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Electronic structures and magnetic properties of RB$_4$ (R=Yb,Pr,Gd,Tb,Dy)

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Most rare-earth tetraborides RB$_4$ have antiferromagnetic ground states except for YbB$_4$ and PrB$_4$. We have investigated the electronic structures and magnetic properties of RB$_4$ (R=Yb,Pr,Gd,Tb,Dy) employing the first-principles total energy band method. It is found that YbB$_4$ has the paramagnetic ground state, while the other tetraborides are in the magnetic ground state, which is in agreement with experiments. We have obtained the spin and orbital magnetic moments and discussed the importance of the spin-orbit interaction and the on-site Coulomb repulsion (U) in these systems. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3058707]

The crystal structure of rare-earth tetraboride RB$_4$ consists of rare-earth (R) ion layers stacked along the c-axis with three kinds of boron (B1, B2, and B3) atoms in-between. B1 and B3 form B$_6$ octahedra with apexes along the c-axis, which are interconnected by B2. Tetragonal unit cell contains 4 f.u. of RB$_4$. There exist only a small number of conduction carriers because most valence electrons participate in bondings between boron atoms. Therefore, the valency of the R ions plays an important role in determining the physical properties of these systems.[1] The plot of lattice constant versus atomic number from Pr to Yb in RB$_4$ reveals an abnormal change at YbB$_4$, reflecting the different valence states of Yb ion from those of other rare-earth ions.[1] The intermediate valence state of Yb ion was proposed for YbB$_4$.[2] Magnetic properties in these systems are determined by 4f electrons of R ions, and so it is required to know the valence states of R ions.

Most rare-earth tetraborides RB$_4$ exhibit the antiferromagnetic ground states, whereas YbB$_4$ and PrB$_4$ are in the paramagnetic and the ferromagnetic ground states, respectively.[1,3] As the rare-earth tetraborides are metallic, the magnetic mechanism is explained by the Ruderman–Kittel–Kasuya–Yosida-type interaction, in which the local 4f magnetic moments of R ions are coupled through the mediating conduction electrons. Based on the resonant x-ray scattering, it was recently proposed that the magnetic state has a strong correlation with the orbital degree of freedom in RB$_4$ (R=Gd,Tb,Dy).[4]

A strong structural anisotropy in these compounds gives rise to the electrical and magnetic anisotropies. PrB$_4$, for example, favors the ferromagnetic spin ordering along the c-axis.[3] On the other hand, for ErB$_4$, the magnetic susceptibility normal to the c-axis is nearly constant up to 70 K, whereas the susceptibility along the c-axis shows a complex temperature dependence.[3] This indicates that the spin-orbit interaction is important in these systems.

In this study, we have investigated the electronic structures and magnetic properties of RB$_4$ (R=Yb,Pr,Gd,Tb,Dy). The band calculations are performed by using the linearized muffin-tin orbital (LMTO) band method in the atomic sphere approximation. The local spin-density approximation (LSDA) is adopted for the exchange-correlation potential. Since the RB$_4$ system has the packing ratio of more than 60%, the LMTO method is expected to produce reliable band structures.[5] The spin-orbit (SO) interaction and the on-site Coulomb repulsion (U) are also considered to describe f states of R ions properly (LSDA+SO and LSDA+SO+U).[6]

First, we have compared the total energies between paramagnetic and ferromagnetic phases of RB$_4$ in the LSDA. We found that YbB$_4$ has a stable paramagnetic state, while all the other RB$_4$ have stable ferromagnetic states. These features are consistent with the Stoner factor calculations. The Stoner factor for YbB$_4$ is less than 0.5, whereas the Stoner factors for the other materials are larger than 2.0. According to the Stoner criterion[7] for metallic systems, the stoner factor larger than 1 will lead to the ferromagnetic instability.

Then we have compared the total energies between ferromagnetic and antiferromagnetic phases for PrB$_4$ and GdB$_4$. We have obtained the ferromagnetic ground state for PrB$_4$ and the antiferromagnetic ground state for GdB$_4$ in agreement with the observation. However, GdB$_4$ is considered to have more complicated noncollinear antiferromagnetic state, which is not described by the simple collinear antiferromagnetic spin configurations. In the following, we will consider the results for the ferromagnetic phases of RB$_4$.

The valence band structure for RB$_4$ is more or less similar to each other, except for the difference in the location of f states of R ions. As the strong hybridization among the B ions is induced by the crystal structure, R ion hardly affects the covalent bonding states among the B ions. Accordingly the f states of R ion could be described by Hund's rule.

Figure 1 provides the local density of states (DOS) for Yb and three types of B ions in the paramagnetic phase of YbB$_4$. In Fig. 1(a), $J_{5/2}$ and $J_{7/2}$ states are split by the SO

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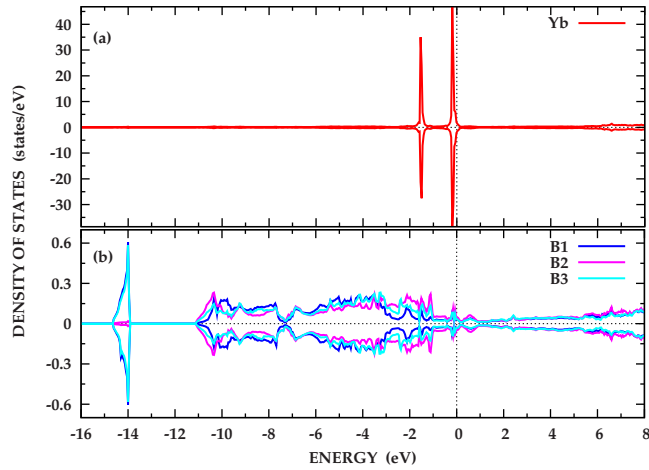[c] Author to whom correspondence should be addressed. Electronic mail: bimin@postech.ac.kr.

FIG. 1. (Color online) DOSs from the LSDA+SO band structure calculation for YbB$_4$: (a) the local DOS for Yb ions and (b) the local DOS of each boron ion. The local DOSs show the nearly divalent nature of Yb ion and the strong covalent bonds among boron ions

interaction with the gap of ~1.5 eV. Divalent Yb^{2+} ion with $4f^{14}6s^0$ electron configuration has no magnetic moment, while trivalent Yb^{3+} with $4f^{13}6s^0$ electron configuration possibly contributes magnetic properties in solid solutions. Therefore, the valency of Yb ion plays an important role in determining the magnetic state of YbB$_4$. In Fig. 1(a), $4f$ states seem to be fully occupied. However, it cannot be simply said that Yb ions are in the divalent state. Since the DOS
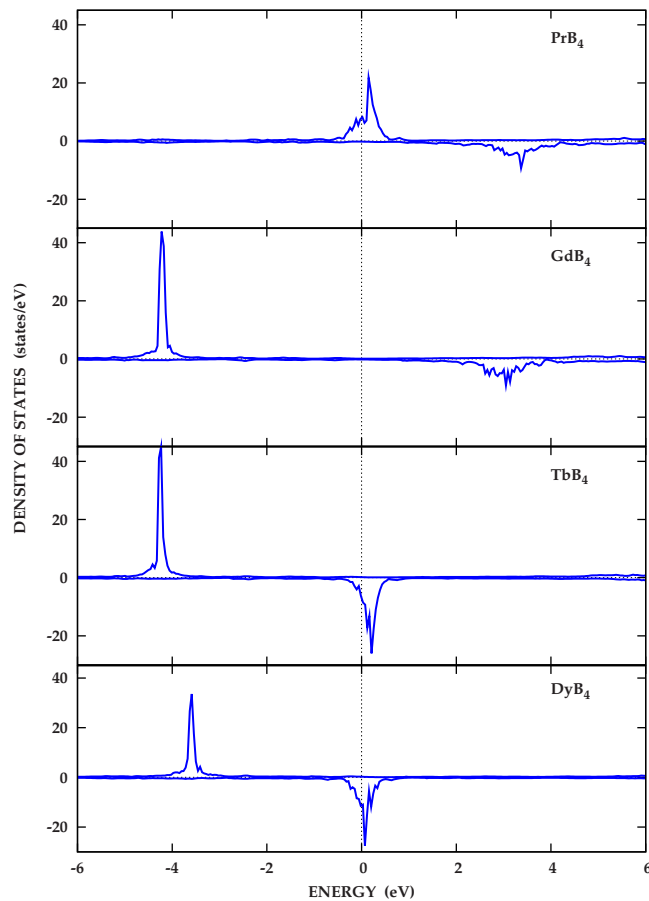

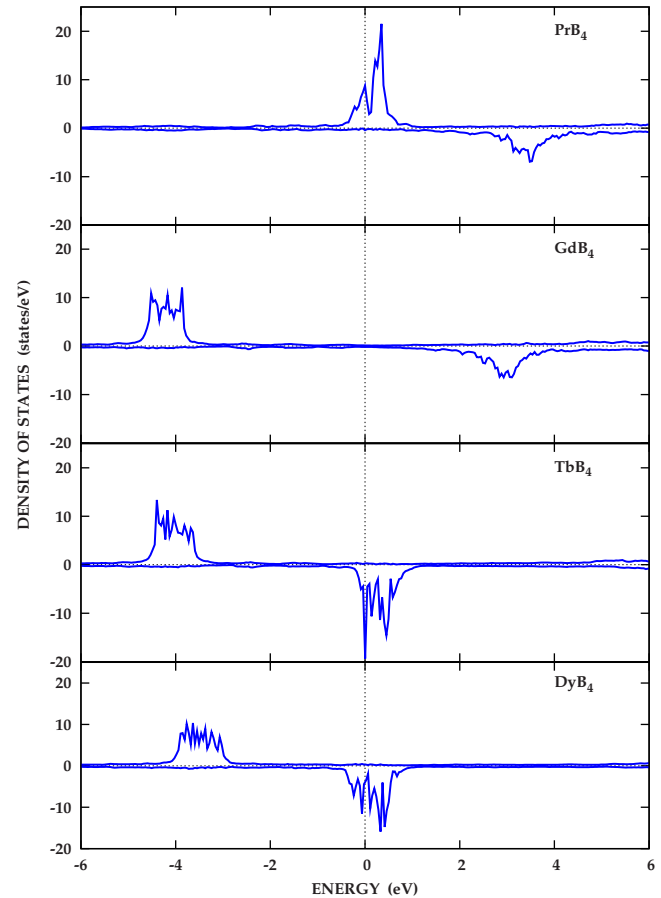FIG. 3. (Color online) The local DOSs of $4f$ for RB$_4$ in the LSDA+SO. The bandwidths are mostly increased by the SO interaction.

of $4f$ states at the Fermi energy (E_F) has nonzero value, Yb ions would be in the nearly divalent state. The local DOSs of B1 and B3 which constitute the B$_6$ octahedra are very similar to that of B2 which bridges the octahedra, suggesting the strong covalent bonding between them. It is noted that the DOSs at around −14 eV correspond to the octahedron molecular orbitals of B1 and B3 ions.

For the cases of RB$_4$ $(R=Pr,Gd,Tb,Dy)$, we will discuss the effects of spin-orbit interaction and on-site Coulomb repulsion (U) on the electronic structures. Figures 2–4 provide the local DOSs $4f$ states for RB$_4$ $(R=Pr,Gd,Tb,Dy)$ in the LSDA, LSDA+SO, and LSDA+SO+U $(U=4$ eV, J $=0.9$ eV), respectively. The SO effect gives rise to the broadened $4f$ state. Noteworthy is that, in the LSDA and the LSDA+SO, the majority spin $4f$ DOS of GdB$_4$ is hardly distinguishable from that of TbB$_4$ but, in the LSDA+SO +U, they become quite distinguishable.

Table I is the summary of calculated spin and orbital magnetic moments for RB$_4$ in the LSDA+SO and the LSDA+SO+U. The differences of the spin magnetic moments are negligible between the LSDA+SO and the LSDA+SO+U. However, the deviations of the orbital magnetic moments between the two are as much as ~2.0μ_B for PrB$_4$ and ~1.0μ_B for TbB$_4$ and DyB$_4$. As the majority spin $4f$ states in PrB$_4$ are located near E_F, the effect of U is relatively larger than in other compounds. Since the LSDA +SO+U describes the localized character of $4f$ electrons
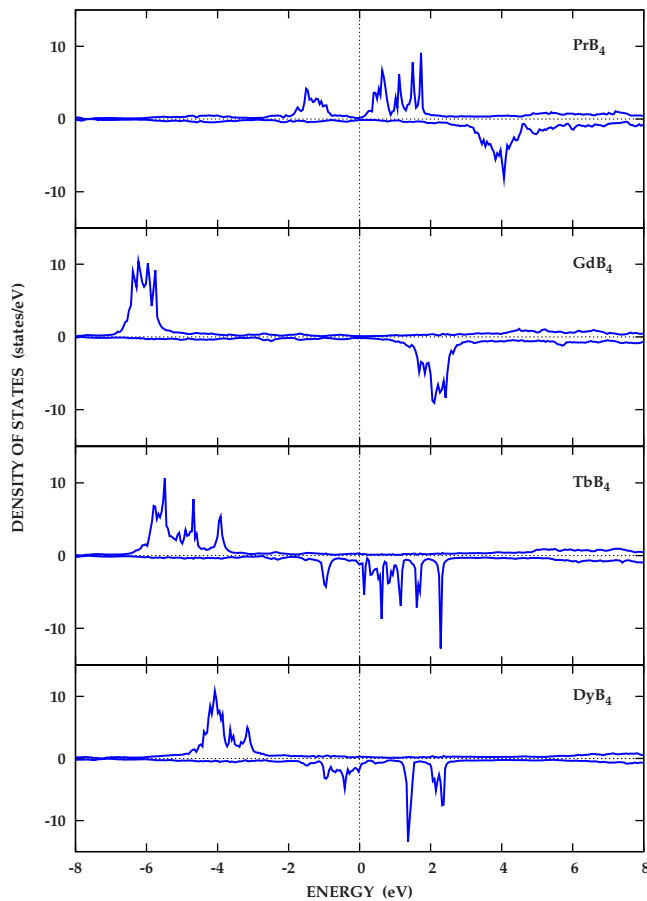

FIG. 2. (Color online) The local DOSs of $4f$ for RB$_4$ in the LSDA.

FIG. 4. (Color online) The local DOSs of $4f$ for $R\mathrm{B}_4$ in the LSDA+SO $+U$ ($U=4.0$ eV, $J=0.9$ eV). The localized character of $4f$ electrons is described well by considering the on-site Coulomb repulsion (U).

TABLE I. The calculated spin magnetic moments (SMs) and orbital magnetic moments (OMs) for $R\mathrm{B}_4$ in the LSDA+SO and the LSDA+SO+U ($U=4.0$ eV, $J=0.9$ eV). The magnetic moment is in units of μ_B per R ion.

	LSDA+SO		LSDA+SO+U	
	SM	OM	SM	OM
PrB$_4$	2.08	−2.15	2.17	−4.10
GdB$_4$	7.00	0.00	7.00	0.01
TbB$_4$	5.75	2.38	5.73	3.38
DyB$_4$	4.59	3.96	4.40	4.98

and boron ions. Therefore the valence states of R ions in $R\mathrm{B}_4$ ($R=\mathrm{Pr,Gd,Tb,Dy}$) are close to the trivalent state.

In conclusion, we have found that YbB$_4$ has a paramagnetic ground state with nearly divalent Yb^{2+} ions, while the other $R\mathrm{B}_4$ ($R=\mathrm{Pr,Gd,Tb,Dy}$) have the magnetic ground states with trivalent R ions. We have confirmed that the strong bonding exists among the B ions, and R ions hardly affect the covalent states among the B ions. The spin and orbital magnetic moments of R ions in the LSDA+SO+U are in good agreement with those from Hund's rule, even though there are small discrepancies due to the existing covalent bonding between R and B ions.

well, it is expected to give the right orbital magnetic moments for $R\mathrm{B}_4$.[6] The trivalent states of Pr^{3+}, Gd^{3+}, Tb^{3+}, and Dy^{3+} have f^2, f^7, f^8, and f^9 electron configurations, respectively. Then, according to Hund's rule, Pr^{3+}, Gd^{3+}, Tb^{3+}, and Dy^{3+} would have the orbital magnetic moments of −5.0, 0.0, 3.0, and 5.0μ_B per R ion, respectively. The spin and orbital magnetic moments obtained from the LSDA+SO+U in Table I are in good agreement with the expected values from Hund's rule. Small discrepancy would be attributed to the band effect, that is, the existing covalent bonding between R

[1] K. H. J. Buschow and J. H. N. Creyghton, J. Chem. Phys. **57**, 3910 (1972).
[2] J. Y. Kim, B. K. Cho, H. J. Lee, and H.-C. Kim, J. Appl. Phys. **101**, 09D501 (2007).
[3] J. Etourneau, J. P. Mercurio, A. Berrada, and P. Hagenmuller, J. Less-Common Met. **67**, 531 (1979).
[4] S. Ji, C. Song, J. Koo, K.-B. Lee, Y. J. Park, J. Y. Kim, J.-H. Park, H. J. Shin, J. S. Rhyee, B. H. Oh, and B. K. Cho, Phys. Rev. Lett. **91**, 257205 (2003); S. Ji, C. Song, J. Koo, J. Park, Y. J. Park, K.-B. Lee, S. Lee, J.-G. Park, J. Y. Kim, B. K. Cho, K.-P. Hong, C.-H. Lee, and F. Iga, Phys. Rev. Lett. **99**, 076401 (2007).
[5] H. L. Skriver, *The LMTO Method* (Springer-Verlag, Tokyo, 1984).
[6] S. K. Kwon and B. I. Min, Phys. Rev. Lett. **84**, 3970 (2000).
[7] D. J. Kim, *New Perspectives in Magnetism of Metals* (Kluwer Academic, New York, 1999).