Fizika Nizkikh Temperatur, 2009, v. 35, No. 7, p. 721–724

Hall effect and magnetic ordering in RB_{12}

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Received March 12, 2009, revised April 13, 2009

The concentration of carriers in LuB_{12} is evaluated theoretically by applying *ab initio* FP-LMTO calculations. Theoretical results are found to be in agreement with high precision measurements of the Hall $R_H(T)$ coefficient which were carried out on single crystals of the rare earth dodecaborides RB_{12} (R = Ho, Er, Tm, Lu) at temperatures 1.8–300 K. A nature of the antiferromagnetic ordering in RB_{12} is investigated within the RKKY-like model, which was supplemented by comprehensive electronic structure calculations for paramagnetic, ferromagnetic and antiferromagnetic phases.

PACS: 71.20.Eh Rare earth metals and alloys;
72.15.Qm Scattering mechanisms and Kondo effect;
75.30.–m Intrinsic properties of magnetically ordered materials.

Keywords: Hall effect, RKKY model, borides, electronic structure, magnetic ordering.

The MB_{12} dodecaborides (M is rare earth, early transition, or actinide metal) are of great scientific interest and technological importance due to their extraordinary electronic, magnetic and structural properties such as peculiar bonding [1], superconductivity (YB_{12} and ZrB_{12} [2,3]), Kondo and valence fluctuation effects (YbB_{12} [4]). The heavy rare earth (R) dodecaborides RB_{12}, close to the famous Kondo insulator YbB_{12}, are of particular interest due to complicated scenario of magnetic ordering at low temperatures and observed peculiar incommensurate magnetic structures (TbB_{12}–TmB_{12} [5]).

Though a number of experimental and theoretical investigations were carried out for RB_{12} [1,5–9], the mechanisms of microscopic magnetic interactions, as well as fine details of the electronic structure in these compounds, are still not clear.

In order to elucidate the origin of principal interactions and electronic states responsible for magnetic ordering in RB_{12}, the high precision measurements of the Hall resistivity $\rho_H(\varphi, T, H)$ were carried out for HoB_{12}, ErB_{12}, TmB_{12} and LuB_{12} compounds within a wide temperature range of 1.8–300 K in magnetic fields up to 80 kOe [6,7].

Based on the measured Hall coefficients of RB_{12} [6,7], the corresponding values of normalized charge carrier concentration $n/n_{4f} = (R_H e n_{4f})^{-1}$ are evaluated and presented in Fig. 1. Here n and n_{4f} are the numbers of carriers and rare earth atoms per the primitive cell correspondingly and R_H is the Hall coefficient.

As can be seen in Fig. 1, the temperature dependences of the charge carrier concentration are distinct from each other for the nonmagnetic LuB_{12} and magnetic dodecaborides. In particular, a pronounced anomaly of $n/n_{4f}(T)$ is revealed in LuB_{12} at $T^* \approx 56$ K, whereas magnetic compounds HoB_{12}, ErB_{12} and TmB_{12} demonstrate a weak enough variation of the carrier concentration n at intermediate temperatures. Indeed, on the average, the n/n_{4f} value is varied within about 10% through the paramagnetic region of RB_{12} series, namely 2.0–2.2. It should be stressed that this result contradicts to the assumption that the conduction band in RB_{12} compounds is formed by only one $5d$ electron of a rare earth element [10]. To shed

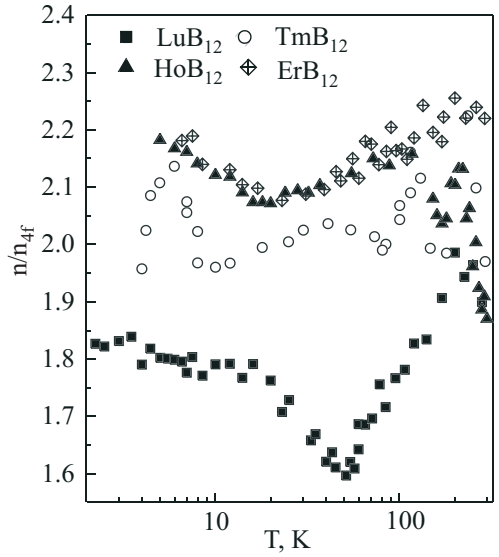

Fig. 1. Temperature dependence of normalized charge carriers concentration $n/n_{4f} = (R_H e n_{4f})^{-1}$ of RB_{12}.

light on the structure and filling of the conduction band in RB_{12} compounds, the experimental study of Hall coefficients was supplemented by *ab initio* calculations of the electronic structure for the paramagnetic (PM) and magnetically ordered (FM and AFM) phases of the RB_{12} dodecaborides. Based on the calculated band structure of the reference LuB_{12} compound, which is supposed to represent a typical electronic configuration within RB_{12} series in the paramagnetic phase, manifestations of magnetic ordering are analyzed and discussed in the framework of the RKKY model.

The stable B_{12} nanoclusters can be considered as basic structural elements of the cubic dodecaborides. The corresponding UB_{12}-type crystal structure is similar to the simple rock-salt lattice, where U atoms and B_{12} cuboctahedrons occupy the Na- and Cl-sites, respectively. The *ab initio* electronic structure calculations were carried out for the paramagnetic, ferromagnetic and collinear antiferromagnetic phases of RB_{12} (R = Ho, Er, Tm) by using the relativistic full potential linear muffin-tin orbital (FP-LMTO) method [11,12] within the local density approximation (LDA) [13] and the generalized gradient approximation (GGA) [11]. With the present FP-LMTO method, one can avoid extra shape approximations imposed on the charge density or potential. The localized 4*f* states of rare earth ions were treated as spin-polarized outer-core wave functions, contributing to the total spin density. The spin occupation numbers were fixed by applying the Russel–Saunders coupling scheme to the 4*f* shell, which was not allowed to hybridize with the conduction band states. Other details of the FP-LMTO method employed in the present work are given in Refs. 11 and 12.

For each RB_{12} compound, the band structure was calculated for a number of lattice parameters close to experimental one. These calculations provided total energies for a ground state and corresponding equations of states $E(V)$ with sufficient accuracy. By this way the magnetic stability of AFM ordering in RB_{12} was confirmed by comprehensive total energy calculations for PM, FM and AFM phases. Also, the detailed calculations of the band structure, Fermi surface, total and partial densities of electronic states (DOS) were carried out for the reference LuB_{12} compound to reveal principal features of electronic spectra, which are common for the whole RB_{12} series. The corresponding band structure and total density of electronic states of LuB_{12} in the close vicinity of the Fermi level E_F are presented in Figs. 2 and 3. According to the present calculations, RB_{12} borides possess a rather complicated Fermi surface (FS) consisting of three principal parts. The first sheet of the FS is multiply connected in the <111> directions (ΓL direction in the Brillouin zone) and topologically similar to the FS of copper. The second part of the FS forms «pancake»-like electron surfaces centred at X symmetry points. And the third Fermi surface sheet consists of small electronic lenses centred at K points of the Brillouin zone. These results are in agreement with the recent FP-LAPW calculations [14], whereas previous band structure calculations for the heavy rare earth dodecaborides provided only two FS sheets [8,15]. As it follows from our calculations, the main features in the band structure of RB_{12} are governed by hybridization of 5*d* states of rare-earth with 2*p* states of boron. These hybridized bands exhibit a strong dispersion at the Fermi level (see Fig. 2), and the calculated effective masses of conduction electrons appeared to be comparatively small ($m^* \sim m_0$), in agreement with results of the experimental studies of the de Haas–van Alphen effect in LuB_{12} [9], HoB_{12}, ErB_{12} and TmB_{12} compounds [16]. For LuB_{12} our evaluation of a volume

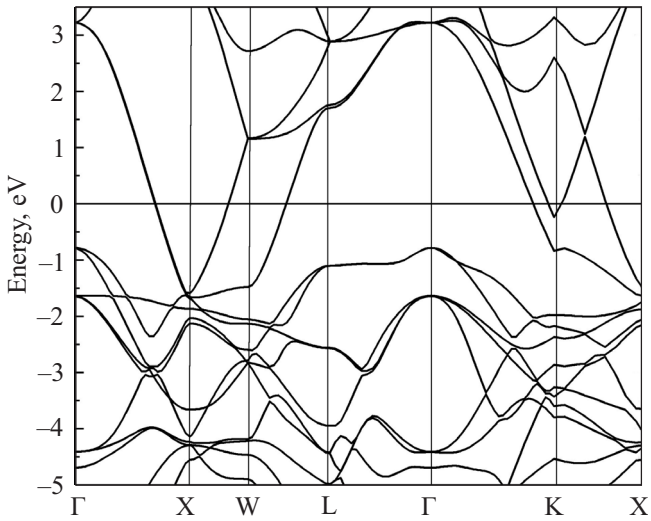

Fig. 2. Band structure for the reference LuB_{12} compound.

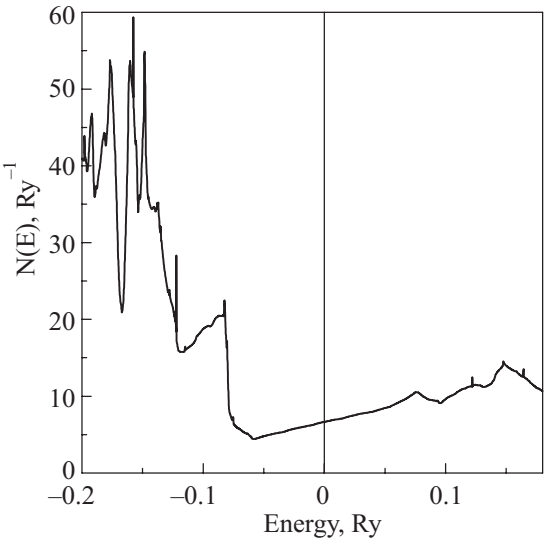

Fig. 3. Calculated total density of state for LuB_{12}.

enclosed by the FS provides the estimated carrier density about two conduction electrons per formula unit.

In order to elucidate a nature of magnetic ordering in RB_{12} a qualitative analysis was carried out here within the framework of the RKKY model [17],

$$\theta \sim Gn^2J^2/E_FSF(n), \qquad (1)$$

where θ is the paramagnetic Curie temperature, G is the De Gennes factor, J is the effective exchange parameter, and $F(n)$ is the RKKY function. As is seen from the calculated dependence of the RKKY function versus carrier concentration n in Fig. 4, for all investigated RB_{12} the $F(n)$ behavior in vicinity of $n/n_{4f} = 2$ appeared to be consistent with the AFM ordering in these borides. Also one can see in Fig. 4, that in the range from $n/n_{4f} = 2$ to 2.2 the RKKY function varies moderately, and relative changes of $F(n)$ do not exceed 30%. Therefore, the paramagnetic Curie temperatures behavior within the RB_{12} series is expected to be predominantly governed by the De Gennes factor, which decreases monotonously for heavy rare-earth ions R. The $\theta(n)$ behavior is in a qualitative agreement with the experimental relative values of the Néel temperature T_N, which are equal to 7.4, 6.7 and 3.3 K for HoB_{12}, ErB_{12} and TmB_{12}, respectively [5,6]. However, an attempt to describe the relative values of T_N more precisely within Eq. (1) presumes that noticeable increase of the effective exchange parameter J with the atomic number of rare earth element should take place in the investigated RB_{12} series. Indeed, the ratios $J_{Er}/J_{Ho} \cong 1.25$ and $J_{Tm}/J_{Ho} \cong 1.5$ have to be valid to satisfy the observed sequence of T_N in the framework of Eq. (1). On the other hand, such increase of J with the atomic number of rare earth element contradicts to the direct *ab initio* calculations for rare earth systems [18,19], which provide changes of the corresponding exchange parameter not exceeding 5%. Therefore, the deviations from De Gennes scaling for magnetic ordering temperatures of RB_{12} occur that are probably due to a mechanism not represented by the RKKY model.

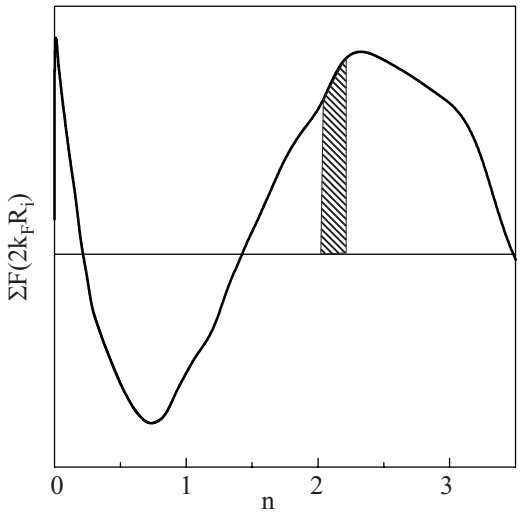

Fig. 4. RKKY function vs normalized carrier concentration n for fcc lattice.

As it follows from results of the recent studies of transport properties in RB_{12} [6,7], an anomalous behavior of transport parameters does not comply with the variation of the De Gennes factor between HoB_{12} and LuB_{12}, and the decrease of charge carrier mobility with the 4*f* occupation number n is presumably related to the enhancement of spin fluctuations (SF) within the HoB_{12} and TmB_{12} series. Accordingly we may also suggest, that the onsite 4*f*–5*d* spin fluctuations can also renormalize the values of the magnetic ordering temperature of RB_{12}, in addition to the RKKY mechanism of Eq. (1) and in line with the suggested SF mechanism of Refs. 20 and 21.

Thus, it is revealed, that 5*d* states of rare earth ions which are hybridized with 2*p* states of boron are playing an important role not only in formation of the electronic structure and bulk properties, but also in the AFM ordering in RB_{12} via both the RKKY-like indirect exchange interaction and the onsite 4*f*–5*d* spin fluctuations effects.

Support by the RAS Program «Strongly Correlated Electrons in Semiconductors, Metals, Superconductors and Magnetic materials» and the RFBR 07-02-90902 grant is acknowledged.

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