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Gadolinium is usually considered as a model system, where the half-filled 4*f* shell provides localized spin-only magnetic moments, which are widely believed to be ordered by means of RKKY type exchange interaction. However, among the heavy rare earth metals, Gd is the only metal which is ferromagnetic down to the liquid helium temperature, and this is not described by the RKKY theory. It is also surprising, that in HCP Gd the easy axis of low temperature magnetization is directed at an angle about 20° from the *c*-axis, exhibiting the preferred orientation of the magnetization. With increasing pressure, the crystal structure of Gd changes in the order HCP-(Sm-type)-DHCP-FCC. Therefore, further detailed experimental and theoretical studies of high pressure effects on magnetic properties and phase transitions in gadolinium (and other rare earths) are required to shed more light on mechanisms of magnetic ordering and electronic structure transformations, the nature and extent of which are not clear.

In this report we are mostly focused on refinement of the experimental dependence of the magnetic transition temperature T_C on pressure under pure hydrostatic (gaseous) conditions. Unlike previously used methods, we employed a new procedure, based on the measurement of pressure effect on the dc magnetic susceptibility of Gd in the paramagnetic state at temperatures above T_C. The *dc* paramagnetic susceptibility of Gd was measured in the temperature range of 295−365 K and under hydrostatic pressure up to 0.16 GPa, yielding values of the paramagnetic Curie temperature Θ and its pressure derivative. Also we explored a possibility to describe pressure effects on magnetism of Gd within simple mean-field approaches, which are based on *ab initio* electronic structure calculations. Based on the results of electronic structure calculations within the density functional theory, the experimental behavior of Θ under pressure was described in the framework of mean-field like approach.

Keywords: gadolinium, electronic structure, magnetic susceptibility, Curie temperature, high pressure

1. Introduction

Among the heavy rare earth metals, Gd is the only metal which undergoes a paramagnetic–ferromagnetic transition at the highest magnetic ordering temperature $T_C \approx$

≈ 293 K and remains ferromagnetic (FM) down to liquid helium temperature [1,2]. The half-filled 4*f* shell of Gd (S = 7/2, L = 0) provides a localized spin-only magnetic moment. Therefore gadolinium is often considered as a model system, where the localized 4*f* spin moments are inserted in a sea of the itinerant electrons. It is believed that 4*f* moments of Gd are ordered in a FM ground state by means of Ruderman-Kittel–Kasuya–Yosida (RKKY)-type exchange interaction [1].

A number of experiments have been performed to study the pressure effect on the Curie temperature of Gd (see, for example, [4] and references therein). With increasing pressure, the crystal structure of Gd changes in the order HCP → Sm-type → → DHCP → FCC and the first HCP → Sm-type transition occurs at about 2.5 GPa [5]. For pressures below the structural transitions, the Curie temperature of Gd was found to decrease monotonically with increasing pressure at the rate within the range of $dT_C/dP = -(10.6–17.2)$ K/GPa [4]. In all cases the value of dT_C/dP was estimated from the pressure-induced shift of peculiarities in the temperature dependences of various properties at the transition point (resistivity, magnetization, *ac* susceptibility, etc.). The methods were of different accuracy, which caused the considerable scatter of the experimental data. Another possible source of errors is a deviation from the hydrostatic conditions. The crucial role of stress homogeneity has been revealed in studies of the uniaxial pressure effects on T_C. These effects appeared to be strongly anisotropic and more pronounced with the stress applied along the *c*-axis [6,7]. This correlates with the anisotropic nature of the spontaneous magnetostriction resulted from the thermal expansion data for Gd in FM state [2].

In this report we are focused on refinement of the experimental dependence of T_C on pressure using pure hydrostatic (gaseous) conditions. Unlike previously used methods, we employed a new procedure, based on the measurement of pressure effect on the *dc* magnetic susceptibility of Gd in the paramagnetic (PM) state at the temperatures above T_C. Also we attempted to describe the pressure effects on magnetism of Gd within a simple mean-field approach, which is based on *ab initio* electronic structure calculations.

2. Experimental

In this study we used the polycrystalline Gd sample of 99.9% purity. The temperature dependence of its magnetic susceptibility χ was measured by a Faraday method between 295 and 365 K in magnetic field $H = 0.1$ T, and a Curie–Weiss behavior

$$\chi(T) = \frac{C}{T - \Theta} \tag{1}$$

has been revealed at $T \geq 320$ K (solid line in Fig. 1). The corresponding values of the paramagnetic Curie temperature and effective magnetic moment were evaluated to be $\Theta \simeq 295$ K and $\mu_{eff} = 8.18 \pm 0.1\mu_B$ in agreement with literature data.

The $\chi(P)$ measurements were performed under helium gas pressure P up to 0.16 GPa at fixed temperatures, $T = 325.5$, 333.5 and 352.1 K, by a levitation-type magnetometer [8,9], using the spherical sample of about 1 mm in diameter. The

relative errors of magnetic measurements under pressure did not exceed 0.1% for the employed magnetic fields close to $H \sim 0.1$ T. The field was produced by a non-superconducting solenoid with geometrical parameters similar to those of the superconducting coil used originally in Refs. [8,9]. The experimental $\chi(P)$ dependencies are presented in Fig. 2 and found to be linear, yielding the pressure derivatives $d\ln\chi/dP$, which are listed in Table 1.

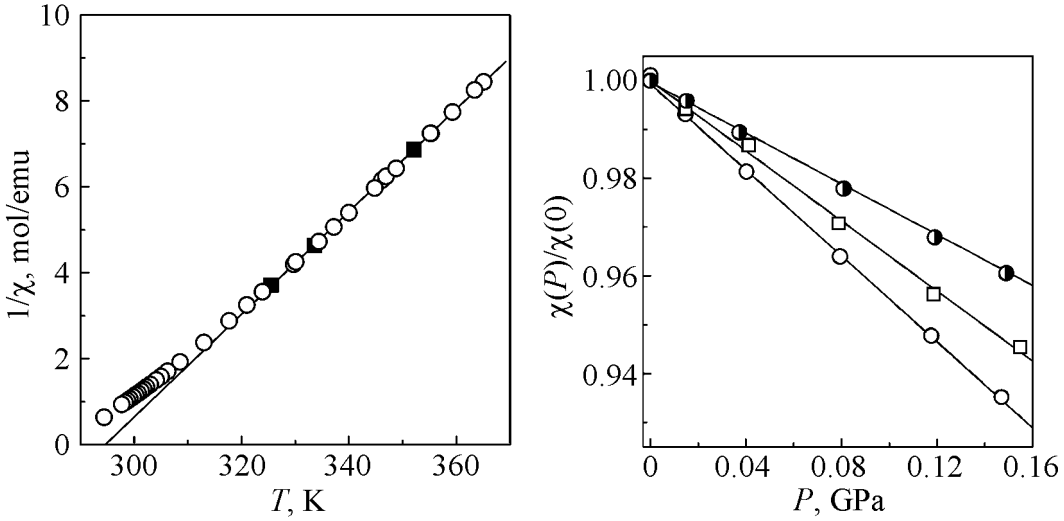

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility for Gd, measured by the Faraday method (○). The data obtained with the levitation method at ambient pressure are represented by black squares. The Curie–Weiss fit is indicated by the solid line

Fig. 2. Pressure dependencies of the magnetic susceptibility of Gd normalized to its value at $P = 0$ at different temperatures, K: ○ – 325.5, □ – 333.5, ◑ – 352.1

Table 1

Magnetic susceptibility χ and its pressure derivative $d\ln\chi/dP$ for Gd at different temperatures

T, K	χ, 10^{-3} emu/mole	$d\ln\chi/dP$, 10^{-2} GPa^{-1}
325.5	269.1	−47.5 ± 1.5
333.5	215.7	−38.5 ± 1.5
352.1	145.5	−28.0 ± 1.5

Based on the Curie–Weiss behavior of $\chi(T)$, the $d\ln\chi/dP$ is assumed to be predominantly governed by the pressure dependence of the paramagnetic Curie temperature Θ:

$$\frac{d\ln\chi}{dP} = \frac{d\ln C}{dP} + \frac{1}{(T-\Theta)}\frac{d\Theta}{dP} \approx \frac{\chi}{C}\frac{d\Theta}{dP} \qquad (2)$$

where the Curie constant C is close to that of free Gd^{3+} ion value and expected to be pressure independent. According to Eq. (2), the value of pressure derivative of

Θ was evaluated from a slope of the linear approximation of the dlnχ/dP vs χ dependence in Fig. 3. The derivative was found to be dΘ/dP = −14.9 ± 0.3 K/GPa, which is in excellent agreement with the most reliable data for polycrystalline sample of Gd from Ref. [10], dT_C/dP = −14.8 ± 0.2 K/GPa. Using the experimental bulk modulus value B = 39 ± 1 GPa for Gd [11], one obtains the corresponding volume derivative, dlnΘ/dln$V$ = 1.97 ± 0.08.

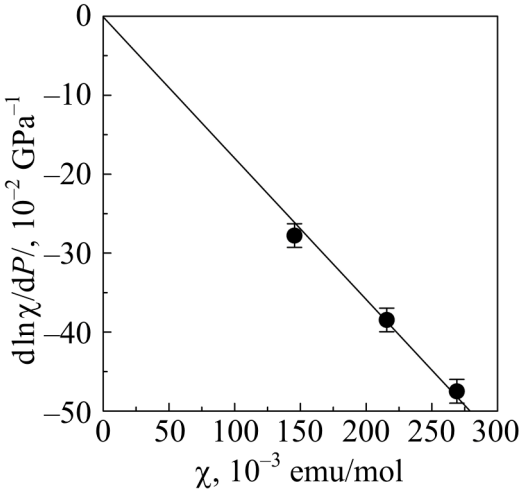

Fig. 3. Dependence of the pressure derivative dlnχ/dP for Gd on the corresponding magnetic susceptibility at different temperatures

3. Computational details and results

In order to analyze the experimental data on the pressure effects, the volume-dependent electronic structures and magnetic properties of Gd were calculated *ab initio*. For these calculations we employed a full-potential relativistic linear muffin-tin orbital method (FP-LMTO, code RSPt [12–14]), and also the LMTO method in atomic sphere approximation (LMTO-ASA code, see Refs. [15,16]. The local spin density approximation (LSDA) of Ref. [17] was employed. In the FP-LMTO calculations the basis set for Gd included 6*s*, 6*p*, 5*d*, and 5*p* orbitals, with the 5*p* orbitals treated as pseudo-valence states. In both FP-LMTO and LMTO-ASA approaches, the 4*f* states were treated fully relativistically as spin polarized open core states, which contribute to the total spin density, but do not hybridize with conduction electrons. The use of this approach was justified by successful description of the FM ground state and the Fermi surface of HCP Gd [18,19].

In the framework of a simple mean-field theory (see Refs. [15,16,20] and references therein), the Curie temperature of the rare-earth metal can be described by a functional relation of the form:

$$k_{\mathrm{B}}T_{\mathrm{C}} \propto \chi_d^{\mathrm{eff}} J_{4f5d}^2 \left(g_J - 1\right)^2 J\left(J+1\right). \qquad (3)$$

Here χ_d^{eff} is the effective *d*-band spin susceptibility, g_J is the Lande factor, J_{4f5d} is the local 4*f*-5*d* exchange integral:

$$J_{4f5d} = \int g\left(p(r)\right)\varphi_{4f}(r)^2\,\varphi_{5d}(r)^2\,\mathrm{d}r\,, \qquad (4)$$

where $\varphi_{4f}(r)$ and $\varphi_{5d}(r)$ are the partial wave functions, and $g(\rho(r))$ is a functional of the electronic density [17]. In this work we used Eq. (3) in order to determine whether the simple mean-field theory is relevant to describe experimental data on the pressure effects on T_C in Gd. In order to evaluate the effective *d*-band susceptibility entering Eq. (3), we carried on *ab initio* calculations of the exchange enhanced spin susceptibility for Gd in the PM state. Within a modified FP-LMTO method [13], the effect of external magnetic field H was taken into account by means of the Zeeman operator $H\left(2\hat{s}+\hat{1}\right)$ included in the FP-LMTO Hamiltonian.

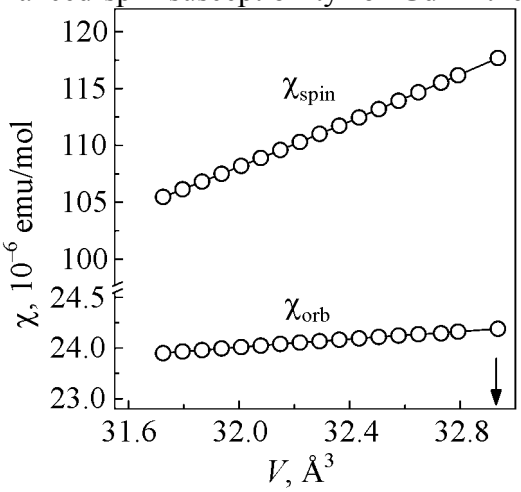

Fig. 4. Calculated dependencies of the main contributions to the magnetic susceptibility of Gd on the atomic volume. Arrow marks the experimental value of volume at ambient pressure

The self-consistent calculations of the field-induced spin and orbital magnetic moments were carried out in an external magnetic field of 10 T. That allowed determining of the corresponding contributions χ_{spin} and χ_{orb} to the paramagnetic susceptibility. These calculations were performed for a number of lattice parameters *a* close to the experimental one. This provided the behavior of χ_{spin} and χ_{orb} in Gd for varying atomic volumes at the fixed experimental HCP lattice parameters ratio, $c/a = 1.59$.

The results of calculations are shown in Fig. 4. It should be noted that the calculated total paramagnetic susceptibility of Gd, $\chi = \chi_{spin} + \chi_{orb} \approx 142 \cdot 10^{-6}$ emu/mole, corresponding to the experimental lattice parameters at ambient pressure, is consistent with the experimental room temperature values of χ for related series of metallic Y, La and Lu which amount (in the same units) to 190, 100 and 180, respectively [21].

Based on the calculated dependence $\chi_{spin}(V)$ for PM Gd, the pressure derivative of χ_{spin} was evaluated and compiled in Table 2. In order to convert the calculated volume derivative into the pressure one, we used the experimental bulk modulus value for Gd (B = 39 GPa [11]).

For calculation of the pressure dependence of the local J_{4f5d} exchange integral (4) of Gd, we employed the atomic sphere approximation (LMTO-ASA) within the open core approach for 4*f* states of Gd, in line with Refs. [15,16]. The calculated J_{4f5d} is about $7 \cdot 10^{-3}$ Ry, and its pressure derivative is also listed in Table 2.

Table 2

Pressure derivatives of magnetic parameters for Gd

Derivative, 10^{-2} GPa^{-1}

Calculated
$d\ln\chi_{spin}/dP = -7.3$ $d\ln J_{4f5d}/dP = 1.3$ $d\ln T_C/dP = -4.7$
Experimental
$d\ln\Theta/dP = -5.05 \pm 0.10$ (present work) $d\ln T_C/dP = -4.78 \pm 0.07$ (single crystal) [10] $d\ln T_C/dP = -5.05 \pm 0.07$ (polycrystal) [10]

Note. Calculations are done for the PM state.

4. Discussion

According to Eq. (3), the pressure dependence of the Curie temperature of Gd can be represented as:

$$\frac{d\ln T_C}{dP} = 2\frac{d\ln J_{4f5d}}{dP} + \frac{d\ln\chi_{spin}}{dP}. \tag{5}$$

By substituting in Eq. (3) the calculated pressure derivatives of J_{4f5d} and χ_{spin} from Table 2, we obtained theoretical estimations of $d\ln T_C/dP$, which are also given in Table 2. The estimated value $d\ln T_C/dP = -4.7\cdot10^{-2}$ GPa^{-1} is in agreement with the present experimental value $d\ln\Theta/dP = -(5.05 \pm 0.10)\cdot10^{-2}$ GPa^{-1}, as well as with the literature data (see Table 2). This supports the validity of the functional relation (3). The agreement also points to a predominant participation of the itinerant 5*d*-electrons in the indirect exchange interaction for Gd. Therefore, the magnetic ordering and peculiar magnetic properties of Gd can be hardly explained within the simple RKKY coupling scheme.

The obtained pressure derivative for the paramagnetic Curie temperature of Gd can be used for evaluation of a spontaneous volume change due to magnetic ordering, $\Delta V/V \equiv \omega_m(T)$, which is related to the squared molar magnetic moment $M^2(T)$ (see Ref. [22] and references therein):

$$\omega_m(T) = \frac{c}{B}M^2(T). \tag{6}$$

Here B is the bulk modulus, and c is the magnetoelastic coupling constant. The latter can be determined for PM Gd within the phenomenological relation [22]:

$$\frac{c}{B} = -\frac{1}{2V\chi}\frac{d\ln\chi}{dP}, \tag{7}$$

where χ and V are the molar susceptibility and volume, respectively. From Eq. (2) it follows:

$$\frac{1}{\chi}\frac{d\ln\chi}{dP} = \frac{1}{C}\frac{d\Theta}{dP}. \tag{8}$$

By using the experimental values of $d\Theta/dP = -14.9$ K/GPa, the Curie constant $C = 8.36$ K·emu/mole and $V = 19.9$ cm^3, one estimates c/B value to be equal

$$\frac{c}{B} = -\frac{1}{2VC}\frac{\mathrm{d}\Theta}{\mathrm{d}P} = \left(4.4 \pm 0.3\right)\cdot 10^{-12}\left(\text{emu/mole}\right)^{-2}. \qquad (9)$$

The substitution of the evaluated c/B value and the experimental molar magnetic moment of Gd at $T \to 0$, $M(0) \approx 4.2\cdot 10^4$ emu/mole (7.63μ_B per Gd atom [3]), in Eq. (6) yields the volume change under magnetic transition to be $\omega_m(0) \sim 0.8\%$. This estimate reasonably agrees with the experimental value $\omega_m(0) \sim 0.5\%$, which resulted from the thermal expansion measurements for Gd [2]. It can be noted, that our *ab initio* calculations of the difference between equilibrium atomic volumes for FM and PM states of Gd ($(V_{FM} - V_{PM})/V_{FM} \approx 0.7\%$) also provided a qualitative agreement with the experimental value of magnetovolume effect.

5. Summary

Measurements of the pressure effect on magnetic susceptibility of Gd in its PM state provided a new experimental method to study the pressure dependence of the Curie temperature. The *ab initio* calculated spin susceptibility and exchange integral were employed to analyze pressure dependence of magnetic properties of Gd within the mean-field approach (3). By this way the reasonable description of the observed uniform pressure effect on T_C was obtained, indicating the decisive role of 5*d*-electrons in the indirect exchange interaction.

However, the mean-field approach (3) leads to overestimated values of T_C. This disagreement is probably related to the assumption that only non-magnetic spin-degenerate states are present above T_C. Also spin fluctuations are obviously of a substantial significance in determining the magnetic properties of heavy rare-earth systems with ferromagnetic ordering.

The magnetovolume effect studies can be applied in future investigations as a useful tool for identification in magnetic systems of the hierarchies of exchange interactions and effects of the magnetic moments disorder. The recent theoretical approaches, using a Monte Carlo simulation [19], seem promising, but require further exploration to shed light on the nature of magnetism and its pressure dependence in the rare-earth systems.

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