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PRESSURE EFFECT ON ELECTRONIC STRUCTURE
AND MAGNETIC PROPERTIES OF RM$_2$ COMPOUNDS

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Effect of pressure on electronic structure and magnetic properties of ferromagnetic GdM$_2$ (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt) compounds and the reference YCo$_2$ compound was studied experimentally and theoretically. Based on results of ab initio electronic structure calculations , the magnetic ordering temperatures and their pressure derivatives are estimated in the framework of the mean field models and appeared to be in improved agreement with experimental data. The origin of anomalous magnetovolume effect in YCo$_2$ is revealed.

Introduction

Rare earth-based metallic compounds RM$_x$ (M − is a simple or transition metal, or their combination) are of considerable technological and scientific interest due to their extraordinary magnetic properties and potential industrial applications. Among these compounds, the RM$_2$ intermetallics with the cubic Laves phase structure C15 exhibit a variety of peculiar magnetic properties. These properties are governed by different types of interactions, involving the highly correlated and strongly localized *4f*-states of rare earth, the *d*-states of transition metal atoms, which are comparatively weakly correlated and more delocalized, and lastly the valence states of R atoms, which are expected to be the mediators of indirect exchange coupling. At the same time, the mechanisms and details of microscopic magnetic interactions in these materials are still not clear.

Few approaches were put forward for calculations of the magnetic ordering temperature T_C in rare-earth systems [1–4]. However, these approaches were applied only for few selected systems, and their validity was not properly tested and confirmed. In addition, a study of pressure (or atomic volume) effects on electronic structure, magnetic properties, and the Curie temperatures can shed more light on a nature of exchange interactions and molecular field parameters

in the rare-earth compounds. In this contribution, the experimental study of the pressure effect on the magnetic susceptibility χ, and Curie temperatures Θ, was carried out for GdM_2 (M = Al, Ni, Rh, Ir, Pt) and YCo_2 compounds. The reference compound YCo_2 is a strongly enhanced Pauli paramagnet, which exhibits a distinct maximum in the temperature dependence of χ, and the itinerant metamagnetic transition at a field of ~70 T. In order to elucidate the origin of the principal interactions and electronic states responsible for magnetic ordering, the *ab initio* calculations of the volume-dependent electronic structure were performed for GdM_2 (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt) and YCo_2 compounds. The calculated magnetic moments, susceptibilities, band and exchange parameters, and their corresponding volume (pressure) derivatives were used to analyze the available experimental data.

Experimental technique and results

The magnetic susceptibility of the rare-earth compounds GdM_2 (M = Al, Ni, Rh, Ir, Pt) was studied under helium gas pressure, P, up to 2 kbar in the temperature range 78 (or T_C) − 330 K. The measurements were made by the Faraday method, using a pendulum magnetometer placed into the pressure cell [5]. The relative errors did not exceed 0.05%. The $\chi(T)$ of GdM_2 compounds investigated obeys the Curie-Weiss law 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. The estimates for the $d\Theta/dP$ derivatives are also given in Table 1. It should be noted that for GdM_2 systems the values of Θ are close to the magnetic ordering temperatures, T_C, and in the following consideration no distinction is made between them. Also, a strong pressure effect on the magnetic susceptibility was observed in YCo_2, providing the volume derivative $d\ln\chi/d\ln V \approx 17$ at $T = 78$ K.

Band structure and exchange parameters calculations

Ab initio band structure calculations have been carried out for the paramagnetic (PM) and ferromagnetic (FM) phases of GdM_2 compounds, as well as for the paramagnetic YCo_2 compound, which crystallize in the cubic Laves phase structure C15. The calculations were performed with the linear muffin-tin orbital method (LMTO) [6,7] in the atomic spheres approximation (LMTO-ASA), where the spin densities and the potential are assumed to be spherically symmetric around each atom, and matrix elements are evaluated over a sphere with the same volume as the primitive cell. The individual atomic radii of the components were chosen following the general rule, proposed in Ref. [7]. The 4*f*-states were treated as spin-polarized open core states with the Hund's rule restriction for the 4*f* spin, according to [8]. Namely, the spin occupation numbers

Table

Calculated PM $N(E_F)$ and FM $N^{\uparrow\downarrow}(E_F)$ DOS at the Fermi level (in states/Ry·cell), magnetic moments M_S (in μ_B/f.u.) and the local J_{fd} and J_{dd} exchange integrals (in mRy) at Gd site. The experimental $d\Theta/dP$ and calculated dT_C/dP pressure derivatives of the Curie temperature, in K/kbar. All experimental saturation moments M_{ST} (in μ_B/f.u.) and the Curie temperatures for GdMg$_2$, GdFe$_2$, GdCo$_2$ are taken from Refs. [14,15], whereas Θ for GdAl$_2$, GdNi$_2$, GdRh$_2$, GdIr$_2$ and GdPt$_2$ are obtained in the present work

Parameter	GdMg$_2$	GdAl$_2$	GdFe$_2$	GdCo$_2$	GdNi$_2$	GdRh$_2$	GdIr$_2$	GdPt$_2$	YCo$_2$
$N(E_F)$	101.3	68.0	207.4	45.4	49.5	36.2	39.2	46.0	79.4
$\dfrac{d\ln N(E_F)}{d\ln V}$	0.8	−4.7	0.84	1.57	5.8	3.8	−0.87	2.1	2.1
$N^{\uparrow\downarrow}(E_F)^1$	134.4	33.8	79.0	95.1	45.1	34.5	30.5	47.4	–
$\dfrac{d\ln N^{\uparrow\downarrow}(E_F)}{d\ln V}$	3.6	0.7	0.38	1.81	0.84	0.29	2,23	−0.18	–
M_S	8.1	7.6	3.5	5.1	7.1	7.05	7.1	7.2	–
$d\ln M_S/d\ln V$	−0.18	−0.04	−0.77	−0.14	0.03	−0.005	−0,012	−0.01	–
J_{fd}	6.44	6.09	6.01	6.09	6.35	6.24	6.06	6.33	–
$d\ln J_{fd}/d\ln V$	−0.5	−0.6	−1.27	−1.3	−1.3	−1.5	−1.65	−1.6	–
J_{dd}	39.06	38.81	39.45	39.32	39.98	39.9	39.69	40.66	41.50
$d\ln J_{dd}/d\ln V$	−0.1	−0.08	−0.26	−0.27	−0.3	−0.26	−0.31	−0.25	−0.3
T_C	367	167	143	112	38	27	57	136	–
dT_C/dP	0.053	0.57	1.72	0.55	−0.31	−0.096	0.36	0.07	–
M_{ST}	7.23	7.1	2.8–3.8	4.3–5.3	7.0–7.2	6.9	6.8	6.3–7.0	–
Θ	81	166	810	420	74	75	90	38	–
$d\Theta/dP$	–	0.69±0.03	–	–	−0.13±0.02	0.06±0.015	0.06±0.06	−0.05±0.02	–

were fixed by applying the Russel-Saunders coupling scheme to the $4f$ shell. Therefore, the $4f$-states were not allowed to hybridize with conduction electrons, contributing to the total spin density, but not being a part of the band structure. This approach is particularly suitable for Gd compounds, where $4f$ spin-up and spin-down occupation numbers are $n_f^+ = 7$ and $n_f^- = 0$. Also, the $4f$ electrons of Gd form the S state, which is not affected by the crystal-field interactions. The exchange and correlation potentials were calculated using the local spin density approximation (LSDA).

The results obtained with the LMTO-ASA method were verified and supplemented by *ab initio* relativistic full-potential LMTO calculations (FP-LMTO) [9]. In this method, the Kohn-Sham equations are solved without any shape approximations imposed on the charge density or potential. An elementary cell is subdivided into muffin-tin (MT) spheres at atomic sites and an interstitial re-

gion. Inside the MT spheres the basis functions, charge density and potential are expanded in spherical harmonic functions multiplied by a radial function, whereas in the interstitial region charge density and potential are expanded in a Fourier series. The paramagnetic and spin-polarized LMTO-ASA and FP-LMTO band structure calculations were performed self-consistently on a uniform mesh of about 1000 k-points in the irreducible wedge of the Brillouin zone for a number of lattice parameters close to the experimental ones. The magnetic susceptibility of PM systems were derived from the field-induced moments, which have been calculated in an external magnetic field of 10 T. Other details of the LMTO methods employed in the present work are given elsewhere [6–9].

Results and discussion

The main results of the calculations together with the available experimental data are presented in Table 1. As one can see, the calculated magnetic moments for the GdM$_2$ compounds are in a fair agreement with the experimental saturation moments. Regarding the calculated local exchange integrals, the values of J_{fd} and J_{dd} at Gd site do not vary substantially over the whole of GdM$_2$ series. On the other hand, the logarithmic volume derivatives of the exchange integrals appeared to be rather large, in comparison with the typical values $\mathrm{d}\ln J/\mathrm{d}\ln V \approx$ ≈ -0.1 in transition metals [6,7]. Remarkably, that the calculated values of $\mathrm{d}\ln J_{fd}/\mathrm{d}\ln V$ (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 CeCo$_2$ from the susceptibility measurements under pressure [10].

Based upon the results of the band structure calculations, the magnetic ordering temperatures T_C can be estimated for GdM$_2$ systems. In the simplest possible mean-field theory [4] the Curie temperature is given by:

$$k_B T_C = \frac{1}{3}\chi_d\, J_{fd}^2 (g_j - 1)^2 J(J + 1),$$

where χ_d is the effective susceptibility, which is proportional to the partial density of d-band states at the Fermi level E_F, J_{fd} – is the exchange integral, g_J and $(g_J{-}1)^2 J(J{+}1)$ are the Lande and de Gennes factors, respectively. This approach, however, usually provides too high values of T_C, and the only good agreement for GdCo$_2$ [4] should be regarded as fortuitous.

The alternative molecular-field approach for T_C calculations has been proposed for ferrimagnetic rare-earth intermetallics [2,11]:

$$T_C = 4\left(\frac{g_J - 1}{g_J}\right)^2 \left(n_{\mathrm{RR}} + n_{\mathrm{RM}}^2 \chi_{\mathrm{M}}'\right) C_{\mathrm{R}}.$$

In this approach the molecular-field coefficients n_{RR} and n_{RM} can be related to the exchange integrals and susceptibilities of conduction electrons at rare

earths and M sites, which in turn can be evaluated *ab initio* in the framework of the LMTO calculations described above (see [2,11] for details). The estimated in this way values of T_C are presented in Table 1. As one can see, this approach yields a qualitative agreement with the experimental T_C and the corresponding pressure derivatives of Θ, though a noticeable difference from the experiment can be also seen in Table 1 for some GdM_2 compounds. Actually, the calculated volume derivatives of T_C had to be converted to the pressure ones for comparison with the experimental data in Table 1, and the only available value of bulk modulus, $B = 0.78$ Mbar for $GdAl_2$ [12], was used for all GdM_2 compounds. This rough estimation for B could contribute to discrepancies between the theoretical and experimental pressure derivatives of T_C, the more so since a good agreement is found just in the case of $GdAl_2$ (see Table 1).

The calculated spin and orbital contributions, and the total susceptibility of YCo_2, are presented in Fig. 1 as functions of lattice spacing, and appeared in agreement with experimental data. A main part of the strongly volume-dependent spin contribution originates from the $3d$ states of Co. These $3d$ states
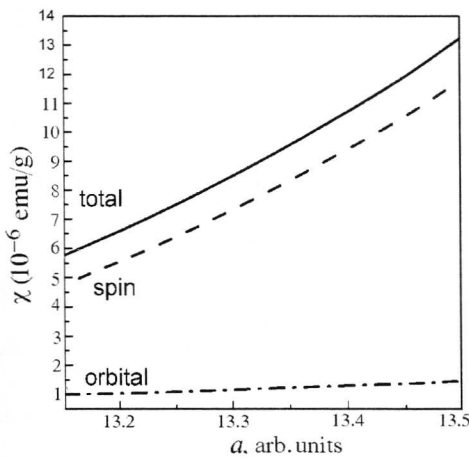

Fig. 1. Calculated magnetic susceptibility of YCo_2 as a function of lattice parameter. The solid line corresponds to the total χ, the dashed and dashed- dotted lines represent spin and orbital contributions, respectively.
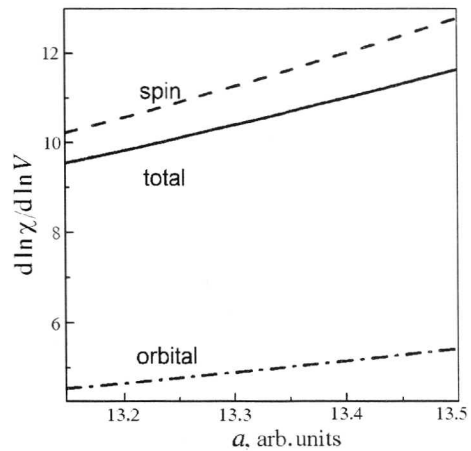
Fig. 2. Calculated logarithmic volume derivatives of the contributions to magnetic susceptibility of YCo_2 versus lattice parameter. The solid line corresponds to the total χ, the dashed and dashed-dotted lines represent spin and orbital contributions, respectively.

are also responsible for the orbital contribution to χ, and probably for other peculiar magnetic properties of the RCo_2 series [1,4,10,13]. The calculated volume derivative of susceptibility, $d\ln\chi/d\ln V$, is presented in Fig. 2 and appeared to be in agreement with experimental data, $d\ln\chi/d\ln V = 17$ at $T = 78$ K, this work, and $d\ln\chi/d\ln V = 14$ at $T = 40$ K, Ref. [13].

Conclusions

It has been demonstrated that the band theory within LSDA provides an adequate description of the electronic structure and peculiar magnetic properties of GdM_2 and YCo_2 compounds. It is found that $3d$ states of Co are responsible for the strongly volume-dependent spin contribution to the magnetic susceptibility of YCo_2. The modified mean-field approach, based on LSDA, gives 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. The results obtained in the present work are expected to encourage further advance in the theory of magnetic ordering in rare-earth systems.

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