concentration. In an external magnetic field, degeneracy grows. The random distribution of gadolinium ions over the lattice forms the inhomogeneous (Gaussian) distribution of the local exchange fields. In a weak exchange field at $H_E \sim kT$, spins become paramagnetic and their contribution to magnetization exceeds the contribution of the antiferromagnetically ordered crystal regions. Therefore it is impossible to determine the concentration interval for the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ samples with the long-range antiferromagnetic order from the integral magnetic characteristics. For these concentrations, the temperature of the magnetic phase transition was determined by the calorimetric study and from the variation in the magnetic entropy calculated from the specific heat.

Figure 3 presents temperature dependences of the specific heat for the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ solid solutions with $X = 0.04$, 0.1, and 0.25. The observed maxima correspond to the Néel temperature T_N ($X = 0$) = 150 K, T_N ($X = 0.04$) = 140 K and T_N ($X = 0.1$) = 127 K. Above T_N , the specific heat at low concentrations is nearly temperature-independent and satisfies the Dulong–Petit law. For gadolinium sulfide, in addition to the phonon contribution in the high-temperature region, the transitions between the 4f multiplets caused by splitting of atomic terms by an internal crystal field and

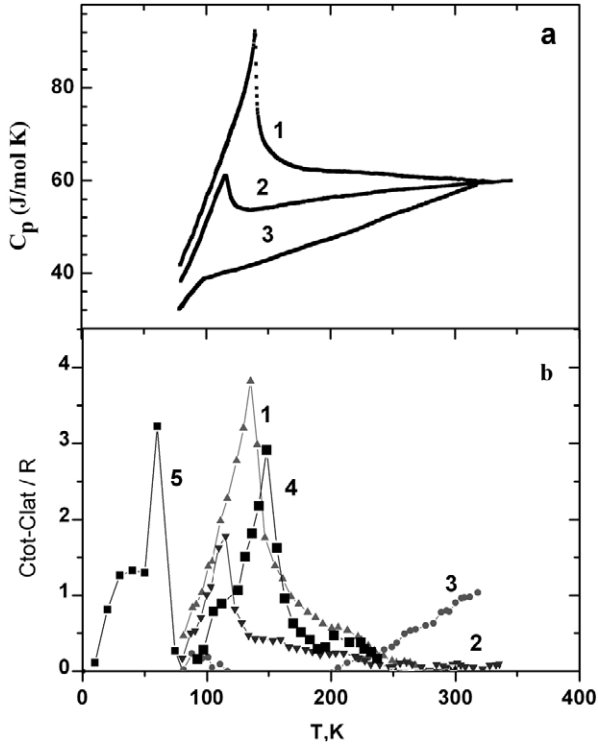


Figure 3. Temperature dependences of (a) specific heat and (b) magnetic specific heat for the $Gd_xMn_{1-x}S$ system with (1) $X = 0.04$, (2) 0.1, and (3) 0.25 and for (4) MnS and (5) GdS.

spin-orbital coupling should be taken into account. The magnetic contribution to the specific heat was determined by subtracting the lattice contribution [8] from the measured (total) specific heat: $C_{tot} - C_{lat}$. Figure 3(b) shows the temperature dependences of the magnetic specific heat for the $Gd_xMn_{1-x}S$ system. In addition, the dependences calculated from literature data for MnS [17] and GdS [18] are presented. The magnetic specific heat of the $Gd_xMn_{1-x}S$ solid solution grows at $X = 0.04$. The slight growth of the specific heat is possibly related to the increase in the spin value upon substitution of $S_{Gd} = 7/2$ for $S_{MnS} = 5/2$ and the occurrence of additional low-frequency oscillation branches. New degrees of freedom lead to the growth of the specific heat.

The temperature dependence of the specific heat for the sample with the substituent concentration $X = 0.25$ at $X = 100$ K exhibits the kink and the monotonic growth both below and above the Debye temperature (figure 3(a)). The growth of the specific heat above the Debye temperature for the compound with $X = 0.25$ is caused by the change in the electronic structure. The density of electron states for small concentration and for $X > 0.2$ is shown in figures 4(a), (b). For $X \ll 1$, the Fermi level lies in the range of impurity states. The energy gap $\Delta E = E_f - E_F$ between the Fermi level E_F and the $4P_J$ multiplet of a rare-earth gadolinium ion decreases with increasing concentration. The Fermi level shifts to the bottom of the conduction band and is localized there at $X = 0.25$ (figure 4(b)).

The specific heat of the electron system is mainly due to the electron density of states, which can be expressed by the

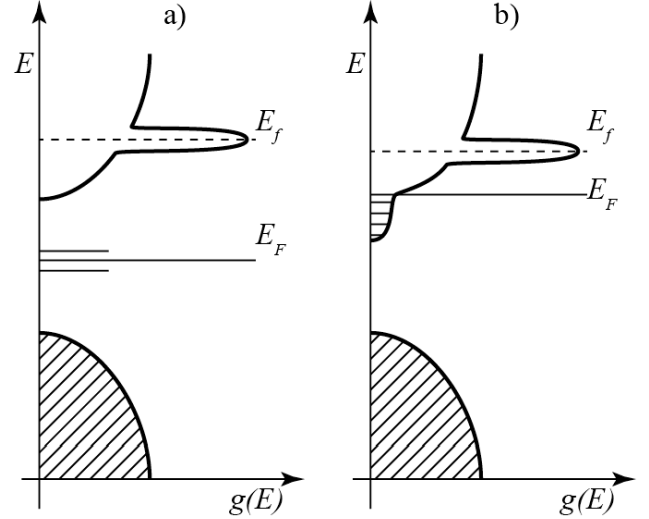


Figure 4. The scheme of the electron density states for small concentration (a) and for $X > 0.2$ (b).

delta function $g(E) = A\delta(E - E_f)$ in the vicinity of the 4f level. We describe the temperature dependence of the specific heat by the model with two levels distant from one another by ΔE . According to [8], specific heat C_f is

$$C_f = R(\Delta E/k_0T)^2 g_1/g_0 (\exp(-\Delta E/k_0T)/[1 + (g_1/g_0) \exp(-\Delta E/k_0T)]^2), \quad (1)$$

where g_1 is the 4f level degeneracy multiplicity.

At low temperatures, the specific heat tends to zero, passes through the maximum as the temperature is increased (at $T = 390$ K), and then smoothly drops. The function $C(T) = XC_f$ satisfactorily describes the experimental data for the parameter $\Delta E = 0.18$ eV with the degeneracy multiplicity $g_1/g_0 = 98$ figure 5. The large degeneracy multiplicity is apparently related to the narrow energy interval near the f level caused by small hybridization of the $4P_J$ multiplet with the d band.

With increasing concentration of the substitute in the $Gd_xMn_{1-x}S$ system, the fraction of magnetic atoms participating in the formation of the magnetic order in the range $80 \text{ K} < T < 150 \text{ K}$ decreases. This follows from the variation in the magnetic entropy calculated from the specific heat $S(T) - S(T = 80 \text{ K}) = \int C dT/T$ for several concentrations figure 6. The concentration of percolation of magnetic atoms in the lattice is $X_c = 2/z$, where z is the number of nearest neighbors; for the fcc lattice, $X_c = 0.16$. The maximum change in the entropy at the antiferromagnetic-paramagnetic phase transition in the molecular field approximation is related to the spin value $\Delta S = Nk_B \ln(2s + 1)$; for manganese sulfide, the maximum change in the entropy is $\Delta S/R = 1.8$. For the compound with $X = 0.25$, the change in the entropy $\Delta S/R = 0.22$ in the temperature range $80 \text{ K} < T < 150 \text{ K}$ is smaller than the critical value $\Delta S/R = 0.29$ found in the percolation region in the molecular field approximation. We can therefore state that the long-range magnetic order vanishes within the concentration range $0.21 \leq X \leq 0.24$.

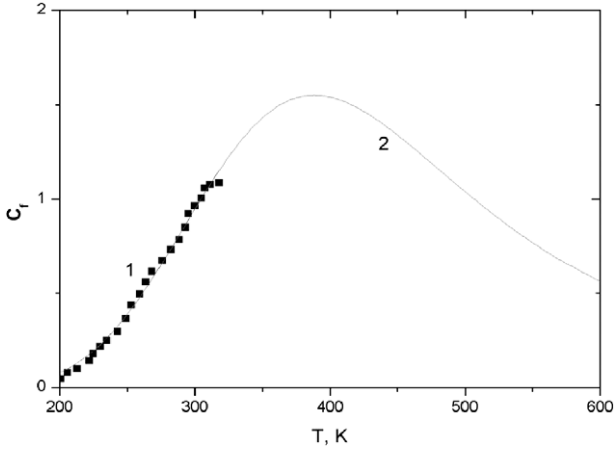


Figure 5. Temperature dependence of specific heat C_f : (1) experimental data calculated by the formula $(C_{\text{tot}} - C_{\text{lat}})/R$ for the $\text{Gd}_{0.25}\text{Mn}_{0.75}\text{S}$ sample and (2) calculated data obtained by formula (1) at the degeneracy multiplicity $g_i/g_0 = 98$ for the two-level model.

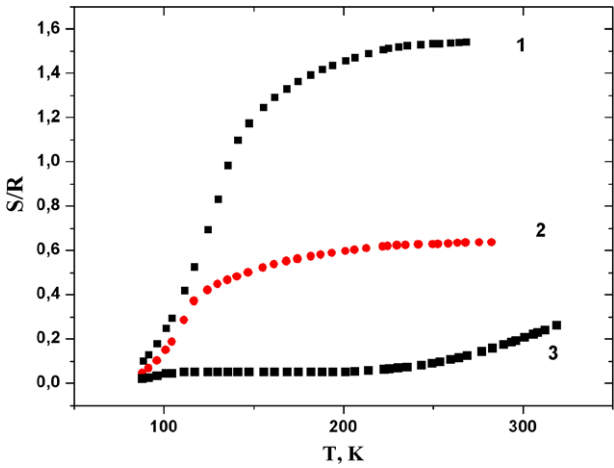


Figure 6. Temperature dependence of magnetic entropy for the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ system with $X = 0.04$ (1), 0.1 (2) and 0.25 (3).

The growth of the specific heat above the Debye temperature can also be caused by enhancement of anharmonicity of the ion oscillations. To verify this fact, we measured the coefficient of thermal expansion of the solid solutions. The results of investigations of coefficient of thermal expansion α and relative elongation $\Delta L/L$ for the two $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ ($X = 0.04$ and 0.2) samples are presented in figure 7. The anomalies of $\alpha(T)$ at $T_N = 142$ and 114 K are observed. As the concentration of the substitute in the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ system is increased, the coefficient of thermal expansion in the magnetically ordered region decreases; in the paramagnetic phase, the values of $\alpha(T)$ are nearly invariable, which implies that the coefficient of the anharmonic interaction does not depend on concentration. At the transition to the magnetically ordered region, the lattice is compressed due to the magnetoelastic interaction, which can be presented in the form $\beta u \langle S(0)S(h) \rangle$, where β is the parameter of the magnetoelastic interaction and u is the relative displacement of ions. Minimization of the intrinsic

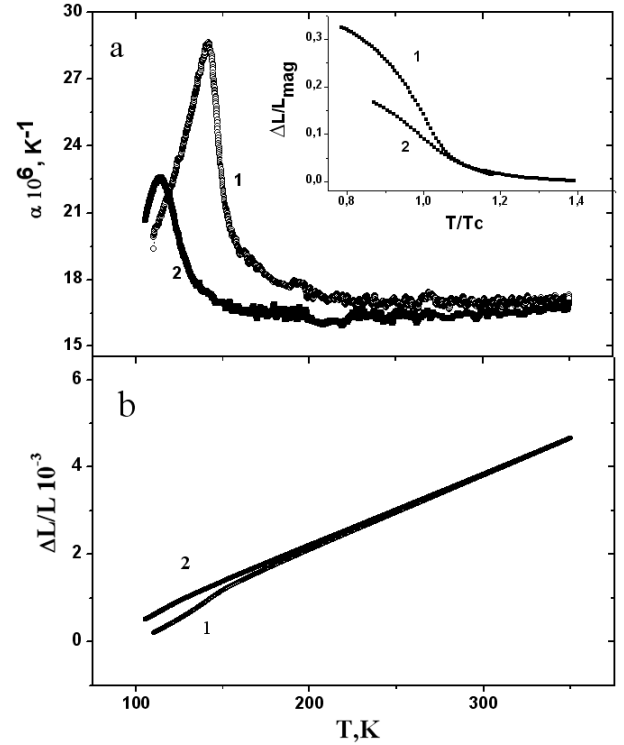


Figure 7. Temperature dependence of (a) coefficient of thermal expansion $\alpha(T)$ and (b) relative elongation $\Delta L/L$ for the $\text{Gd}_X\text{Mn}_{1-X}\text{S}$ samples with (1) $X = 0.04$ and (2) 0.2. The inset shows relative elongation of the sample below the Néel temperature.

energy dE/du in the molecular field approximation.

$$E = -Jz \langle S(0)S(h) \rangle - \beta u \langle S(0)S(h) \rangle + 1/2ku^2, \quad (2)$$

where J is the exchange interaction, k is the elastic constant, and z is the number of interacting ion spins, yields the displacement value $u = \beta \langle S(0)S(h) \rangle / k$. Compressibility of the lattice in the magnetically ordered region can be caused by two factors: variation in the elastic parameters β/k and the spin correlation function $\langle S(0)S(h) \rangle$. The variation in the parameter of the magnetoelastic interaction can be estimated knowing the behavior of the effective exchange and the lattice parameter in the solid solution with the change in the concentration of gadolinium ions. Since the parameter $\beta = dJ/du$ characterizes the variation in the exchange value with the lattice parameter, the variation in the exchange is proportional to the Néel temperature: $dJ/dX \sim (2/3S(S+1)z)^{-1} dT_N/dX = 0.02$. The lattice parameter grows with the concentration: $da(X)/dX = 0.063$. As a result, the parameter of the magnetoelastic interaction decreases by 35%. At the same time, the elasticity modulus for gadolinium sulfide exceeds that for manganese monosulfide; i.e. $k_{\text{GdS}}/k_{\text{MnS}} = 1.17$. The decrease in the linear size of the sample figure 7 in the low-temperature region related to the variation in the elastic parameters is $\Delta L(x=0.2)/\Delta L(x=0.04) = \beta/k = 0.65$, which exceeds the experimental value $\Delta L(x=0.2)/\Delta L(x=0.04)_{\text{exp}} = 0.58$. The reduction of the spin correlations $\langle S(0)S(h) \rangle(x)/\langle S(0)S(h) \rangle(x=0) = 0.88$ upon substitution of gadolinium for manganese yields good

agreement with the experimental data. In other words, the main contribution to the drop of the magnetoelastic energy is made by the variation in the magnetoelastic constant. The extrapolated change of the relative size of the sample can be presented in the form $\Delta L(x)/\Delta L(x=0) = (1 - 2.2x)\langle S(0)S(h) \rangle(x)/\langle S(0)S(h) \rangle(x=0)$.

The Néel temperature is determined by measuring the susceptibility, specific heat, and coefficient of thermal expansion of the $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ samples. The boundary of the antiferromagnetic–paramagnetic transition is approximated well by the linear dependence $T_N(x)/T_N(x=0) = 1-1.3x$. In the region of the critical concentration of the break of the long-range magnetic order, the Néel temperature sharply drops. Using the phase diagram of the disordered binary alloy A_xB_{1-x} for an antiferromagnet with fcc lattice having the second type of ordering [19], one can estimate the value of the exchange interactions between the nearest neighbors $J_{\text{MnCd}}/J_{\text{MnMn}} \sim 4$ and the next-nearest neighbors $K_{\text{MnCd}}/J_{\text{MnMn}} \sim 1$.

3. Conclusions

Structural, magnetic, and thermophysical studies of the $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ system allowed us to establish the region of existence of the long-range antiferromagnetic order $0 \leq X \leq 0.2$. Enhancement of the magnetic specific heat in the solid solution at small doping concentrations and growth of the specific heat above the Debye temperature at high concentrations have been found. The anomaly of the specific heat caused by the transition of electrons between the 4f level and the d electron in the conduction band has been found. It has been established that the coefficient of thermal expansion of the samples decreases with increasing concentration of gadolinium in the antiferromagnetic region and remains invariable in the paramagnetic region. The relative variation in the sample size has been attributed to weakening of the spin correlations in the solid solution and a decrease in the magnetoelastic coupling constant.

Acknowledgments

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