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PRESSURE EFFECT ON MAGNETIC SUSCEPTIBILITY AND EXCHANGE INTERACTIONS IN GdM_x (x = 1, 2, 3, 5) SYSTEMS

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Effect of pressure on electronic structure and magnetic properties of GdM_x (x = 1, 2, 3, 5) systems is studied experimentally and theoretically. By employing the ab initio electronic structure calculations, the magnetic susceptibilities, saturation moments, exchange parameters, magnetic ordering temperature and their pressure derivatives are evaluated and appeared to be consistent with available experimental data. The obtained results are expected to promote further advance in the theory of magnetic ordering in rare-earth systems.

Introduction

The rare-earth intermetallics and alloys RM_x (M is *sp*- or *d*-metal) are of considerable interest due to a large variety of magnetic properties. It is commonly believed, that peculiar magnetic properties of RM_x are governed by different types of interactions [1,2], involving the highly correlated and strongly localized 4*f*-states of rare earth, the *d*-states of transition metal atoms, which are comparatively weakly correlated and more delocalized, and also the valence states of R atoms, which are expected to be the mediators of indirect exchange coupling. However, many principal details of microscopic magnetic interactions in these materials are still unclear. Some more or less successful approaches to the evaluation of magnetic ordering temperatures T_C in rare earths [3–7] have been put forward recently. These theories were applied only for selected systems, and they have not been properly tested and validated because of the lack of adequate description of the electronic structure.

The experimental study of the magnetic susceptibility in the paramagnetic state provides an appropriate tool for evaluation of different contributions to the magnetic coupling in RM_x compounds. Also, the pressure derivatives of the paramagnetic Curie temperature, Θ, taken from these measurements, are of particular interest owing to their assumed sensitivity to the nature of the exchange interaction.

The studies of pressure effects on the magnetic susceptibility can, therefore, stimulate the development of new theoretical models for band structures, exchange interactions and crystal-field (CEF) parameters in rare-earth compounds. In this connection, a study of pressure effects on the electronic structure and magnetic properties can shed more light on the nature of exchange interactions in RM_x compounds. Also, magnetization studies under pressure are useful tools to obtain information on hybridization effects between electronic states. In this work, the experimental studies of pressure effect on the magnetic susceptibility, χ, and the paramagnetic Curie temperatures, Θ, were carried out for a number of GdM_x (x = = 1, 2, 3, 5) compounds and pseudo-binary alloys. In order to elucidate the origin of the interactions and electronic states responsible for magnetic ordering, the *ab initio* calculations of the volume-dependent electronic structures were also performed for GdM_x systems. The calculated magnetic moments, susceptibilities, band and exchange parameters, and their volume (pressure) derivatives were employed to analyze available experimental data.

Experimental and theoretical details

The cubic single-crystalline samples of GdM (GdMg, GdZn, and GdCd, CsCl-type structure) and GdM_2 ($GdMg_2$, $GdAl_2$, $GdCo_2$, and $GdNi_2$, C15-type structure) were made from the high-purity materials (the rare earths were at least 3N (99.9)), as described in detail in Refs. [8] and [9], respectively, where some preliminary measurements were carried out. The polycrystalline $GdIn_{3-x}Sn_x$ samples (the cubic $AuCu_3$-type structure, $0 < x < 3$) were prepared in the Institute of Low Temperatures and Structure Research (Wroclaw, Poland) by arc-melting of the constituent elements under argon atmosphere, followed by annealing at 800°C for 7 days. The single crystals of the hexagonal $GdNi_5$ compound ($CaCu_5$-type structure) were analogous to the samples previously investigated in Ref. [10]. The magnetic susceptibilities of the GdM_x systems were studied under helium gas pressure, P, up to 2 kbar in the temperature range 78(or T_C)–330 K. The measurements were carried out by the Faraday method, using a pendulum magnetometer placed into the pressure cell [11]. The relative measurement errors did not exceed 0.05%. The $\chi(T)$ of investigated Gd-based compounds obeys the Curie-Weiss law

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

with the effective magnetic moment close to its value for the free Gd^{3+} ion, and the corresponding paramagnetic Curie temperatures Θ are listed in Table 1. Within the experimental accuracy, the linear change of magnetic susceptibility with pressure was observed for all studied GdM_x systems. According to Eq. (1), the corresponding values of the pressure derivative $d\ln\chi/dP$ are governed by the pressure dependence of Θ, assuming the Curie constant C to be pressure independent:

$$\frac{d\ln\chi}{dP} = \frac{\Theta}{T - \Theta}\frac{d\ln\Theta}{dP}. \tag{2}$$

Table 1

The magnetic parameters and their pressure/volume derivatives in GdM_x compounds. Calculated total M_t and experimental saturation M_S magnetic moments (in μ_B/f.u.) and calculated local J_{fd} and J_{dd} exchange integrals (in mRy) at Gd site, together with their respective volume derivatives and the theoretical bulk moduli B (in kbar). The experimental paramagnetic Curie temperatures Θ, the calculated T_C, and their pressure derivatives, dΘ/dP and dT_C/dP in K/kbar. All data on Θ for GdMg, GdZn, GdCd, $GdAl_2$, $GdNi_2$, $GdIn_3$ and $GdNi_5$ are obtained in the present work, whereas the Curie temperatures for $GdMg_2$ and $GdCo_2$ are taken from Refs. [1,2,16]

Parameter	GdMg	GdZn	GdCd	$GdMg_2$	$GdAl_2$	$GdCo_2$	$GdNi_2$	$GdIn_3$	$GdNi_5$
M_S	5.6–7.6	7.5	7.2	7.3	7.1	4.3–5.3	7.0–7.2	–	6.0–6.9
M_t	7.6	7.7	7.8	8.1	7.6	5.1	7.1	–	6.3
$d\ln M_t/d\ln V$	0.12	0.04	0.03	–0.18	–0.05	–0.14	0.03	–	–0.6
J_{fd}	7.3	7.1	7.3	6.45	6.1	6.1	6.35	7.7	7.9
$d\ln J_{fd}/d\ln V$	–0.3	–0.5	–0.45	–0.5	–1.3	–1.3	–1.3	–0.7	–0.6
J_{dd}	39.0	36.4	36.9	39.1	38.8	39.3	40.0	42.1	41.50
$d\ln J_{dd}/d\ln V$	–0.29	–0.25	–0.17	–0.27	–0.30	–0.26	–0.31	–0.33	–0.09
B	490	570	660	460	870	1110	1190	570	1700
Θ	116	270	265	81	167	400	75	–96	33
dΘ/dP	–1.25	0.05	1.1	–	0.73	–1.1	–0.13	–0.38	0.013
T_C	180	400	385	360	180	120	40	–	170
dT_C/dP	–1.0	0.3	0.6	0.1	0.6	–0.6	–0.3	–	0.1

The corresponding estimates for the dΘ/dP derivatives are given in Table 1. It should be noted that for Gd-based systems the values of Θ are close to the experimental magnetic ordering temperatures, T_C, and in the following consideration no distinction is made between them.

Ab initio band structure calculations have been carried out for the paramagnetic (PM) and ferromagnetic (FM) phases of GdM_x compounds and alloys. The calculations were performed with the linear muffin-tin orbital (LMTO) method [12–15]. The 4*f*-states of rare-earths were treated as spin polarized open core states with the Hund's rule restriction for the 4*f* spin, according to [12]. This approach is particularly suitable for Gd-based compounds, where 4*f* spin-up and spin-down occupation numbers are $n_f^+ = 7$ and $n_f^- = 0$. Also, the 4*f* electrons of Gd form the *S* state, which is not affected by the CEF interactions. The exchange and correlation potentials were calculated using the local spin density approximation (LSDA). The atomic sphere approximation (LMTO–ASA) [12,13] was employed together with the *ab initio* relativistic full-potential (FP–LMTO) method [14,15]. The spin polarized and paramagnetic band structure calculations were performed self-consistently for a number of lattice parameters close to experimental ones. Also, the band structures of the pseudo-binary alloys $GdIn_{3-x}Sn_x$ were calculated within the virtual-crystal approximation. Namely, the true atom in the alloy was replaced by an «average» atom which is interpolated in charge between the corresponding pure atoms, and the band-filling effects are accounted properly. Other details of the LMTO methods employed in the present work are given elsewhere [12–15].

Results and discussion

The main results of the calculations together with available experimental data are presented in Table 1. As one can see, the calculated magnetic moments for the ferromagnetic GdM and GdM_2 compounds are in a fair agreement with the available experimental saturation moments. It should be taken into account that for some GdM_x systems the saturation of magnetic moments has not been achieved in available fields. Also, in some cases, like e.g. GdMg [17], the canted ferromagnetic structure is expected at low temperatures. Regarding the calculated local exchange integrals, the values of $J_{\rm fd}$ and $J_{\rm dd}$ at Gd site do not vary substantially over the GdM, GdM_2, GdM_3, and GdM_5 series. At the same time, the volume derivatives of exchange integrals appeared to be rather large in some systems, in comparison to the typical values of $\mathrm{d}\ln J/\mathrm{d}\ln V \approx -0.1$ for transition metals and compounds [15]. In particular, some calculated values of $\mathrm{d}\ln J_{\rm fd}/\mathrm{d}\ln V$ (see Table 1) appeared to be close to the volume derivative of the averaged exchange interaction parameter, $\mathrm{d}\ln J/\mathrm{d}\ln V = -1.5$, evaluated for the paramagnetic compound $CeCo_2$ from the susceptibility measurements under pressure [15].

By using the results of the band structure calculations, the magnetic ordering temperatures $T_{\rm C}$ for GdM, GdM_2 and $GdNi_5$ can be estimated within the simplest possible mean field theory [3,7] by:

$$k_{\rm B}T_{\rm C} = \frac{1}{2}\chi_d J_{\rm fd}^2 (g_J - 1)^2 J(J+1) \qquad (3)$$

where χ_d is the effective susceptibility, which is proportional to the partial density of d-band states at the Fermi level $E_{\rm F}$, $J_{\rm fd}$ – is the exchange integral, g_J and $(g_J - 1)^2 J(J + 1)$ are the Lande and de Gennes factors, respectively. However, this approach, which is basically related to the assumption by Campbell [18] that 5d-electrons at R play a dominant role in magnetic ordering, provided too high values of $T_{\rm C}$, and the only good agreement obtained for $GdCo_2$ [7] should be regarded as fortuitous.

The alternative molecular field approach for $T_{\rm C}$ calculations has been proposed for ferrimagnetic rare-earth intermetallics [5,12,19]:

$$T_{\rm C} = 4\left(\frac{g_J - 1}{g_J}\right)^2 \left(n_{RR} + n_{RM}^2 \chi'_M\right) C_R \,. \qquad (4)$$

In this approach the molecular-field coefficients n_{RR} and n_{RM} [2] can be related to the exchange integrals and susceptibilities of conduction electrons at R and M sites, which in turn can be evaluated *ab initio* in the framework of the LMTO calculations described above (see Ref. [19] for details). The estimated by this way values of $T_{\rm C}$ and their derivatives are given in Table 1. As one can see, this approach yields a qualitative agreement with the experimental Θ and the corresponding pressure derivatives, though a noticeable difference with the experiment can be also noted in Table 1 for some GdM_x compounds.

Actually, the calculated volume derivatives of T_C are converted to the pressure ones for comparison with the experimental data in Table 1, and the corresponding bulk moduli, B, were calculated *ab initio* (see Ref. [14] for details) and also listed in Table 1. One should take into account, however, the overbonding tendency of LSDA calculations, which often provides overestimated bulk moduli (up to 10%). This could contribute to discrepancies between the theoretical and experimental pressure derivatives of magnetic ordering temperatures in Table 1.

The $GdIn_{3-x}Sn_x$ alloys ($0 < x < 3$) order antiferromagnetically with the Neel temperatures T_N below 50 K, which show a complex W-shaped variation with composition x. Their magnetic susceptibility is studied under hydrostatic pressure at fixed temperatures (78 and 300 K) above T_N. This study revealed well defined peculiarities in the concentration dependences $T_N(x)$, the paramagnetic Curie temperature $\Theta(x)$, as well as the pressure effect $d\ln\chi(x)/dP$ (see Fig. 1). The values of $d\ln\chi(x)/dP$ and $d\ln\Theta(x)/dP$ at 77.3 K, shown in Fig. 1, demonstrate a strong variation with x. The calculated volume derivative of the concentration dependence of the partial density of s-states (DOS) at the Fermi level, $d\ln N(E_F)/d\ln V$, is shown in Fig. 1. The experimental estimates of the volume derivative $d\ln\Theta(x)/d\ln V$ and results of *ab initio* calculations of the volume-dependent electronic structure of the alloys were used to analyze the nature of exchange interactions in $GdIn_{3-x}Sn_x$. The calculated bulk moduli for $GdIn_3$ and $GdSn_3$ appeared to be 570 and 610 kbar, and their average value $B = 590$ kbar was accepted for $GdIn_{3-x}Sn_x$ alloys.

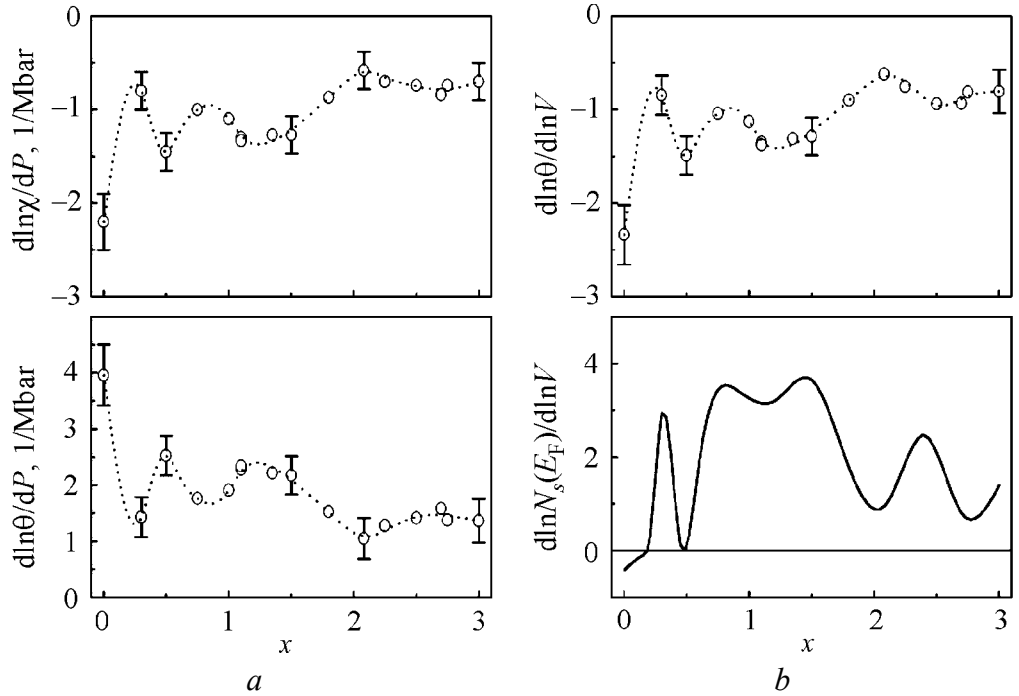

Fig. 1. (a) Experimental values of the pressure effects on magnetic susceptibility at 77.3 K and the Curie temperature Θ in $GdIn_{3-x}Sn_x$ alloys. (b) Volume derivatives for Θ and the calculated partial DOS at the Fermi level for s-states at Gd ($N(E_F)$, solid line) versus composition. Dashed lines are guides for the eye

The interaction between localized *f*-moments in rare-earth compounds can be described within the RKKY model of indirect exchange via the conduction electrons. In its simplest form [1,18] this model gives:

$$\Theta \propto I^2 N(E_F), \tag{5}$$

where I is a strength of exchange interaction between *f*- and conduction electron spins, and pressure independent factors are omitted. Thus one obtains:

$$\frac{d\ln\Theta}{d\ln V} = 2\frac{d\ln I}{d\ln V} + \frac{d\ln N(E_F)}{d\ln V}. \tag{6}$$

In agreement with Eq. (6), a clear correlation between the concentration dependences of $d\ln\Theta(x)/d\ln V$ and $d\ln N(E_F)/d\ln V$ derivatives is seen in Fig. 1(b). This indicates the validity of the RKKY-type model of indirect interaction in the $GdIn_{3-x}Sn_x$ system, presumably due to a substantial contribution of *s*- and *p*-states to $N(E_F)$. By estimating a vertical shift which drops off $d\ln N(E_F)/d\ln V$ into approximate coincidence with $d\ln\Theta(x)/d\ln V$ dependence, we obtained average volume derivative of I, $d\ln I/d\ln V = -1.2$, which is close to the corresponding value evaluated in Ref. [15] for the effective exchange coupling between the *d*-band electrons.

The hexagonal RNi_5 compounds, having relatively simple structure and uniaxial anisotropy, are especially suited for studies of both the exchange interactions and the CEF effects [2]. Here we report experimental and theoretical results on the pressure effects on the magnetic properties of $GdNi_5$, which order ferromagnetically at 33 K. The observed pressure derivative of the paramagnetic Curie temperature appeared to be small (Table 1). According to our calculations, the itinerant magnetism of $GdNi_5$ is dominated by spin-polarized Gd 5*d*- and Ni 3*d*-states. There is no charge transfer of the Gd outer electrons to the 3*d*-band, and the filling of this band is not complete. The Fermi level is situated within the predominantly Ni 3*d*-band at the local peak of the density of states $N(E)$. As is seen in Fig. 2, at

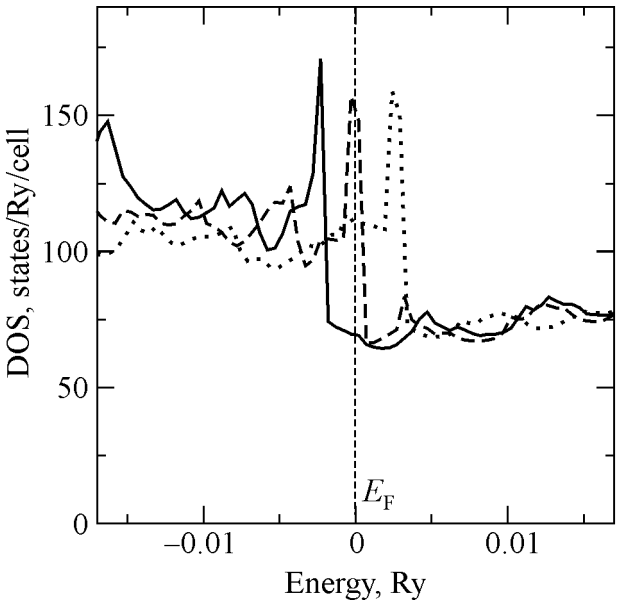

Fig. 2. Fine structure of the density of states (DOS) of ferromagnetic $GdNi_5$ in the vicinity of the Fermi level E_F (marked with a vertical dashed line). The solid line corresponds to the ambient atomic volume, whereas the dashed and dotted lines represent DOS for the lattice parameters reduced by 1 and 2%, respectively

high pressures (i.e. at reduced atomic volumes) the Fermi level is expected to pass through the DOS peak, and this can affect substantially the magnetic state of $GdNi_5$. The volume dependence of the Curie temperature, calculated for $GdNi_5$ within the approach (6), appeared to be weak in agreement with the experiment (see Table 1).

Conclusions

It is demonstrated that the band theory within LSDA provides an adequate description of the electronic structure and peculiar magnetic properties of GdM_x. Our experimental magnetovolume data together with the results of first-principles band structure calculations point to a predominant participation of *d*-electrons in the indirect exchange interaction for GdM, GdM_2, and $GdNi_5$ compounds, where ferromagnetic ordering can be hardly explained within the conventional RKKY coupling scheme. The ferromagnetic instability in these compounds is apparently induced by the local 4*f*–5*d* exchange interaction. It is shown that band structure details, as well as a more general theory for the indirect exchange interactions are required for an *a priori* description of the magnetic properties of these compounds. The modified mean field approach, based on LSDA, gives a reasonable description of T_C and their behavior with pressure, indicating that the *f*–*d* exchange interaction can contribute substantially to magnetic ordering phenomena in rare-earth systems. Also, one should expect a significance of spin fluctuations in magnetic properties of *R* compounds with ferromagnetic ordering, and a suitable spin-fluctuation theory (e.g. [4]) can be applied to these systems. This might provide a reduction of T_C, and perhaps a better description of the experimental $d\Theta/dP$ derivatives in ferromagnetic GdM_x compounds. Most likely an interplay between different kinds of magnetic interactions takes place in heavy rare-earth compounds, and the magnetovolume effect can be applied in future investigations as an efficient tool for identification of exchange interactions, as well as CEF effects.

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