Origin of the magnetism in CaB_6: A first-principles study

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Through systematic density functional calculations, we revealed that the weak ferromagnetism in CaB_6 and related materials stems from the joint effect of boron vacancies and impurities. Each boron vacancy introduces strongly localized gap states around its first-neighbor B atom right above the Fermi level. The partial occupation of these gap states caused by either lattice distortion or addition charge triggers magnetic instability and the local magnetic moment can be as large as $0.8-1.2\mu_B$ in various cases.

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I. INTRODUCTION

The intriguing discovery of Young *et al.*[1] that semimetal $Ca_{0.995}La_{0.005}B_6$ possesses weak ferromagnetism at remarkably high temperature has fueled extensive studies of various magnetic hexaborides.[2–7] Since none of their constituents has partially filled *d* or *f* orbitals, it is significant to investigate if the conventional band magnetism theory still applies to these systems. Matsubayashi *et al.* suggested that ferromagnetism observed in these materials stems from the presence of transition-metal impurities.[8] However, Maiti *et al.*, who made sure that no magnetic ingredient was involved in the procedure of fabricating their magnetic CaB_6 samples, challenged this conjecture.[9] Density-functional calculations found zero local magnetic moment in these systems even with dopants, Ca vacancy, and boron vacancy (V_B), unless the entire B_6 octahedron is removed under a huge energy penalty of 50.7 eV.[20] The calculated Fermi surface that nests around the *X* point in the Brillouin zone[10,11] was utilized by Zhitomirsky *et al.*[12] and by Barzykin and Gorkov as the driving factor for either excitonic instabilities or structural deformation, and both may lead to weak magnetization. However, these models lost their grounds since GW calculations as well as photoemission and x-ray emission experiments indicate a sizeable energy gap at the *X* point. Therefore, is still an open question: What is the governing factor for the "unusual" ferromagnetism observed in hexaborides? Although the details have never been clearly elucidated, several groups recognized the significance of lattice imperfections in the past. This case was reinforced by recent experimental findings of Maiti *et al.*, who explicitly pointed out that deficiencies in the *B* sublattice is the prime factor for the ferromagnetism in their samples. In particular, they found that ferromagnetism in CaB_6 vanishes if 99.9999% highly pure boron powder was used instead of the 99.7% one.[9] Several other authors also reported that magnetic moment of CaB_6 strongly depends on the defect and impurity concentration.[13–16]

In this Brief Report, we found sizable magnetization in CaB_6 because of the formation of V_B-V_B and V_B-impurity (e.g., carbon or nitrogen) pairs. Systematic density functional calculations clearly demonstrated that each V_B-impurity pair might produce a local magnetic moment up to $1.3\mu_B$ as a result of alternation of lattice distortion mode and charge transfer toward the gap states. The magnetic instability can be explained in the framework of the Stoner model. Interestingly, the presence of C or N impurities not only enhances the spin polarization around the V_B site, but also promotes the formation of V_B in a large vicinity.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The calculations were performed with the all-electron full potential linearized augmented plane wave (FLAPW) method[17]as well as the Vienna *ab initio* simulation package (VASP).[18] The generalized gradient approximation in the formula of Perdew-Burke-Ernzerhof[19] was adopted to describe the exchange-correlation interaction. No shape approximation was assumed in charge, potential, and wave-function expansions. In the FLAPW calculations, the energy cutoffs of 225 and 16 Ry were chosen for the charge potential and basis expansions in the interstitial region. Spherical harmonics with a maximum angular-momentum quantum number of $l_{max}=8$ were used in the muffin-tin region ($r_{Ca}=2.3$ a.u. and $r_B=r_C=r_N=1.3$ a.u.). In the VASP calculations, an energy cutoff of 350 eV was chosen for the basis set and the projector augmented wave (PAW) pseudopotentials were used for the description of electron-ion interaction. The lattice constants and the atomic positions were fully relaxed through the VASP calculations with a criterion that requires the maximum force on atoms smaller than 0.01 eV/Å. The magnetic properties were calculated with the FLAPW code. The optimized lattice constant for the bulk CaB_6 is 7.84 a.u., in good accordance with the experimental data, 7.86 a.u.[10]

III. RESULTS AND DISCUSSIONS

We first reexamined results of Monnier and Delley[20] for CaB_6 with a single V_B, C, or N in the $3\times3\times3$ supercell through the FLAPW calculations. Indeed, none of these systems carries meaningful magnetic moment as shown in Table I. Nevertheless, it is interesting to note that the presence of V_B produces a pronounced peak in the band gap, as shown in Fig. 1(a). From their charge-density distributions given in Fig. 2 and also through the band-structure analysis, we found that these gap states are associated with two dangling bonds

TABLE I. Local magnetic moments and relative energies of CaB_6 in different configurations for which more details are provided in Fig. 4(a).

Defect	Magnetic moment (μ_B)	Energy (eV)
	$(2\times2\times2)$ Supercell	
Single V_B	0.31	
Single C_B	0.00	
Single N_B	0.00	
V_B+V_B	0.48	
V_B+C_B	0.62	
V_B+C_B	0.26	
C_B+N_B	1.00	
	$(3\times3\times3)$ Supercell	
Single V_B	0.00	
Single C_B	0.00	
Single N_B	0.00	
V_B+C_B *A*	1.26	0.646
V_B+C_B *B*	1.01	0.561
V_B+C_B *C*	0.00	0.401
V_B+C_B *D*	1.04	0.547
V_B+C_B *E*	1.00	0.492
V_B+C_B *F*	1.00	0.281
V_B+C_B *G*	0.41	0.145
V_B+C_B *H*	0.00	0.000
V_B+C_B *I*	0.84	0.111
V_B+C_B *J*	0.82	0.218
V_B+N_B	0.38	

centered on the B atom that is the nearest to the void, denoted as B_N henceforth. According to the Stoner model, magnetic instability is expected on B_N if these gap states are partially filled by adding electrons into the system or by altering their energies. Practically, these are achievable through introducing La, C, Si, and N impurities as well as through slightly changing atomic arrangements with another V_B nearby.

To test this idea, we performed calculations by moving the two adjacent B_6 cages that comprise either V_B or B_N along the joint line. The changes of total energy and magnetic moment are presented in Fig. 3 for two distortion modes, respectively. The first mode has two cages moved together, denoted as the α mode in inset in Fig. 3, whereas in the second mode they move in the opposite directions, denoted as the β mode in the inset in Fig. 3. The most striking finding is that the system possesses a large magnetic moment before relaxation, $\sim 0.45\mu_B$ per vacancy, regardless the size of the cell. This magnetic moment is rather stable in a large range of distortion in the α mode, which is preferential in the $2\times2\times2$ supercell. In the fully relaxed structure, the presence of a single V_B in the $2\times2\times2$ supercell bestows a magnetic moment of $0.31\mu_B$, very substantial for a system without *d* and *f* elements. Since B atoms in CaB_6 are negatively charged, the presence of each V_B provides 1/3 extra electron

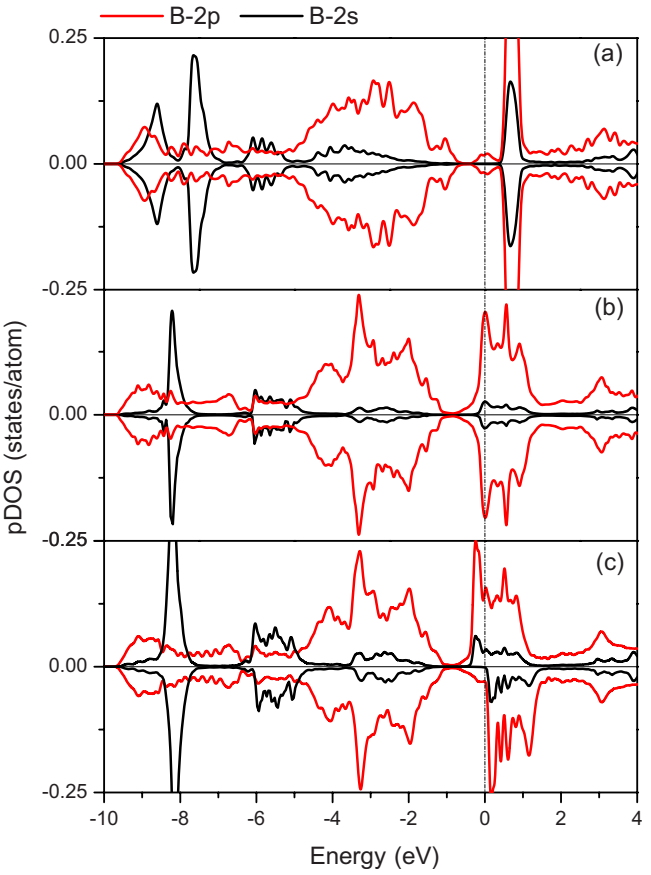

FIG. 1. (Color online) Projected density of states of the B_N atom in CaB_6 calculated with (a) $3\times3\times3$ supercell, (b) $2\times2\times2$ supercell without spin polarization, and (c) $2\times2\times2$ supercell with spin polarization. Zero energy indicates the position of the Fermi level.

in its vicinity and hence produces ferromagnetism in hexaborides. The projected density of states (PDOS) curves of B_N in Figs. 1(b) and 1(c) clearly indicate that the magnetization can be explained in the framework of the Stoner model, namely, the magnetic instability is triggered by the presence of high peak of PDOS at the Fermi level in calculations without spin polarization.

Nevertheless, the β mode leads to much lower energy if a $3\times3\times3$ supercell is adopted and, furthermore, the magnetic moment gradually disappears when V_B and B_N are set to

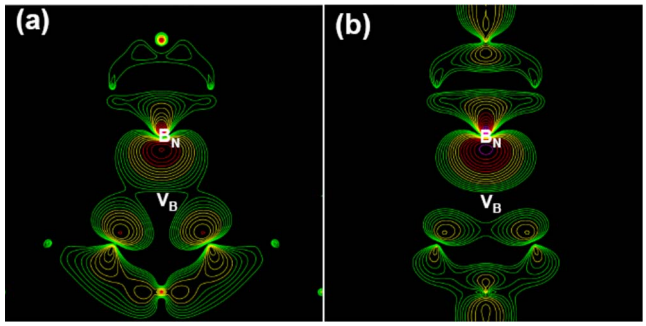

FIG. 2. (Color online) Charge density distribution of two gap states. Contours start from 1.0×10^{-4}e/a.u.^{3} and increase consecutively by a factor of 1.2.

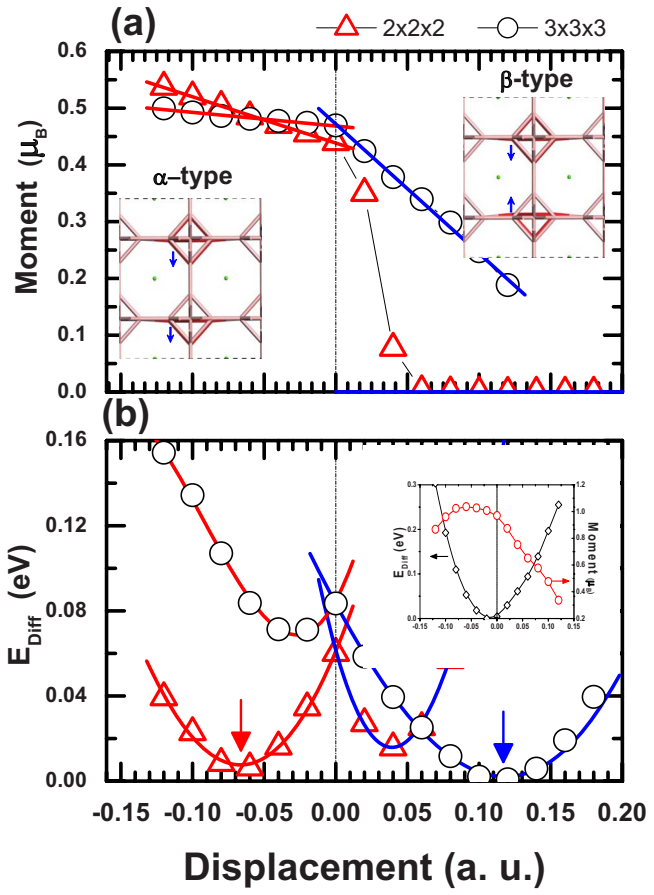

FIG. 3. (Color online) (a) Magnetic moments and (b) energy changes of CaB_6 for two possible distortion modes as shown in the insets in panel (a) for the V_B-B_N pair in either the $2\times2\times2$ or $3\times3\times3$ supercell. The inset in panel (b) shows results in the $3\times3\times3$ supercell with the presence of a carbon impurity in the B cage opposite to V_B.

relax toward each other. Therefore, as was already stated before and also as reported by Monnier and Delley,[20] the magnetic moment vanishes in a fully relaxed structure if only a single V_B is involved in the $3\times3\times3$ supercell. It is clear now that the magnetization of CaB_6 is driven by the formation of V_B, in conjunction with an appropriate local lattice distortion, rather than by dopants such as La as believed before. Therefore, the key issue is to find means that promote the α-mode distortion around V_B and, furthermore, to provide additional electrons to B_N so as to activate the magnetic instability by shifting the Fermi level to the PDOS peak of the gap states.

To elucidate the effect of C or N impurities, we deliberately arrange a V_B together with a carbon-dopant (C_B) along a chain and redo the calculations. The inset in Fig. 3(b) shows that the V_B-B_N pair prefers the α-mode relaxation in the $3\times3\times3$ supercell, with the aid of C_B at site D shown in Fig. 4(a). Meanwhile, as a result of partial charge transfer from C_B toward B_N, the magnetic moment enhances to larger than $1.0\mu_B$ in several cases in Table I. The magnetization vanishes only when (1) the C dopant directly replaces the B_N atom because the Fermi level lies above the gap states with the availability of excessive electrons on that site; or (2) the

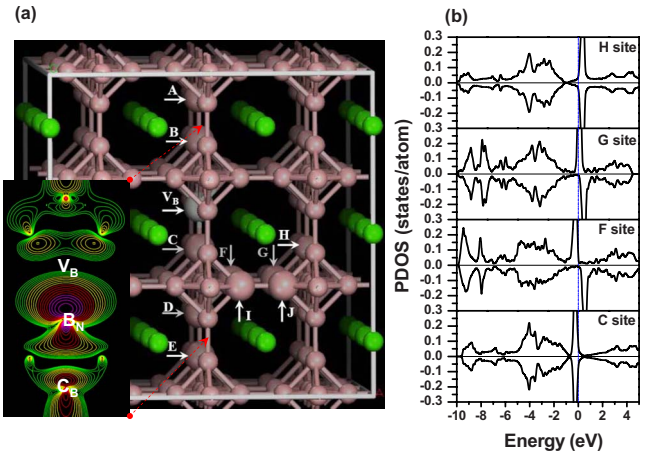

FIG. 4. (Color online) (a) The atomic arrangements of V_B and C_B in the $3\times3\times3$ supercell and (b) the projected density of states of B_N for several configurations. The inset in panel (a) shows the spin density, with contours starting from $1.0\times10^{-4}e^3/a.u.^3$ and increasing consecutively by a factor of 1.2.

C dopant is too far away from B_N so the additional electron can hardly reach the B_N site. The spin-density distribution in the inset of Fig. 4 shows an apparent similarity to the wave function of the V_B-induced gap state in Fig. 2(b). The presence of C_B also leads to expansion of the B–B bonds. In the bulk CaB_6, the B–B bond lengths are 1.75 and 1.67 Å within and across the B_6 octahedra, respectively. In comparison, they expand to ~1.86–1.88 Å near V_B and C_B, and the B_6 cages also deform accordingly.

It is obvious that the energy position and the shape of the PDOS curve of the gap states around B_N are very sensitive to the location of C_B in Fig. 4. The correlation between large magnetic moments in Table I and the high PDOS peak at E_F in Fig. 4 for different V_B+C_B configurations indicates that the Stoner instability is responsible for the magnetization observed in CaB_6. C_B needs to take appropriate position for the efficient concurrence of charge transfer and structural distortion, necessary for the magnetization at B_N. Furthermore, the dopant should be placed in an octahedron other than the one that already hosts the primary V_B to avoid the missing link toward B_N. In several cases, the gap states are fully occupied in the majority-spin channel and the magnetic moment reaches $1.0\mu_B$. C_B induces sizable magnetic moment on the B_N site as far as from the G and J sites. The energy differences between different configurations are rather small so these different V_B+C_B configurations have comparable chance to form during fabrication. We found that the best configuration for facilitation of magnetization is to arrange V_B and C_B along a chain. However, if the carbon impurity directly takes the site of B_N, the gap states are fully occupied in both spin channels as shown in Fig. 4 for the C site. The magnetic moment is also negligible if C_B takes the H site, which is too far from B_N for the electron to get through. Interestingly, we found that the gap states of B_N are partially occupied and the magnetic moment can be as large as $\sim0.4\mu_B$, as listed in Table I, if N instead of C is used in this configuration.

Finally, the calculated formation energy of a single V_B in the $3\times3\times3$ supercell is about 11.0 eV, in agreement with

the results obtained by others.[20] Although the formation energy is quite large, it is perceivable that the density of V_B is still reasonably high in samples.[9] What makes it interesting is that the presence of carbon impurity at the *F*, *G*, *H*, *I*, and *J* sites lowers the formation energy of V_B in CaB_6 by 0.07–0.35 eV. This may facilitate the concurrence of V_B and C_B (or N_B) in a short distance and hence promote the magnetization around B_N as discussed above. We would expect that it is easier to form V_B and C_B pairs on the surface than in the interior region, due to availability of free space for relaxation, and hence may lead to stronger surface magnetization.

IV. CONCLUSIONS

In summary, we have revealed the likely origin of the "unusual" magnetization in CaB_6 through extensive density-functional calculations. The presence of V_B produces a strongly localized gap state around its first neighboring *B* site and the Stoner instability is then triggered by appropriate charge transfer and lattice relaxation. Carbon or nitrogen impurities also play an important role in the magnetism in CaB_6 through (i) promoting the α-mode distortion, (ii) donating charge to B_N, and (iii) enhancing the chance for the formation of V_B.

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