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PRESSURE EFFECT ON ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF MB$_6$ AND MB$_{12}$ BORIDES

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Theoretical and experimental studies of the pressure effect on electronic structure and magnetic properties of MB_6 and MB_{12} borides are carried out to determine the electronic ground states and interactions responsible for the bulk and magnetic properties of these compounds. The band structure and total energy E were calculated ab initio for a number of atomic volumes, providing the equation of states, E(V), bulk moduli B, magnetic moments and susceptibilities. The temperature and pressure dependencies of magnetic susceptibility were also experimentally studied for a number of borides using a pendulum-type magnetometer. In semimetallic EuB_6 the paramagnetic Curie temperature is found to be increasing with pressure, $d\theta/dP = 0.44 \pm 0.03$ K/kbar, whereas in closely related GdB_6 compound the pressure effect is lower in magnitude but opposite in sign: $d\theta/dP = -0.17 \pm 0.03$ K/kbar. The peculiar details in electronic structures are found to be responsible for distinctions in magnetic ordering and the pressure effects on indirect f–f interactions.

Introduction

The MB$_6$ hexaborides and MB$_{12}$ dodecaborides (M is rare-earth, early transition, or actinide metal) are known for their peculiar physical properties, such as superconductivity (YB$_6$, LaB$_6$ and ZrB$_{12}$) [1,2], Kondo and valence fluctuation effects (CeB$_6$, SmB$_6$ and YbB$_{12}$) [3], and anomalous magnetism (EuB$_6$) [4]. Also, narrow gap semiconductors were found among hexaborides with rare earth (YbB$_6$) and alkaline earth (CaB$_6$, BaB$_6$, SrB$_6$) elements [5]. The basic structural elements of cubic dodecaborides are the stable cubooctahedral boron clusters. The structure is described in terms of simple rock-salt lattice, where M occupies Na sites and B$_{12}$ cubooctahedra are located at Cl sites. The CaB$_6$-type structure can

be described in terms of a simple CsCl lattice, where *M* atoms occupy Cs sites, while B_6 octahedra are in Cl sites. Hence the boron atoms produce a rigid cage whereas metallic elements are situated inside the cavities, which are formed by B_6 or B_{12} clusters. Therefore, these compounds can be considered as hard and refractory materials, and their structural and elastic properties are mainly related to the peculiar chemical bonding. At the same time, the electronic and magnetic properties are expected to be governed by the states of metallic bonds. In general, the MB_6 and MB_{12} borides are of great scientific interest and technological importance due to their extraordinary electronic, magnetic and structural properties.

In the present work we are mostly focused on a pressure effect on magnetic properties of two closely related hexaborides, EuB_6 and GdB_6. In addition, the bulk and volume dependent (elastic) properties of selected hexa- and dodecaborides are studied experimentally and theoretically.

Experimental and computational details

The process of sample preparation consists of the synthesis of dodecaborides by a barothermal reduction of the metal oxides in vacuum at 1900 K, the compacting of these powders into rods and their subsequent sintering, and of inductive zone melting. The purity of the initial oxides M_2O_3 was 4N. The content of the main substance in the initial amorphous boron was not less than 99.5%. Highly volatile impurities in boron were deleted partially during the synthesis procedure and partially during zone melting. The total content of impurities in samples studied was not higher than 10^{-3} mass%.

The low-temperature ultrasound studies were performed on samples cut from the zone-melted single crystals. The lattice parameters of the single crystal borides coincide with the powder ones due to the rigid boron sublattice, and are also in a qualitative agreement with published results (see. Ref. [6] and references therein).

The pressure effect on the magnetic susceptibility χ was measured under helium gas pressure up to 2 kbar at two fixed temperatures, $T = 78$ and 300 K, using a pendulum magnetometer placed into the non-magnetic pressure cell [7]. The relative errors of our measurements did not exceed 0.05%. The magnetic susceptibilities in EuB_6 and GdB_6 are found to obey the Curie–Weiss law with the effective magnetic moment value close to that expected for Gd^{3+} state. Based on the $\chi(P)$ measurements the paramagnetic Curie temperatures θ and their pressure derivatives were evaluated.

The *ab initio* band structure calculations were carried out for the paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AFM) phases of MB_6 and MB_{12} by using the full potential linear muffin-tin orbital (FP-LMTO) method within the local spin density approximation (LSDA) [8,9]. The localized 4*f* states were treated as spin polarized outer core wave functions, and the spin occupation numbers were fixed by applying the Russel–Saunders coupling scheme to the 4*f* shell. The bulk moduli *B* and theoretical lattice parameters *a* are evaluated from the calculated total energies as functions of volume, i.e. from the corresponding equations of states (EOS) $E(V)$, and listed in Table 1.

Table 1

Lattice constants (in Å) and bulk moduli (in GPa) of MB_6 and MB_{12} borides

Parameters	MB_6				MB_{12}					
	Y	La	Eu	Gd	Zr	Ho	Er	Tm	Lu	U
a_{exp}	4.1002	4.1565	4.1845	4.107	7.4077	7.4923	7.4841	7.4752	7.4644	7.470
a_{theor}	4.080	4.130	4.164	4.112	7.331	7.45	7.443	7.424	7.413	7.399
B_{exp}	154	184	167	173	234	213	214	233	232	249
B_{theor}	179	185	159	175	249	215	217	220	223	250

Results and discussion

EuB_6 is a FM compound with two consecutive phase transitions at T_{c1} = 15 K and T_{c2} = 12.5 K [3,4]. Our calculations provided a semimetallic state in PM (see Fig. 1 and Table 2) and FM phases, and the total energy appeared to be minimal for the FM phase with magnetic moment of 7.03 μ_B. The paramagnetic Curie temperature of EuB_6 is found to be positive, and increasing with pressure (see Table 2), in agreement with results of the transport measurements under high pressure [3]: $d\ln T_c/dP$ = 24 $Mbar^{-1}$. The trivalent hexaboride GdB_6 has the same *f*-shell configuration, f^7, and a higher band filling (see Fig. 1). The AFM total energy appeared to be minimal for GdB_6 with the calculated magnetic moment of 7.1 μ_B. In contrast to EuB_6, our studies revealed the negative θ and also negative pressure effect on θ for GdB_6 (Table 2). This indicates the effect of electronic structure peculiarities on the effective interaction between 4*f* ions.

Table 2

Calculated DOS at the Fermi level (in states/Ry f.u.) and the corresponding volume derivatives. Experimental values of Curie temperature (in K), as well as experimental and theoretical pressure derivatives, $d\ln\theta/dP$ (in $Mbar^{-1}$), for paramagnetic EuB_6 and GdB_6

Paramagnetic	$N(E_F)$, $(Ry\ f.u.)^{-1}$	$d\ln N(E_F)/d\ln V$	θ, K	$d\ln\theta/dP$, $Mbar^{-1}$	
				exp.	theor.
EuB_6	0.8	–3.1	15	29	15
GdB_6	9.9	0.51	–65	–3	–2

The magnetic ordering in rare earth compounds is usually interpreted in the framework of various mean-field models [10–12], according to which the Curie temperature is approximated by $\theta \sim J^2 N(E_F)$, where $N(E_F)$ is the electronic density of states at the Fermi level, and *J* is the effective exchange parameter. Assuming dJ/dP values to be close and small for both investigated compounds, one might expect that $d\ln\theta/d\ln V \approx d\ln N(E_F)/d\ln V$. However, the calculated volume dependencies of $N(E_F)$ in Table 2 do not follow the experimental pressure effect on θ for both EuB_6 and GdB_6.

It has been suggested [3] that magnetic moments in EuB_6 can be ordered ferromagnetically due to the RKKY-type indirect exchange mediated by conduction

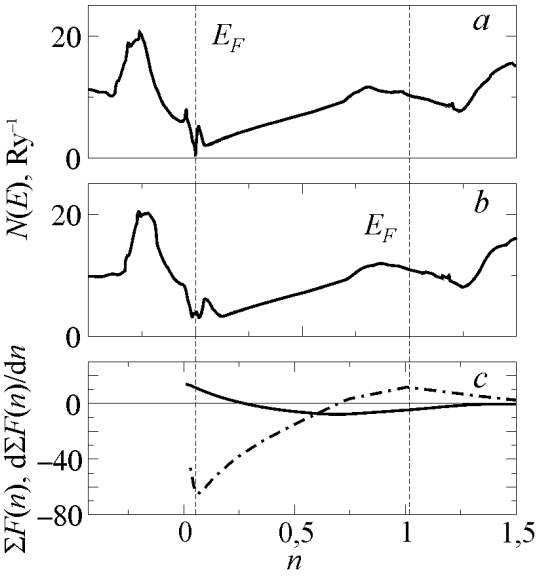

Fig. 1. Calculated DOS for PM phases of EuB_6 (*a*) and GdB_6 (*b*), and the RKKY sum (*c*) with its volume derivative (dashed-dotted line) versus the conduction band filling *n*

electrons [13]. This assumption is in line with our band structure calculations for EuB_6, which revealed a free-electron like behaviour of $E(k)$ dispersion curves in vicinity of the Fermi level. In this case the paramagnetic Curie temperature is given by: $\theta \sim J^2 k_F / a^4 F(n)$ [13], where k_F – a radius of the Fermi sphere, n – the number of conduction electron states, and $F(n)$ – the RKKY function. In the free-electron approximation the quantities n and k_F are related as: $n = \frac{8\pi}{3}\left(\frac{k_F}{2\pi}\right)^3$ (here the lattice parameter is assumed to be $a = 1$).

Though *ab initio* calculations of θ itself still represent a challenging task, it seems more feasible to evaluate the corresponding logarithmic derivative in the framework of the RKKY approach as follows:

$$\frac{d\ln\theta}{d\ln V} = 2\frac{d\ln J}{d\ln V} + \frac{4}{3n}\frac{dn}{d\ln V} + \frac{d\ln F(n)}{dn}\frac{dn}{d\ln V}. \qquad (1)$$

According to our calculations for the PM phase of EuB_6, the number of «light» *sp*-states in the conduction band can be estimated between $n = 0.230$ (for the experimental lattice parameter) and $n = 0.225$ (for the theoretical *a*). Indeed, as one can see in Fig. 1, the overlap of the valence and conduction bands is very small, and the Fermi level is situated just above a bottom of the conduction band in EuB_6. This naturally explains a small value of the band filling *n*.

The calculated DOS of GdB_6 compound in PM state is also presented in Fig. 1. One can see that main features of the $N(E)$ curve are similar to those obtained for EuB_6. Actually, the density of states versus *n* behaves in a free-electron manner between EuB_6 and GdB_6. However, Gd atom is in the trivalent state in GdB_6, and it donates one more electron to the conduction band. The value of *n* calculated in this way for GdB_6 compound varies from $n = 1.309$ (for the experimental lattice parameter) to $n = 1.304$ (for the theoretical *a*).

The calculated for the simple cubic structure RKKY function $F(n)$ [13] is presented in Fig. 1 versus the conduction band filling *n* (predominantly *sp*-electrons). Ibidem, the *n* values corresponding to the band filling in EuB_6 and GdB_6 compounds are also shown as vertical dashed lines. In this way, the RKKY model describes qualitatively a character of magnetic ordering, i.e. the sign of Curie tem-

perature in these compounds: FM in EuB_6 ($\theta > 0$) and AFM in GdB_6 ($\theta < 0$). Moreover, the pressure derivatives of θ, estimated by employing (1) and the corresponding bulk moduli from Table 1, amount to $d\ln\theta/dP = 15$ and $d\ln\theta/dP = -2$ for EuB_6 and GdB_6 compounds, respectively (see Table 2). The agreement between experiment and theory concerning the pressure derivatives of θ can be regarded as very good, taking into account the experimental precision, as well as all approximations related to the simplified RKKY approach employed in this study.

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