Formation of mid-gap states and ferromagnetism in semiconducting CaB₆

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Abstract

We present a consistent overall picture of the electronic structure and ferromagnetic interaction in CaB₆, based on our joint transport, optical, and tunneling measurements on high-quality defect-controlled single crystals. Pure CaB₆ single crystals, synthesized with 99.9999 %-pure boron, exhibited fully semiconducting characteristics, such as monotonic resistance for 2–300 K, a tunneling conductance gap, and an optical absorption threshold at 1.0 eV. Boron-related defects formed in CaB₆ single crystals synthesized with 99.9 %-pure boron induced mid-gap states 0.18 eV below the conduction band and extra free charge carriers, with the transport, optical, and tunneling properties substantially modified. Remarkably, no ferromagnetic signals were detected from single crystals made with 99.9999 %-pure boron, regardless of stoichiometry, whereas those made with 99.9 %-boron exhibited ferromagnetism within a finite range of carrier density. The possible surmise between the electronic state and magnetization will be discussed.
The hexaboride compounds $R\text{B}_6$ ($R = \text{Ca}, \text{Sr}, \text{La}, \text{Ce}, \text{Sm}, \text{Eu}, \text{and} \text{Gd}$) have been studied extensively over the last few decades because of their distinctive physical properties. Recently, it was found that $\text{CaB}_6$ doped with a small amount of $\text{La}$ exhibits a weak ferromagnetism at a high temperature ($T_c \approx 600 \text{ K}$) without the constituent elements being partially filled with $d$ or $f$ orbitals, which are usually required for ferromagnetism \[1\]. Substantial theoretical and experimental efforts have been devoted to clarify this intriguing property \[2, 3, 4, 5, 6\]. Based on the early band structure calculations of $\text{CaB}_6$ \[5\], from which the compound’s apparent semimetallic character could be derived, many theoretical models, such as the ferromagnetic phase of a dilute electron gas (DEG), the doped excitonic insulator (DEI), and the conventional itinerant magnetism, have been suggested to explain the weak ferromagnetism observed at a high temperature \[2, 3, 4\]. However, a more detailed calculation employing the so-called $GW$ approximation \[6\] predicted that $\text{CaB}_6$ has a sizeable semiconducting band gap of about 0.8 eV at the $X$ point in the Brillouin zone and suggested that the magnetism in $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ occurs just on the metallic side of a Mott transition in the La-induced impurity band. Experimental investigations of the predicted band gap with angle-resolved photoemission spectroscopy (ARPES) supported the results of the $GW$ calculation \[7, 8\]. The mapped band structure and the Fermi surface were in good agreement with the $GW$ scheme, and a semiconducting band gap at the $X$ point, estimated to be 1 eV \[8\] or larger \[7\], was reported. In addition, a small electron pocket found at the $X$ point was thought to originate from boron vacancies and to cause the previously reported metallic conductivity in $\text{CaB}_6$, $\text{SrB}_6$, and $\text{EuB}_6$. A more direct signature of a semiconducting band gap, such as in optical absorption and tunneling conductance, would be highly desirable.

Regarding the magnetic properties of La-doped $\text{CaB}_6$, there have been a lot of debates on the origin of the magnetic moment and on the mechanism of the exotic ferromagnetism. Recently, $\text{FeB}$ and $\text{Fe}_2\text{B}$, which have critical temperatures of about 598 K and 1,015 K, respectively, were suggested to be responsible for the high-temperature weak ferromagnetism in $\text{CaB}_6$ \[9\], while the evidence against the argument was presented by Young et al. on an experimental basis \[10\]. However, it was also suggested that defects, possibly driven by La doping and randomly distributed in the lattice, generate free charge carriers that simultaneously create local magnetic moments \[11\]. The defects likely involve sites in the boron sublattice rather than those in the cation sublattice since excess Ca or La ions are
not likely to be placed into the rigid network of B octahedra. Indeed, the formation energy and local magnetic moment of a series of possible point defects in CaB$_6$ were calculated [12]. However, the exact nature of the hypothetical defects is still not clear and it should be confirmed experimentally, in particular whether the defects really induce local magnetic moments and possibly free charge carriers as well.

We synthesized our CaB$_6$ single crystals using the high-temperature flux method, described in detail elsewhere [13]. In order to initiate a variation in the relative concentration of Ca and B, we started the single-crystal growth process with the initial molar ratios of Ca:B = 1:5, 1:6, and 1:6.05. We denote the B-deficient single crystal as CaB$_{6-\delta}$, the stoichiometric one as CaB$_6$, and the B-rich one as CaB$_{6+\delta}$, depending on the initial molar ratio of Ca and B. For the growth of each single-crystal species, we used two different types of boron, one with 99.9999 % purity (6N) (EAGLE PIPHER, USA) and the other with 99.9 % purity (3N) (Target Materials Inc, USA). In the following, a single crystal denoted as CaB$_{6-\delta}$(6N) is a nominally B-deficient sample made with 99.9999 %-pure boron, and likewise CaB$_{6-\delta}$(3N) for one made with 99.9 %-pure boron. Similar notations are used for the stoichiometric and the nominally B-rich single crystals. The 6N and 3N boron contain Fe impurities of order of 0.01 ppm/mg and 1.0 ppm/mg, respectively, and other major non-magnetic ones of C, and Si was found in 3N boron. No magnetic signals were detected in our magnetization measurements of both 3N and 6N boron precursors before and even after heat treatment at 1,450 °C for 12 hr. We conducted our optical measurements using FTIR and grating spectrometers covering the spectral range of 5 meV–6 eV. For tunneling measurements we used the in-situ (breakage at 4 K) break-junction method [14, 15], which protects the samples from serious environmental defects.

Figure 1 displays the temperature-dependent resistivity $\rho(T)$ of CaB$_6$(6N) and CaB$_6$(3N) on a log scale. The $\rho(T)$ of CaB$_6$(6N) was much higher in magnitude than that of CaB$_6$(3N) and exhibited typical semiconducting behavior in the entire temperature range of 2–300 K. However, the $\rho(T)$ of CaB$_6$(3N) revealed metallic temperature dependence except at very low temperatures. The insets of Fig. 1 display the infrared reflectivity of CaB$_6$(6N) and CaB$_6$(3N) at room temperature. The reflectivity of CaB$_6$(6N) reveals its insulating nature: the overall shape of the spectrum, dominated by a single optical phonon mode at 150 cm$^{-1}$, is a typical characteristic of an insulator or a pure semiconductor. We were not able to detect a clear signature of a Drude-like feature of free carriers down to 40 cm$^{-1}$.
(5 meV) (the low-frequency region somewhat obscured by noisy interference fringes). On the other hand, CaB\(_6\)(3N) exhibited a clear Drude-like feature below about 60 cm\(^{-1}\) (7.5 meV) in addition to the aforementioned phonon mode. Hence our optical data are consistent with the temperature dependence of the resistivity of CaB\(_6\)(6N) and CaB\(_6\)(3N) described above. Similar features were observed in the transport and optical measurements on boron-deficient and boron-rich single crystals. Our observations suggest that boron-related defects (or chemical impurities) present in CaB\(_6\)(3N) are closely associated with carrier doping and hence with the semiconducting/metallic characteristics of the resistivity. These results are in contrast to earlier reports in Ref. \[16\] (a high-alloy semiconductor model) and \[17\] (a doped semimetal model) but are compatible with Ref. \[18\] with only subtle differences. Thus, it is essential to employ high-purity boron for careful studies of the intrinsic properties of CaB\(_6\). The effect of the boron purity in alkaline-earth hexaborides has not yet been seriously addressed despite numerous references in the literature which argue that the experimental data on these compounds were quite sensitive to the sample quality.

We have performed electron-tunneling experiments on CaB\(_6\)(6N) and CaB\(_6\)(3N) using a break junction to identify the difference in their electronic structure. The \(dI/dV\) versus applied voltage is plotted in Fig. 2(a) and (b) for CaB\(_6\)(6N) and CaB\(_6\)(3N), respectively. The overall shape of the tunneling conductance curve for CaB\(_6\)(6N) shows a well-defined large gap structure of size \(2\Delta \approx 2\) eV and a weak sub-gap anomaly of size \(2\Delta^* \approx 0.4\) eV. The non-zero \(dI/dV\) at zero bias and the broad maximum on the shoulder at both bias indicate that the electronic states are not completely depleted inside the large gap. The observed large gap feature \(\Delta \approx 1\) eV is most likely a manifestation of the bulk semiconducting band gap of pure CaB\(_6\) corresponding to the 1 eV \(X\)-point band gap reported in the ARPES measurements of Ref. \[7\] and \[8\].

We noted a drastic change in the tunneling conductance spectrum for CaB\(_6\)(3N) as shown in Fig. 2(b). The sub-gap structure \(2\Delta^*\) was strongly enhanced, while the large gap feature \(2\Delta\) was sharply depressed. The marked enhancement of the sub-gap structure is probably linked to the induced free carriers in CaB\(_6\)(3N), but this distinct effect is not precisely in accordance with the electron pocket picture at the \(X\) point observed in the ARPES measurements of Ref. \[7\] and \[8\]. We argue that boron-related defects in CaB\(_6\)(3N) not only induced free carriers but also created \textit{mid-gap states} at about 0.2 eV below the conduction band \[19\]. The sub-gap feature can be then naturally interpreted as representing tunneling...
of the induced free carriers at the mid-gap states across an energy gap of $\Delta^* \approx 0.2$ eV between the highest-occupied mid-gap states and the bottom of the conduction band. This assignment also explains why the sub-gap feature is strongly enhanced in CaB$_6$(3N) but is weakly present in CaB$_6$(6N): the boron-related defects are far more abundant in CaB$_6$(3N). Understandably, even the CaB$_6$(6N) single crystals studied in this work possess such defects to some extent, as reflected by a small trace of the sub-gap feature in Fig. 2(a).

Clear evidence for the bulk semiconducting band gap of 1.0 eV in CaB$_6$(6N) and for the mid-gap states at 0.18 eV below the conduction band in CaB$_6$(3N) comes from direct optical absorption measurements. The optical absorption coefficients of CaB$_6$(6N) and CaB$_6$(3N) are plotted in Fig. 3. The CaB$_6$(6N) and CaB$_6$(3N) samples exhibited optical absorption onsets at 1.0 eV and 0.82 eV, respectively. This observation directly confirms that pure CaB$_6$ is a semiconductor with a band gap of 1.0 eV. The band gap of 1.0 eV is consistent with our break-junction tunneling results discussed above and coincides with the band gap observed by ARPES. The red shift of 0.18 eV in the optical absorption threshold for CaB$_6$(3N) implies that the boron-related defects cause either band-gap narrowing or mid-gap state formation, the latter explanation being favored by our tunneling results above.

By combining the results of our optical and tunneling measurements, we acquire a consistent overall picture of the electronic structure and the band gap of CaB$_6$ as described by a schematic diagram in the inset of Fig. 3. The energy gap $\Delta = 1.0$ eV is common to the optical absorption spectra and to the tunneling conductance spectra of CaB$_6$(6N). The changes noted for CaB$_6$(3N) can be understood in terms of mid-gap states generated at 0.18 eV below the conduction band by boron-related defects. We assign the optical absorption threshold at 0.82 eV for CaB$_6$(3N) to the transition from the valence band to the mid-gap states at $E_{VM} = 0.82$ eV above the valence band. The sub-gap feature $\Delta^* = 0.18$ eV in $dI/dV$, which was strongly enhanced in CaB$_6$(3N) but weakly present in CaB$_6$(6N), represents tunneling from the mid-gap states to the conduction band.

We also conducted isothermal magnetization measurements at 5 and 300 K for the single crystals in Fig. 1, CaB$_{6-\delta}$(6N,3N), CaB$_{6+\delta}$(6N,3N), and also Ca$_{1-x}$La$_x$B$_6$ with $x = 0.005$ (6N,3N), 0.01 (6N,3N), 0.02 (3N), 0.03 (3N), and 0.04 (3N). Surprisingly, no single crystals made with 6N boron exhibited any detectable magnetic signal in the entire temperature range of 5–300 K. CaB$_6$(3N), CaB$_{6+\delta}$(3N), and Ca$_{1-x}$La$_x$B$_6$(3N) with $x = 0.005$, 0.01, and 0.02 revealed ferromagnetism, as can be inferred from a hysteresis loop in the
isothermal magnetization. In contrast, there was no trace of magnetism in CaB$_{6-\delta}$ (3N) and Ca$_{1-x}$La$_x$B$_6$ (3N) with $x = 0.03$ and 0.04. As a representative set of data, the hysteresis loops of Ca$_{0.99}$La$_{0.01}$B$_6$ (3N) at 5 and 300 K are plotted in the inset of Fig. 4. We estimate the carrier density in the relevant samples by converting the Hall resistivity data into the effective number of free carriers using the single-carrier (electron) model. The presence of a single carrier species in hexaborides was already established by Hall measurements on Eu$_{1-x}$Ca$_x$B$_6$ [20, 21] and by ARPES measurements on CaB$_6$, SrB$_6$, and EuB$_6$ [7, 8]. Figure 4 presents the most important correlation between the saturated magnetization $M_{sat}$ and the carrier density. We believe that the exotic ferromagnetism in CaB$_6$ requires simultaneous presence of the localized magnetic moments and free carriers within a finite range of density (Fig. 4). Most importantly, this indicates that the formation of the ferromagnetic state is established through the induced free carriers occupying the mid-gap states. This fact can possibly explain the disappearance of magnetic signal at relatively high carrier density in Ca$_{1-x}$La$_x$B$_6$ ($x \gtrsim 0.03$), which can cause the mid-gap states to merge or hybridize with the conduction band.

Regarding the formation of a localized magnetic moment, it is not clear at present whether it comes from simple magnetic impurities, such as Fe, FeB, and Fe$_2$B, or is indeed associated with boron-related defects as theoretically considered in Ref. 12. However, it was found from micro-chemical analysis of both 3N and 6N compounds that there is no correlation between the Fe content on the sample surface and the emergence of ferromagnetism [22]. Because we have not detected any magnetic signals in our magnetization measurement of both 3N and 6N boron precursors (even after heat treatment), we certainly believe that ferromagnetism is related to impurities, probably not magnetic, in the boron precursor material. It will be very important to precisely identify these impurities and the nature of the associated defects.

In conclusion, we believe our reports are the first to experimentally discover the creation of mid-gap states and extra free carriers therein by boron-related defects in CaB$_6$. In addition, we showed that the exotic ferromagnetism in CaB$_6$ has non-magnetic-impurity origin, contrary to the previous reports. It will be a critical issue to understand the nature of the impurity and the relation between the mid-gap state and ferromagnetism in CaB$_6$.

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FIG. 1: Electrical resistivity $\rho$ versus temperature for CaB$_6$, prepared with boron of 99.9999 % purity (6N) (square) and 99.9 % purity (3N) (circle). Insets: Infrared reflectivity (300 K) of CaB$_6$(6N) and CaB$_6$(3N).

FIG. 2: Tunneling conductance $dI/dV$ versus applied voltage of CaB$_6$, prepared with boron of (a) 99.9999 % purity and (b) 99.9 % purity.

FIG. 3: Absorption coefficient versus photon energy for CaB$_6$ prepared with boron of 99.9999 % purity and 99.9 % purity. The dotted lines are the fits to the data for a direct band gap. Inset: schematic plot of the electronic structure and the band gap along with mid-gap states (VB for valence band, CB for conduction band, and $E_F$ for Fermi level).

FIG. 4: Saturated magnetization $M_{\text{sat}}$ versus carrier density for CaB$_6$, CaB$_{6\pm\delta}$, and Ca$_{1-x}$La$_x$B$_6$, prepared with boron of 99.9 % purity. The solid line is to guide the eye. Inset: Hysteresis curve for Ca$_{0.99}$La$_{0.01}$B$_6$ at 5 and 300 K.
(a) CaB$_6$ (6N)

(b) CaB$_6$ (3N)

Voltage (V)

d$dV$ (mS)
