Functional Materials 11, No.3 (2004)

Electronic structure and magnetic properties of rare-earth RM_2 and RM_3 compounds

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Ab initio calculations of the electronic structure and magnetic properties are carried out for the ferromagnetic GdM_2 compounds (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt), and also for the $La(In_{1-x}Sn_x)_3$ system. Pressure effects on the band structure and magnetic properties of GdM_2 have been evaluated and supplemented experimentally by magnetic susceptibility χ measurements under pressure in the paramagnetic phase. The peculiarities of $\chi(x)$ in $La(In_{1-x}Sn_x)_3$ alloys are found to originate from the band degeneracy points near the Fermi level. Experimental $\chi(x)$ data are analyzed in the framework of modern band and orbital magnetism theories.

Проведены расчеты из первых принципов электронной структуры и магнитных свойств ферромагнитных соединений $GdMV_2$ (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt) и системы $La(In_{1-x}Sn_x)_3$. Эффекты давления на зонную структуру и магнитные свойства $GdMV_2$ изучены теоретически, а также экспериментально на основе измерений магнитной восприимчивости χ под давлением в парамагнитной фазе. Показано, что особенность $\chi(x)$ в сплавах $La(In_{1-x}Sn_x)_3$ обусловлена наличием точки вырождения зон в окрестности уровня Ферми. Анализ экспериментальной зависимости $\chi(x)$ проведен в рамках современных теорий орбитального и зонного магнетизма.

Rare-earths (R) based intermetallics RM_x (M — is a simple or transition metal, or their combination) are of considerable technological and scientific interest due to extraordinary magnetic properties and industrial applications. These properties are governed by different types of interactions, 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 [1, 2]. Among RM_x compounds, the cubic intermetallics RM_2 and RM_3, having relatively simple C15 and $AuCu_3$ structures, respectively, exhibit a variety of unusual magnetic properties and provide a possibility to test various indirect exchange interaction models.

In the present contribution we studied two peculiar groups of these rare-earth intermetallics. Firstly, there are ferromagnetic GdM_2 compounds (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt) with the cubic Laves phase structure. Since the 4*f* sub-shell of Gd is completely filled (empty) for the majority (minority) spin channels, the magnetic anisotropy and magnetostriction in these compounds depend mainly on the itinerant conduction states. The second group is presented by $La(In_{1-x}Sn_x)_3$ pseudobinary alloys with the Cu_3Au structure. This reference paramagnetic system demonstrates the strong oscillations of the magnetic susceptibility with concentration x [3, 4], and such anomalous behavior of χ can have relevance to magnetic ordering in related RM_3 systems.

In order to shed light on the origin of the anomalous behavior of magnetic characteristics in these systems, the *ab initio* calculations of the band structures and mag-

netic properties are carried out for the paramagnetic and ferromagnetic phases of GdM_2 compounds, as well as for the series of solid solutions $La(In_{1-x}Sn_x)_3$. The calculations are carried out by using the linear muffin-tin orbital method (LMTO) in the atomic spheres approximation (ASA), where the spin densities and potentials are assumed to be spherically symmetric around each atom [5]. The results obtained with the LMTO-ASA method were supplemented by relativistic full-potential LMTO (FP-LMTO) calculations [6, 7], where the Kohn-Sham equations can be solved without any shape approximations imposed on the charge density or potential. The exchange and correlation potentials were calculated using the local spin density approximation (LSDA) [8]. In both LMTO-ASA and FP-LMTO calculations, the 4*f*-states of Gd were treated as spin polarized open core states with Hund's rule restriction for the 4*f* spin, analogously to Refs.[7, 9]. The LMTO-ASA and FP-LMTO band structure calculations were performed self-consistently for a number of lattice parameters close to experimental ones.

For each specific compound, studied in the present work, the calculated density of electronic states (DOS) in the vicinity of the Fermi level E_F appeared to be similar within the LMTO-ASA and FP-LMTO calculations. As an example, the DOS for the paramagnetic state of $GdFe_2$, $GdCo_2$ and $GdNi_2$, calculated within LMTO-ASA, are presented in Fig. 1. These DOS curves look rather similar, except that E_F positions correspond to different occupations of conduction band. On the other hand, the $GdFe_2$ and $GdCo_2$ compounds posses high but opposite in sign magnetostriction coefficients. Therefore, the magnetic ordering in these compounds is expected to be strongly influenced by the transition metal sub-lattice.

The evaluated magnetic and band structure characteristics for all GdM_2 compounds are listed in Table. The bulk moduli were evaluated from first principles for all investigated GdM_2 compounds. In Table one can see, that the calculated magnetic moments are in a reasonable agreement with the experimental ones, with allowance made for experimental discrepancies [1, 2, 9, 10]. Regarding the calculated local exchange integrals, the values of J_{fd} and J_{dd} at the Gd site, as well as their volume derivatives, do not vary substantially over the whole GdM_2 series. Remarkably, that the calculated values of $d\ln J_{fd}/d\ln V$ (see Table) appeared to

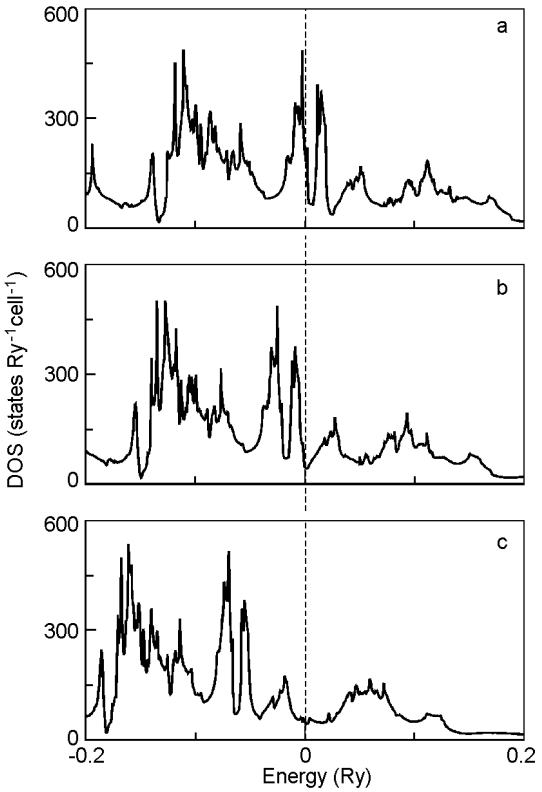

Fig. 1. Paramagnetic densities of states in the vicinity of E_F for: (a) $GdFe_2$, (b) $GdCo_2$ and (c) $GdNi_2$ compounds.

be close to the volume derivative of the averaged exchange interaction parameter, $d\ln J/d\ln V = -1.7$, evaluated for the isostructural $CeCo_2$ compound [11]. According to the calculations, the exchange integrals remain almost unchanged under the paramagnetic-ferromagnetic phase transition. This confirms that exchange integrals are predominantly intra-atomic characteristics, which are not affected by magnetic ordering.

To elucidate a nature of interactions responsible for magnetic ordering, the magnetic susceptibility of GdM_2 compounds (M = Al, Ni, Rh, Ir, Pt) was measured by the Faraday method under helium gas pressure (up to 2 kbar) in the temperature range 78 (or T_C) — 330 K, using the pendulum magnetometer placed into the pressure cell [12]. The $\chi(T)$ obeys the Curie-Weiss law, and the corresponding paramagnetic Curie temperatures, Θ, together with the estimated $d\ln\Theta/d\ln V$ derivatives, are listed in Table. A substantial volume effect on the Curie temperature has been observed in $GdAl_2$ and $GdCo_2$ compounds, whereas it is appeared to be small in other investigated GdM_2. The sign of volume derivatives of Θ is presum-

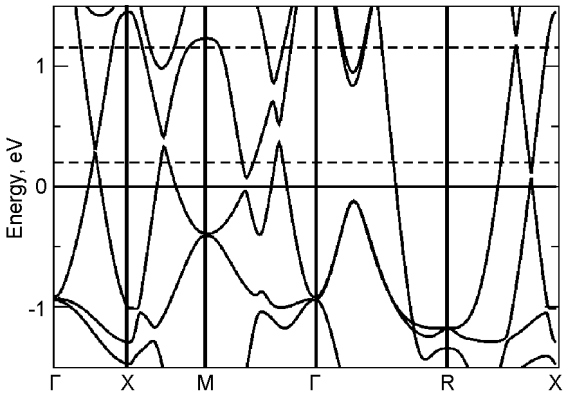

Fig. 2. Band structure of $LaIn_3$ compound. Two dashed lines mark E_F corresponding to (a) $La(In_{0.9}Sn_{0.1})_3$ and (b) $La(In_{0.3}Sn_{0.7})_3$ alloys.

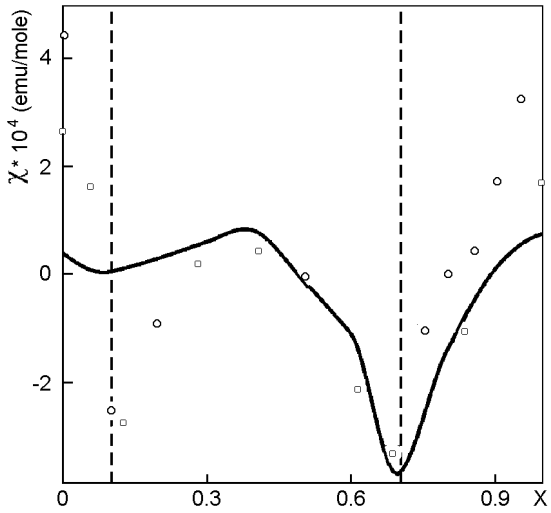

Fig. 3. Experimental (□ [3], o [4]) and calculated (solid line) magnetic susceptibilities of $La(In_{1-x}Sn_x)_3$ alloys.

ably governed by peculiarities of *sp-d*-hybridization.

The second system investigated is $La(In_{1-x}Sn_x)_3$, which demonstrates anomalous $\chi(x)$ behavior [3, 4]. It is known, that some band degeneracy points close to the Fermi level are related to anomalously high diamagnetic contributions to the magnetic susceptibility [13]. This effect was revealed in beryllium [14], alluminium [15], and also in some alloys of bismuth [16]. It was also shown [17], that such points of degeneracy at the XR symmetry lines of the cubic Brillouin zone govern the temperature dependent diamagnetic susceptibility of $CaPb_3$ and $YbPb_3$ compounds, which crystallize in the $AuCu_3$ structure. This effect is expected to take place in more complicated systems, such as isostructural and isovalent pseudo-binary alloys.

The calculated band structure of $LaIn_3$ is given in Fig. 2. In the framework of the rigid band approximation we estimated two Fermi levels (marked with the dashed lines in Fig. 2), corresponding to $La(In_{1-x}Sn_x)_3$ alloys, which are expected to exhibit the $\chi(x)$ minima (see Fig. 3). As one can see, three suitable band degeneracy points, which can

Table. Calculated bulk modules B; paramagnetic $N(E_F)$ and ferromagnetic $N\uparrow\downarrow(E_F)$ DOS and their volume derivatives; J_{fd} and J_{dd} exchange integrals and their volume derivatives; calculated M_t and experimental M_s saturation magnetic moments; experimental values of paramagnetic Curie temperatures Θ and their volume derivatives.

Parameter	$GdMg_2$	$GdAl_2$	$GdFe_2$	$GdCo_2$	$GdNi_2$	$GdRh_2$	$GdIr_2$	$GdPt_2$
B (Mbar)	0.46	0.87	0.9	1.11	1.19	1.66	1.86	2.00
$N(E_F)$ (Ry^{-1})	104.4	64.6	207.4	49.6	48.0	33.5	39.2	46.1
$d\ln N(E_F)/d\ln V$	0.8	−4.7	0.8	1.6	5.8	3.8	−0.9	2.1
$N\uparrow\downarrow(E_F)$ (Ry^{-1})	132.8	33.8	79.0	96.6	49.5	32.7	30.5	47.8
$d\ln N\uparrow\downarrow E_F)/d\ln V$	3.6	0.7	0.4	1.81	0.84	0.29	2.23	−0.18
J_{fd} (mRy)	6.44	6.09	6.01	6.09	6.35	6.39	6.06	6.33
$d\ln J_{fd}/d\ln V$	−0.5	−0.6	−1.3	−1.3	−1.3	−1.5	−1.65	−1.6
J_{dd} (mRy)	39.06	38.81	39.45	39.32	39.98	40.31	39.69	40.66
$d\ln J_{dd}/d\ln V$	−0.1	−0.08	−0.26	−0.27	−0.3	−0.26	−0.31	−0.25
M_t (μ_B)	8.1	7.5	3.5	5.1	7.1	7.0	7.1	7.2
M_s (μ_B)	7.23 [1]	7.25 [9]	2.8–3.8 [1]	4.96 [10]	7.1 [10]	6.9 [1]	6.8 [1]	6.3–7.0 [1]
Θ (K)	100 [1]	167	803 [18]	410 [19]	75	75	90	38
$d\ln\Theta/d\ln V$	–	−3.4±0.2	−0.04 [18]	6.8 [19]	1.7±0.3	−0.8±0.3	−0.7±0.7	1.3±0.5

be related to corresponding diamagnetic peaks, are found in the vicinity of these E_F. We were able to evaluate the only diamagnetic contribution to χ in the framework of the available theory [13], namely, originating from the degeneracy points at XR line, which are close to E_F in $La(In_{0.3}Sn_{0.7})_3$ (see Fig. 2). In Fig. 3 the experimental susceptibilities are presented for the $La(In_{1-x}Sn_x)_3$ system together with the calculated χ, which include diamagnetic and paramagnetic contributions, evaluated analogously to [13, 17] and [20], respectively. It is seen, that the calculated and experimental $\chi(x)$ curves are in a reasonable agreement, confirming validity of the theories [13, 17, 20]. Therefore, the oscillatory behavior of magnetic susceptibility in $La(In_{1-x}Sn_x)_3$ alloys can be explained by competition between the spin paramagnetic and anomalous diamagnetic contributions to χ.

References

1. K.H.J.Buschow, in: Ferromagnetic Materials, v.1, ed. E.P.Wohlfarth, North-Holland, Amsterdam (1980), p.297.
2. J.J.M.Franse, R.J.Radvansky, in: Ferromagnetic Materials, v.7, ed. K.H.J.Buschow, North-Holland, Amsterdam (1993), p.307.
3. E.E.Havinga, H.Damsma, M.H.Van Maaren, *J. Phys. Chem. Solids*, **31**, 2653 (1970).
4. A.M.Toxen, R.J.Gambino, *Phys. Rev. B.*, **8**, 90 (1973)
5. H.L.Skriver, The LMTO Method, Springer, Berlin (1984).
6. J.M.Wills, O.Eriksson, ed. by H.Dreysse, Electronic Structure and Physical Properties of Solids, Springer, Berlin (2000), p.247.
7. K.H.J.Buschow, G.E.Grechnev, A.Hjelm et al., *J. Alloys and Compounds*, **244**, 113 (1996).
8. U.von Barth, L.Hedin, *J. Phys. C*, **5**, 1629 (1972).
9. M.Bauer, M.S.S.Brooks, E.Dormann, *Phys. Rev. B*, **48**, 1014 (1993).
10. T.Kaneko, K.Marumo, S.Miura et al., *Physica B*, **149**, 334 (1988).
11. A.S.Panfilov, G.E.Grechnev, I.V.Svechkarev et al., *Physica B*, **319**, 268 (2002).
12. A.S.Panfilov, *Fizika i Teknika Vysokih Davleniy*, **2**, 61 (1992).
13. G.P.Mikitik, I.V.Svechkarev, *Fiz. Nizk. Temp.*., **15**, 165 (1989).
14. G.E.Grechnev, I.V.Svechkarev, Yu.P.Sereda, *Zh. Eksp. Teor. Fiz.*, **48**, 502 (1978).
15. S.A.Vorontsov, I.V.Svechkarev, *Fiz. Nizk. Temp.*, **13**, 155 (1987).
16. G.P.Mikitik, Yu.V.Sharlai, *Low Temp. Phys.*, **26**, 39 (2000).
17. A.E.Baranovskiy, G.E.Grechnev, G.P.Mikitik et al., *Low Temp. Phys.*, **29**, 356 (2003).
18. M.Brouha, K.H.J.Buschow, *J. Appl. Phys.*, **44**, 1813 (1973).
19. M.Brouha, K.H.J.Buschow, *J. Phys. F: Metal. Phys.*, **3**, 2218 (1973).
20. G.E.Grechnev, R.Ahuja, O.Eriksson, *Phys. Rev. B*, **68**, 064414 (2003).

Електронна структура та магнітні властивості рідкісно-земельних сполук RM2 та RM3.

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Зроблені теоретичні розрахунки електронної структури та магнітних властивостей феромагнітних сполук GdM_2 (M = Mg, Al, Fe, Co, Ni, Rh, Ir, Pt) та системи $La(In_{1-x}Sn_x)_3$. Вплив тиску на зонну структуру та магнітні властивості GdM_2 сполук було вивчено теоретично та експериментально, грунтуючись на вимірах магнітної сприятливості χ під тиском у парамагнітній фазі. Знайдено, що особливість $\chi(x)$ у сплавах $La(In_{1-x}Sn_x)_3$ визначається виродженими електронними станами біля рівня Фермі. Аналіз експериментальної залежності $\chi(x)$ був проведений за допомогою сучасних теорій зонного та орбітального магнетизму.