Formation of midgap states and ferromagnetism in semiconducting CaB_6

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We present a consistent overall picture of the electronic structure and ferromagnetic interaction in CaB_6, based on our joint transport, optical, and tunneling measurements on high-quality *defect-controlled* single crystals. Pure CaB_6 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 CaB_6 single crystals synthesized with 99.9% pure boron induced *midgap 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.

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The hexaboride compounds RB_6 (R=Ca, Sr, La, Ce, Sm, Eu, and Gd) have been studied extensively over the last few decades because of their distinctive physical properties. Recently, it was found that CaB_6 doped with a small amount of La exhibits a weak ferromagnetism at a high temperature ($T_c \approx 600$ 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.[2–6] Based on the early band-structure calculations of 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, the doped excitonic insulator, and the conventional itinerant magnetism, have been suggested to explain the weak ferromagnetism observed at a high temperature.[2–4] However, a more detailed calculation employing the so-called GW approximation[6] predicted that 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 $Ca_{1-x}La_xB_6$ 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 (Ref. 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 CaB_6, SrB_6, and 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 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, FeB and Fe_2B, which have critical temperatures of about 598 K and 1015 K, respectively, were suggested to be responsible for the high-temperature weak ferromagnetism in 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 PICHER, 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. Major impurities were identified to be C and Si in $3N$ boron and relatively negligible Fe impurity was found for both $6N$

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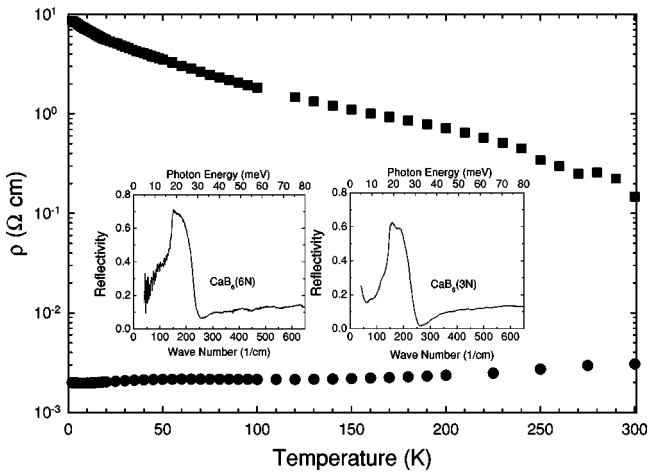

FIG. 1. Electrical resistivity ρ vs temperature for CaB_6, prepared with boron of 99.9999% purity ($6N$) (square) and 99.9% purity ($3N$) (circle). Insets: Infrared reflectivity (300 K) of $CaB_6(6N)$ and $CaB_6(3N)$.

and $3N$ borons. No magnetic signals were detected in our magnetization measurements of both $3N$ and $6N$ boron precursors before and even after heat treatment at 1450°C for 12 h. 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 Ref. 17 (a doped semimetal model) but are compatible with Ref. 18 with only subtle differences. Thus, it is essential to employ high-purity

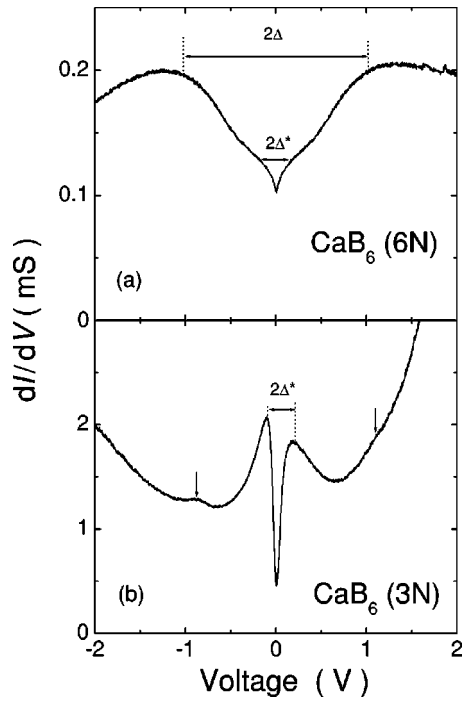

FIG. 2. Tunneling conductance dI/dV versus applied voltage of CaB_6, prepared with boron of (a) 99.9999% purity and (b) 99.9% purity.

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 Figs. 2(a) and 2(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 subgap anomaly of size $2\Delta^* \approx 0.4$ eV. The nonzero 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 Refs. 7 and 8.

We noted a drastic change in the tunneling conductance spectrum for $CaB_6(3N)$ as shown in Fig. 2(b). The subgap structure $2\Delta^*$ was strongly enhanced, while the large-gap feature 2Δ was sharply depressed. The marked enhancement of the subgap 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 Refs. 7 and 8. We argue that boron-related defects in $CaB_6(3N)$ not only induced free carriers but also created *midgap states* at about 0.2 eV below the conduction band.[19] The subgap feature can

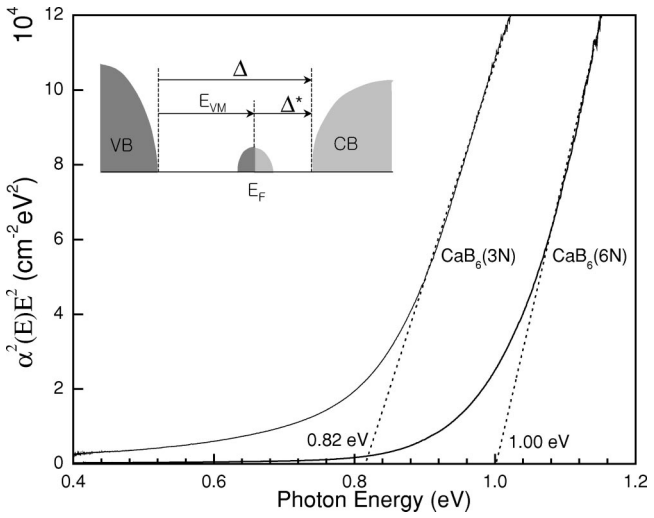

FIG. 3. Absorption coefficient versus photon energy for CaB_6 prepared with boron of 99.9999% purity and 99.9% purity. The dotted lines are the fits to the data for a direct band gap. Inset: schematic plot of the electronic structure and the band gap along with *midgap states* (VB for valence band, CB for conduction band, and E_F for Fermi level).

be then naturally interpreted as representing tunneling of the induced free carriers at the midgap states across an energy gap of $\Delta^* \approx 0.2$ eV between the highest-occupied midgap states and the bottom of the conduction band. This assignment also explains why the subgap 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 subgap feature in Fig. 2(a).

Clear evidence for the bulk semiconducting band gap of 1.0 eV in $CaB_6(6N)$ and for the midgap 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 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.[7,8] 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 *midgap 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 midgap 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 midgap states at $E_{VM} = 0.82$ eV above the valence band. The subgap 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 midgap 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 $Ca_{1-x}La_xB_6$ 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 $Ca_{1-x}La_xB_6(3N)$ 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 $Ca_{1-x}La_xB_6(3N)$ with $x = 0.03$ and 0.04. We estimated 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 measurement on $Eu_{1-x}Ca_xB_6$[20,21] and by ARPES measurements on CaB_6, SrB_6, and EuB_6.[7,8] It was found that the effective carrier density and the electric conductivity scaled well with the La-doping level.

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_2B, or is associated with nonmagnetic origin, such as boron-related defects as theoretically considered in Ref. 12. However, we had a few evidences, partially supporting the nonmagnetic origin of the magnetic moments. First, because we have not detected any magnetic signals in our magnetization measurement of both $3N$ and $6N$ boron precursors (even after heat treatment), it is not likely that magnetism in CaB_6 is related to magnetic impurities in the boron precursor. Second, it is not likely, either, that the observed magnetism is simply due to magnetic impurities from Al flux because the same Al flux were used for the growth of non-magnetic single crystals, such as CaB_6 with $6N$ boron and $Ca_{1-x}La_xB_6$ ($x \geqslant 0.03$) with $3N$ boron. Finally, we found that the magnetic signal could not be removed completely by the chemical etching as in Ref. 9 in some of the crystals. In addition, it is worthwhile to note that the disappearance of ferromagnetism in $Ca_{1-x}La_xB_6(3N)$ ($x \geqslant 0.03$) may be related with the midgap states, which would merge or hybridize with the conduction band at relatively higher carrier density. It will be very important to precisely identify these impurities and the nature of the associated defects.

In conclusion, to the best of our knowledge our reports are the first to experimentally discover the creation of midgap states and extra free carriers therein by boron-related defects in semiconducting CaB_6 with gap of ≈ 1 eV. In addition, we showed that the exotic ferromagnetism in CaB_6

can have, in part, non-magnetic-impurity origin. It will be a critical issue to understand the nature of the impurity and the relation between the midgap state and ferromagnetism in CaB_6.

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