First - principles investigation of magnetism of the rare - earth hexaboride RB_6 (R = La, Ce, Nd, Sm, Eu)

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Electronic and magnetic properties of the RB_6 (R = La, Ce, Nd, Sm and Eu) crystals were investigated by using the first - principles method within the framework of the density functional theory. The ground state of lanthanum hexaboride (LaB_6) is nonmagnetic crystal, while the others RB_6 (R = Ce, Nd, Sm and Eu) are ferromagnetic crystal due to the partial occupations of electrons on 4f orbital for rare – earth atoms. We have done the prediction of lattice parameters, magnetic moments of magnetic ions and total magnetizations of the RB_6 crystals.

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I. INTRODUCTION

Rare - earth hexaborides have been attracting much attention because of their interesting electronic and magnetic properties, which include metallic, semiconducting [1], superconducting [2], fluctuating valence [3] and heavy fermion behavior [4].

Patil *et al.* experimentally studied the electronic property of BR_6 using the high resolution X - ray photoemission spectroscopy (XPS) [5–7]. They observed the influence of 4f states on the surface state [5] and unusual line shape of core B(1s) states of rare - earth hexaborides [6]. Singh *et al.* have studied the optical and electronic properties of the rare - earth hexaborides BR_6 (R = La, Ce, Pr, Nd, Sm, Eu and Gd) using the full potential linearized augmented plane wave method [8]. Their electronic structure calculations were shown that the R(5d) and B(2p) - states are to be overlap at the X symmetry point and the magnetic moment of the ferromagnetic (FM) rare - earth hexaborides increases with increasing 4f occupation.

The samarium hexaboride (SmB_6) is a candidate material for a new topological Kondo insulator and the first strongly correlated heavy fermion material to exhibit topological surface states [9–14]. In early studies of topological insulators, due to the absence of realistic materials, most discussions were based on the model Hamiltonians. The modern theoretical studies on the topological insulators been intensively developing by both the Model Hamiltonian and first - principles methods in solids [15–17].

In this paper, we present the results of electronic and magnetic properties of the rare - earth hexaboride BR_6 (R = La, Ce, Nd, Sm and Eu) crystals investigated by using the first - principles method within the framework of density functional theory (DFT) [18, 19].

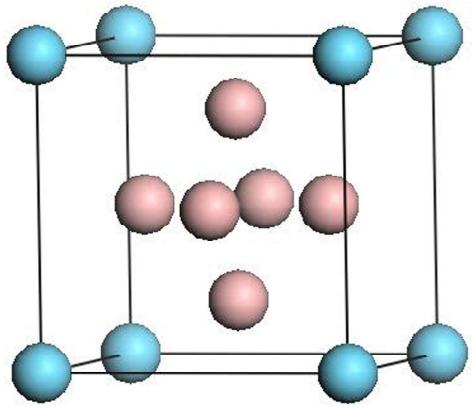

FIG. 1: (Color online) The unit cell of rare - earth hexaborides RB_6 (R = La, Ce, Nd, Sm and Eu) crystals. The rare - earth magnetic ion is sited at the cube corners and the six boron atoms are sited at the body – center position.

II. COMPUTATIONAL DETAILS

The rare – earth hexaborides crystallize in a cubic structure with the space group $Pm\bar{3}m$ (No. 221 in the International Tables of Crystallography) with rare – earth atoms occupying the cube corners while boron octahedral at the body – center position [20]. In these structures, each rare - earth magnetic ion is surrounded by eight boron octahedral, as shown in Figure 1.

Our calculations are based on the projector augmented wave (PAW) method [21] using the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) [22] within the frame-

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work of DFT [18, 19], as implemented in the QUANTUM ESPRESSO package [23]. The interaction between the ions and valence electrons is expressed as the ultrasoft pseudopotential [24]. The following electronic states are treated as valence states: B($2s^2$, $2p^1$), La($5s^2$, $5p^6$, $5d^1$, $6s^2$), Ce($4f^2$, $5s^2$, $5p^6$, $6s^2$), Nd($4f^4$, $5s^2$, $5p^6$, $6s^2$), Sm($4f^6$, $5s^2$, $5p^6$, $6s^2$) and Eu($4f^7$, $5s^2$, $5p^6$, $4s^2$) for atoms. The wave functions are expressed as plane waves up to a kinetic energy cutoff of 40 Ry. The summation of charge densities is carried out using the special k - points generated by the (14 x 14 x 14) grid of Monkhorst - Pack scheme respectively [25]. The tetrahedral method is used [26] when the electronic density of state (DOS) is evaluated. For the self - consistent cycle the total energy convergence is 10^{-8} eV. The occupation numbers of electrons are expressed Gaussian distribution function with an electronic temperature of $kT = 0.001$ Ry. We performed the variable cell optimization and fixed the crystallographic angles. The atomic ionic positions were relaxed until the residual forces were less than 0.05 eV/Å. In order to find the magnetic ground state of the rare - earth hexaboride RB_6 (R = La, Ce, Nd, Sm and Eu) crystals, the spin polarized calculations to find the magnetic energy gain ($\Delta E = E_{FM} - E_{NM}$) between the FM and nonmagnetic (NM) states were performed in all the cells.

III. RESULTS AND DISCUSSION

We have first performed the calculations of atomic and variable cell optimizations of RB_6 (R = La, Ce, Nd, Sm and Eu) crystals. We predicted the lattice parameters to be 4.15, 4.12, 4.14, 4.14 and 4.16 Å in the RB_6 (R = La, Ce, Nd, Sm and Eu) crystals respectively. Overall, our predicted structure properties reproduce quite well the other theoretical and experimental results [12, 27–29], which are shown in the parentheses in Table I. Note that the structural parameters of rare - earth hexaboride crystals are not strongly altered in the rare - earth atoms due to atomic radii of La, Ce, Nd, Sm and Eu atoms being similar.

We estimated the magnetic energy gains between the FM and NM states and predicted the magnetic moments of magnetic ions and total magnetizations of the RB_6 crystals. For the LaB_6 crystal, the magnetic energy gain is not observed and the magnetic moment of La atom and total magnetization is found to be zero. It is related to following the two points. The 4f ornital of La ion has not an electron occupation and the valence electrons are symmetrically fully occupied on the majority and minority states of other orbitals (We did not show the total and orbital projected DOS). Therefore, the NM state is favored in the lanthanum hexaboride (LaB_6) crystal. For the other RB_6 (R = Ce, Nd, Sm and Eu) crystals, the magnetic energy gain is observed and these magnetic energy gain between the FM and NM states is obtained to -0.03, -1.79, -4.90 and -6.96 eV/cell for the CeB_6, NdB_6, SmB_6 and EuB_6 crystals respectively. Therefore, the FM state is favored in the RB_6 (R = Ce, Nd, Sm and Eu) crystals (See Table I).

The origin of the magnetic energy gain is related to the unbalance on the majority and minority spin states of electrons on the 4f orbital of rare - earth atoms in the RB_6 (R = Ce, Nd, Sm and Eu). We have shown the total and orbital projected DOS in Figure 2. The majority and minority states of B(2p) orbital are symmetrically spreading from -10 eV to -1.0 eV below the Fermi level. It is shown that B atoms are nonmagnetic ions. But the 4f state of rare - earth atoms is strongly localized nearly the Fermi level. The electrons are partially occupied on the minority state of 4f orbital and its majority state is empty in the CeB_6 crystal. The 4f electrons are partially occupied on the majority spin state and the minority spin states for RB_6 (R = Nd, Sm and Eu) are fully empty, i.e. the major contribution to the total magnetization is from the spin polarization of 4f state of rare - earth atoms.

For the CeB_6 crystal, the magnetic energy gain is very small and found to be -0.03 eV/cell. It is shown the CeB_6 crystal is a weak FM crystal and the total magnetization is found to be 0.75 μ_B/cell due to the magnetic moment of 0.72 μ_B/atom for Ce atom. For the EuB_6 crystal, the FM state of EuB_6 crystal is more favorable than that of other RB_6 (R = Ce, Nd and Sm) because of the energy difference of -6.96 eV/cell. Therefore, the total magnetization is found to be 6.78 μ_B/cell, which is quite high. It is shown us that the EuB_6 crystal is strong FM crystal. This magnetization is defined by the value of magnetic moment for Eu atom and its value is found to be 6.81 μ_B/atom. These values of total magnetization for rare - earth hexaborides are well in agreement with those of other researchers [30, 31]. Here we should note that the difference of these values is related to the weak induced magnetic moment of non magnetic B atoms. It does not affect the spin polarization of B(2p) state.

For the NdB_6 and SmB_6 crystals the total magnetizations and magnetic moments are reasonable and the total magnetization were found be 3.45 and 5.73 μ_B/cell, respectively, which correspond to the magnetic energy gains of -1.79 and -4.90 eV/cell respectively. These total magnetization generates by the magnetic ions of Nd and Sm atoms and their magnetic moments is found to be 3.43 and 5.74 μ_B/atom respectively.

IV. CONCLUSION

In conclusion, we have shown that the ground state of lanthanum hexaboride (LaB_6) is nonmagnetic state and the partial occupation of electrons on the 4f orbital of rare - earth atoms creates ferromagnetic state in the RB_6 (R = Ce, Nd, Sm and Eu) using the first - principles method within the framework of DFT. We have predicted the lattice parameters, magnetic moments of magnetic ions and total magnetizations of the RB_6 crystals.

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TABLE I: For the rare - earth hexaboride RB_6 (R = La, Ce, Nd, Sm and Eu) crystals, the lattice parameter, the energy gains between the FM and NM states ($\Delta E = E_{FM} - E_{NM}$), the spin states, magnetic moments of magnetic ions and total magnetizations. The experimental lattice parameters and total magnetizations are in the bracket.

	LaB_6	CeB_6	NdB_6	SmB_6	EuB_6
a (Å)	4.15(4.16)[27]	4.12(4.14)[28]	4.14	4.14(4.13)[12, 29]	4.16
ΔE (eV/cell)	0.0	-0.03	-1.79	-4.90	-6.96
Spin state	NM	FM	FM	FM	FM
m (μ_B/atom) (R)	0.0	0.72	3.43	5.74	6.81
M_{tot} (μ_B/cell)	0.0	0.75(1.00)[30]	3.45	5.73	6.78(7.30)[31]

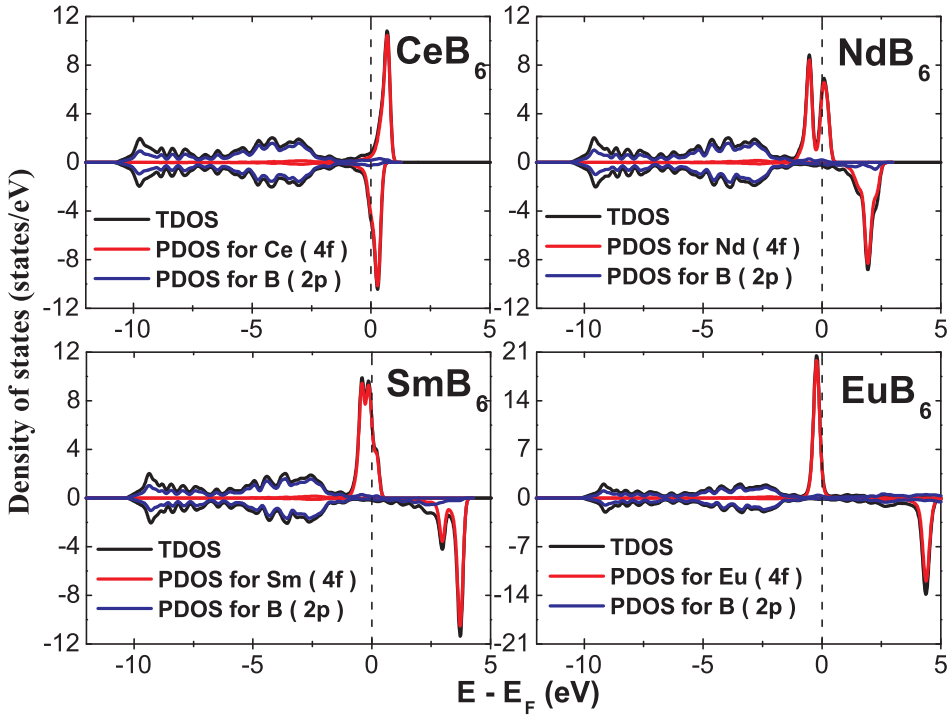

FIG. 2: (Color online) The total and orbital projected DOS for the rare - earth hexaborides RB_6 (R = Ce, Nd, Sm and Eu) crystals. The Fermi level corresponds to the dashed line.