Electronic Structure and Origin of Ferromagnetism in CaB$_6$

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Electronic structure calculations using quantum Monte Carlo (QMC) methods conclusively show that pure CaB$_6$ is a narrow-gap semiconductor with an X-point gap $\sim$ 1.3 eV. This should put to rest controversies as to whether the compound is a semimetal or a semiconductor, as also theories suggesting it to be an excitonic insulator. Our extensive Hartree-Fock (HF) and density functional theory (DFT) calculations support the view that the hexaboride ferromagnetism can be induced by contamination with magnetic element atoms like Fe and that presence of La is not essential for this. La impurity, however, gives rise to a metallic state with a small electron-like Fermi surface as seen in ARPES experiments.

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Recently, a great deal of interest has been generated in divalent hexaboride CaB$_6$ mainly due to observation of unusual ferromagnetism (FM) in the system supposedly with Lanthanum doping [1]. The unusual feature of this ferromagnetic state is that it has very small moment $\sim 0.07 \mu_B$ per La atom and yet has very high Curie temperature, $T_C \sim 600K$. Theoretical models with unconventional many-body mechanisms were proposed as explanation for this FM in absence of d- or f-electrons in the system. For example, it was suggested [1, 2] that doped hexaboride forms the magnetically ordered ground state of a dilute electron gas while Zhitomirsky et al. and other workers [3] suggested it to be an excitonic insulator. Central to the idea of excitonic insulator is the assumption of a small band overlap of top of the B p valence states and bottom of the Ca d conduction states. This band overlap was suggested by early density functional theory (DFT) band structure calculations [4]. It is well-known by now that DFT in local density approximation seriously underestimates the band gap, hence models based on a small band overlap in these calculations are somewhat questionable. Going beyond DFT, the perturbational GW method band structures, which incorporate self-energy corrections, have been calculated for the system. Though one of them predicts a large band gap at the X-point of the Brillouin zone (BZ) of this simple cubic system [5], another shows a small overlap [6]. A very recent calculation using weighted density approximation predicts a band gap of $\sim 0.8$ eV at the X-point [7]. These conflicting results clearly point out that our understanding of basic properties of this interesting material is still rather limited.

Theoretical calculations reported in the literature show considerable controversy regarding metallic/semiconducting character of CaB$_6$ in the experimental results, too. Semimetal nature is supported by observation of metallic resistivity [8, 9], the de Haas-van Alphen effect [8, 10], and Shubnikov-de Haas results [11]. On the other hand, NMR [12], angle resolved photoemission spectroscopy (ARPES) [13], and thermopower experiments [14] suggest that CaB$_6$ is a narrow-gap semiconductor. Some recent high resolution ARPES [17] and combined transport, optical and tunneling measurements [16] very strongly suggest that pure CaB$_6$ is a semiconductor, while metallic character and FM in the system originate from boron-related defects.

While the pure system is poorly understood, there is very little understanding of the origin of FM in the system. Authors in ref. [17] proposed a scenario for FM in La-doped samples over a small concentration range by studying formation energies and associated moments of various defects. However, given the large formation energy of B$_6$ octahedron vacancy they found, and observation of FM in systems even without La-doping, make their proposal less likely. Various experimental groups have suggested, and there is growing consensus on this point, that FM in CaB$_6$ is an extrinsic effect related to magnetic impurities such as Fe and Ni [15, 19, 20], probably coming from B used in sample preparation. The most convincing argument for this is provided by the experiments of Cho et. al [16].

Hoping to clarify some of these issues, we did a detailed first principles electronic structure calculation of pure CaB$_6$ using Hartree-Fock (HF), DFT and quantum Monte Carlo (QMC) methods, and also did an analysis of the X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) data. This work is still in progress and will be reported in a future publication.
fects include substitutional impurities—Fe and La in the cation sublattice, and vacancies—a single missing B. For the first time, through the use of explicitly correlated many-body wavefunctions in variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) calculations, we conclusively show that pure CaB₆ is a semiconductor with an X-point gap of ~1.3 eV. Using HF and DFT methods, we have shown that i) La is not essential for ferromagnetism in the system, while ii) Fe substitutional impurities give rise to ferromagnetism, iii) B vacancy, and Fe and La substitutional impurities make the system metallic, iv) CaB₆ with La substitutional impurities has a small electron-like Fermi surface (FS), explaining some of the observations in ARPES experiments [13, 15]. Since experimental information about atomic structure around these defects is essentially absent, our studies should be understood as an exploration of various possible scenarios. Nevertheless, we believe our results suggest explanations to most of the experimental observations at least qualitatively, and give an accurate quantitative estimate of the gap in the pure system, thus clarifying the overall physics of CaB₆.

We performed our HF and DFT calculations using CRYSTAL98 and CRYSTAL03 codes [21, 22]. We used both all electron basis sets and ECPs in our calculations and they gave similar results. For QMC calculations we used the same basis sets with ECPs as used in HF. For QMC calculations, we used a Slater-Jastrow wavefunction of the form

$$\Psi = D^\dagger D^\dagger \exp \left[ \sum_{i,j,l} u(r_{ij}, r_{il}) \right].$$  (1)

The Jastrow correlation part depends on electron-ion distances r_{ij} and electron-electron distances rij and the term includes electron-electron coulomb terms and altogether contains 10 variational parameters. In the first step, these variational parameters are optimized by minimizing the variance in the local energy, E_L = \frac{1}{N} \sum_i |H_i - E_i|, H being the Hamiltonian of the system in which the core electrons are replaced by pseudopotentials (for Ca the Ne-core electrons were eliminated). Finally, a large part of the variational bias is eliminated by fixed-node DMC. Details of these methods have been discussed in the literature [23].

**Pure CaB₆**: As is typical with these methods, HF gave a large X-point gap of ~5.50 eV, while the use of hybrid functional B3LYP reduced the gap to ~0.86 eV. PW91 generalized gradient approximation (GGA) gave a conducting state and a small band overlap at the X-point, as found in all other such calculations in the literature (see fig. 1). For QMC calculations we used a 2 x 2 x 2 supercell so that the X-point of the primitive BZ is folded on to the Γ-point of the BZ corresponding to the simulation cell. Since we are interested in the gap at the X-point of the primitive BZ, we can work with wavefunctions at the Γ-point of the supercell BZ. The wavefunction is shifted for the Slater part of the many-body wavefunction for our QMC calculations were taken from HF calculations. For the ground state wavefunction, the N lowest energy orbitals were included. For the excited state, we promoted one electron from the top of the valence band to the bottom of the conduction band at the Γ-point of simulation BZ which corresponds to the folded X-point. Variational principle guarantees that the calculated energy is a strict upper bound for the lowest energy state of the symmetry imposed by the trial function. Since we are interested in direct gap, the excited state of interest in not the ground state of the particular symmetry (which is determined by the k-point occupation in a solid). It is well known that in such cases the DMC energy is not necessarily a strict upper bound of the excited state energy. However, fixed-node DMC gives a good estimate of the excited state energy. In fact, it is exact if the nodal structure of the trial function \(\Psi(R)\) is exact, and in most practical cases the fixed-node constraint is dominant and leads to energies which are higher than the exact energies for a given state (see ref. [24], for example). We optimized the variational parameters in the Jastrow part only for the ground state wavefunction, and used the same set for the excited state. The precise value of the gap we obtained in our DMC calculations is 1.3(2) eV. This is in very good agreement with all the experiments that give an estimate of the bulk band-gap [13, 14, 16]. Obviously, this result is based on fixed-node DMC single determinant trial wavefunctions.

Our results based on the fixed-node single-determinant trial wave function DMC method, which is a many-body approach different from previous calculations, suggest that the pure CaB₆ compound is a narrow-gap semiconductor. Hence we conjecture that the metallic character seen in transport measurements have originated from defects in the system. This result also suggests that the theories with unconventional mechanisms explaining FM in this system using early DFT band structures might not be correct and we believe that our calculations support the concept of certain impurities. Therefore, we conclude that CaB₆ is a narrow-gap semiconductor with both metallic and ferromagnetic character. Figure 1 shows the band structure of pure CaB₆ calculated with HF, B3LYP functional and PW91 GGA functional.
follow with calculations of CaB$_6$ with defects, proposing explanations for the origin of FM and metallic behavior as observed. As we mentioned, experimental information about atomic structures of possible defects in hexaborides is not available. Therefore our calculations of the hexaboride with defects only serve as models to illustrate the qualitative impact of imperfections on the electronic structure.

**CaB$_6$ with defects**: We present here results from our calculations of three different defects in CaB$_6$. We consider substitution of Ca in the lattice by Fe and La, and an isolated B vacancy. The first one is motivated by the suggestions that magnetic ions, possibly Fe or Ni, are responsible for FM in this system. Although there have been indications that Fe and Ni reside close to the surface layer [20], there are also experiments suggesting that they penetrate substantially into the bulk [25]. We treat these as bulk substitutional impurities to avoid complications of surface effects such as relaxation and reconstruction in our calculations. It has also been speculated that FM with high T$_c$ is due to boride formation–FeB or Fe$_2$B–which have T$_c$’s of 598 K and 1015 K respectively. However, this has been contradicted by other works [18]. Since the experimental evidence is not conclusive, we do not consider any possible boride formation either. B vacancy would presumably be the most natural defect in a nominally B deficient sample. Although no FM was seen in B deficient samples in ref. [17], we still study this system to understand its electronic properties. La substitution is motivated by the original observation of FM in the La substituted compound Ca$_{1−x}$La$_x$B$_6$.

Concentrations of various defects in conditions of thermal equilibrium depend on their formation energies (FE). The defect formation energy is defined in the usual way, as the difference between the binding energies of the pure solid and the solid with defect. Since there are no hints about structural relaxations around defects from experiments we did not consider such relaxations. At least in some cases these have been shown to be negligible [17]. However, such relaxations cannot be ruled out a priori and therefore our formation energies (Table I) are most probably biased towards the defect formation being less favorable. Nevertheless, since we are interested in a basic, qualitative understanding of the electronic structure changes in presence of defects, we believe that our model calculations are sufficient for this purpose.

From impurities in boron, or by some other means during sample preparation, would be present in minute amounts because of its relatively large FE. The smallest impurity concentration we have been able to study is ~3.7% of Fe doping (one Ca replaced in a 3 × 3 × 3 supercell) because of system size limitations. Going down from 12.5% to 3.7%, an Fe impurity always stabilizes a FM state over a paramagnetic one. As an origin of this FM state, we note that there is a splitting of Fe d states due to the ligand field of the B octahedra. In presence of this cubic field, the five degenerate d states split into two different energy levels: triply degenerate t$_{2g}$ states, and doubly degenerate e$_g$ states. The result is a 3/2 spin on Fe with a ~1/2 spin over surrounding B atoms that forms a local magnetic moment. A FM state will form when these local moments interact either through hybridized Fe-B states, or in regions where there is a high Fe concentration, such as near the surface.

**TABLE I**: Defect formation energies in eV calculated with HF and B3LYP.

| Defect        | HF  | B3LYP |
|---------------|-----|-------|
| Fe-substitution | 15.6 | 6.9   |
| B-vacancy     | 15.8 | 14.8  |
| La-substitution | -0.5 | -2.8  |

**Fig. 2**: (Color online) Band structure of CaB$_6$ with 3.7% Fe impurity with HF, B3LYP and PW91 functionals. Black(solid) and red(dotted) lines represent up and down spin energies in the FM ground state. Fermi energy in all cases has been set to 0.
moving a B has the effect of taking away a B p valence electron from top of the valence band. The system becomes metallic and the position of the Fermi energy tells that it has a hole-like FS at the Γ-point of the BZ of the 2 × 2 × 2 cell. Although our calculations show that a magnetically ordered state is favored, the energy difference with a paramagnetic state is only ∼ 0.05 eV per primitive cell. This energy difference is too small to be taken as an indication of a magnetic ground state, and in fact, can be an artifact of the B3LYP method. This conjecture is supported by the GGA results in ref. [17] where B vacancy is not seen to give rise to any appreciable magnetic moment.

Now we come to our study of La substitution of Ca. Because of the initial observation of magnetism in Ca$_{1−x}$La$_x$B$_6$, it was thought that La plays a role in the origin of FM in the system. This makes the study of La substitution particularly interesting. Also note that the formation energy of a La substitutional impurity turns out to be negative indicating that any La atoms present during sample preparation would readily get incorporated into CaB$_6$. In our HF calculations we find that La-doped CaB$_6$ down to an impurity concentration of 1.6%, has a paramagnetic ground state. This is found to be the case also at the B3LYP level of approximation. In any case, since HF is known to favor a high-spin state, one can reasonably expect the La-doped system to be nonmagnetic. This, along with our prediction of FM in Fe doped CaB$_6$, lends support to the claims that FM in this system is an extrinsic effect due to some magnetic atoms, and is not related to the presence of La. In Fig. 3 we show the band structure and density of states for a system with 3.7% La-doping. The system is found to be metallic. From the position of the Fermi surface we find that the system has a small electron-like FS at the Γ-point in the BZ. Comparing band structure in Fig. 3 with that of a (3 × 3 × 3) supercell (not shown) of pure CaB$_6$, we find that there is a small shift of the Fermi energy with only minor changes in energy bands. Thus La replacing a Ca atom acts as an electron donor in the system. We believe that the electron-like Fermi surface seen in ARPES measurements might have originated from La substitutional impurities.

Finally we study the effects of a B vacancy and a Fe substitutional impurity being present together in CaB$_6$. This is motivated by the observation in ref. [16] that although CaB$_6$, CaB$_{6+δ}$ and Ca$_{1−x}$La$_x$B$_6$ prepared with lower purity B exhibit FM, no such effect is seen in CaB$_{6−δ}$. This suggests that although Fe substitutional impurities give rise to FM, B vacancies neutralize that effect and when both are present in the system it is no longer FM. This is precisely borne out by our calculations. We have studied two extreme scenarios as far as the positions of the B vacancy and Fe impurity are concerned—i) they are on neighboring sites, and ii) they are as far apart as possible in our 3 × 3 × 3 simulation cell. In both cases a nonmagnetic state is preferred over a FM state in our HF calculations. Again, HF typically preferring a high-spin state, we can take this as a reasonable indication that a B vacancy destroys the FM state created by a Fe impurity.

In conclusion, using explicitly correlated many-body wavefunctions, we have conclusively shown that pure CaB$_6$ is a narrow-gap semiconductor with an X-point gap of 1.3(2) eV. Our HF and DFT calculations show that possible imperfections in the crystal—B vacancy, Fe or La substitutional impurities—drive the system metallic, explaining the apparent anomalies in the experimental results. Out of these, La substitutional impurities give rise to a small electron-like Fermi surface, which was seen in experiments but had no clear explanation. We have also shown that FM in this system is related to magnetic impurities, e.g., Fe and probably has no relation with the presence of La. Another interesting fact emerging from our calculations, explaining the fact that FM was never seen in CaB$_{6−δ}$ samples in Ref. [16], is that a B vacancy destroys any magnetic moment created by Fe impurities.

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