Pressure-Induced Metallization and Electrical Phase Diagram for Polycrystalline CaB_6 under High Pressure and Low Temperature *

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The electrical properties of polycrystalline CaB_6 are revealed by in-situ resistance measurements under high pressure and low temperature. Due to the existence of grain boundaries, polycrystalline CaB_6 behaves with semiconducting transport properties, which is different from the semimetallic CaB_6 single crystals. The temperature-dependent resistance measurement results show that before the structural phase transition at 12.3 GPa the high pressure first induces the metallization at 6.5 GPa for CaB_6. Moreover, the phase diagram for CaB_6 is drawn based on the investigated electric conducting properties and at least three different conducting phases are found even at moderate high pressure and low temperature, indicating that the electric nature of CaB_6 is very sensitive to the environment.

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CaB_6, one kind of alkaline-earth hexaborides, has gained intensive research for decades, not only due to its significant values in technical applications, but also unsettled puzzles in fundamental physical research.[1−3] With the merits of high hardness, high melting point, chemical stability, and high electrical conductivity, CaB_6 can be widely used in the fields of wear resistant coatings, cutting tools, and high capacity batteries.[4−7] Therefore, finding methods for synthesizing high-quality CaB_6 with various forms became a hot topic, aiming to realizing its superlative effectiveness in different applications.[8−12]

In the process of further promoting and expanding the physical properties of CaB_6, weak ferromagnetism was found in La-doped CaB_6,[13−15] which is very rare for materials without partly filled $3d$, $4f$, or $5f$ shells. Initially, the weak ferromagnetism was suspected to originate from the transition-metal impurities.[16,17] However, later experiments with high-purity crystal samples confirmed that it is an intrinsic property.[18,19] Theoretical predictions have attributed the weak ferromagnetism in CaB_6 to boron vacancies, where flat bands near the Fermi level spin-split due to the strong exchange interaction in the B p-shell. Tromp *et al.* reported that CaB_6 is not a semimetal, but a semiconductor with a band gap of 0.8±0.1 eV from the results of parameter free quasiparticle calculations of the single-particle excitation spectrum, and predicted that it should even be possible to make the spin analogs of bipolar devices if a p-type hexaboride with some of the Ca replaced by a monovalent ion is also found to be ferromagnetic.[3]

For an amazing material such as CaB_6 valuable in both industry techniques and basic physical research, studying it from as wide a point of view as possible is necessary and is never obsolete. Especially for the potential application of CaB_6 in spin electronics, the physical properties should not only be known at room temperature, but also be clear under low temperature. Moreover, pressure is another factor to tune the band gap of materials sensitively, which could endow CaB_6 with unexpected change in physical properties, e.g., Kolmogorov *et al.* found that CaB_6 undergoes $cP7 \rightarrow oS56 \rightarrow tI56$ transformation at 13 and 32 GPa, respectively.[20] However, such studies are rare and therefore many properties of CaB_6 under high pressure or/and low temperature still remain unknown, which obstructs its further use. In this Letter, we study the electrical transport properties of CaB_6 at high pressure and low temperature. We find one pressure-driven metallization and two semiconducting phases for CaB_6 by measuring the temperature-dependent resistivity at various pressures, and then obtain its electrical p–T phase diagram. This study will be a reference for CaB_6 applications in spin electronics and other electrics under extreme conditions.

The CaB_6 sample was obtained from high-pressure and high-temperature synthesis. Electrical resistance measurements under high pressure were conducted in a diamond anvil cell with the culet of diameter of 500 μm. Similar to works reported before, no pressure medium was used in the electrical measurements to ensure all resistance signals were coming from the sample itself. The pressure-dependent resistance was measured under high pressure up to 22.0 GPa. The temperature-dependent resistance was measured un-

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der various pressures and low temperature down to 4 K, where Pt foil was used as the electrodes as shown in the inset of Fig. 1. The structure of synthesized CaB_6 was characterized under high pressure by x-ray diffraction with $\lambda = 0.6199$ Å at Beijing Synchrotron Radiation Facility. For comparison with the electrical measurements, the structural studies were also performed without putting the pressure medium into the sample.

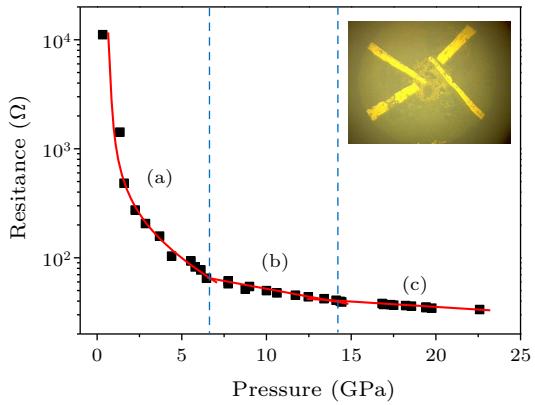

Fig. 1. The pressure dependence of CaB_6 resistance at ambient temperature. The solid and dashed lines are the guidance for eyes. Here (a), (b) and (c) denote three different pressure-dependent resistances. Inset: the electrode configuration in diamond anvil cell.

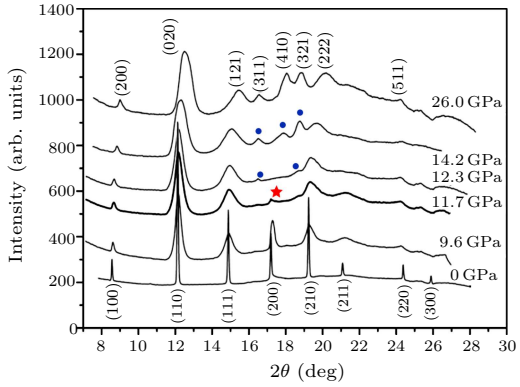

Fig. 2. XRD spectra for CaB_6 powder under various pressures. The asterisk and circle dots highlight the disappearance of the diffraction peak (200) for phase $cP7$ and the appearance of (311), (410) and (321) for phase $oS56$.

Figure 1 shows the pressure-dependent resistance of the synthesized CaB_6 sample. As illustrated in Fig. 1, the resistance in the mass decreases with the pressure, while in three different laws, i.e., (1) very quick drop between ambient and 6.5 GPa, (2) slow linear drop between 6.5 GPa and 14.0 GPa, and (3) relatively slower linear drop at the pressures larger than 14.0 GPa. To figure out the origin of the abnormal resistance change, the structure of the synthesized CaB_6 sample was characterized by x-ray diffraction at various pressures as shown in Fig. 2. The diffraction spectrum at ambient pressure can be definitely indexed as the $cP7$ structure of CaB_6. As the pressure increases to the region between 11.7 and 12.3 GPa, the feature of the spectrum changes with the disappearance of the diffraction peak at $2\theta = 17.2°$ and the appearance of two new peaks at $2\theta = 16.5°$ and 18.6°, indicating that the pressure-induced structure phase transition occurs around 12.3 GPa and the structure of the new phase is $oS56$. Comparing the result with the structure characterization, it can be concluded that the change of the resistance drop laws at 14.0 GPa is caused by the pressure-induced phase transition of CaB_6 from the $cP7 \rightarrow oS56$ structure. However, it is still difficult so far to explain the abnormal resistance variation at 6.5 GPa from the result of structure characterization due to the fact that only one new phase can be observed in the x-ray diffraction spectra at 14.0 GPa.

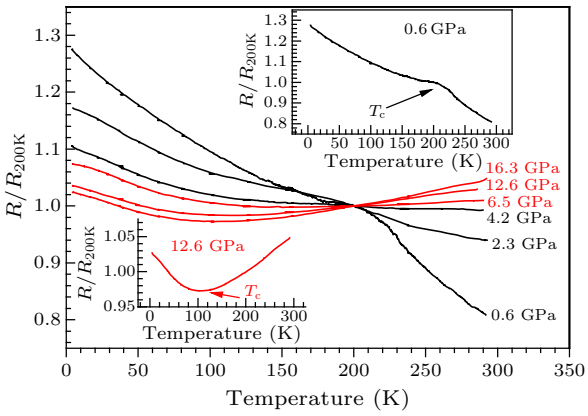

Fig. 3. The temperature dependence of resistance for CaB_6 under various pressure. Inset: the definition of T_c.

For those semiconducting or insulating materials with abnormal changes in resistance but without pressure-induced structural phase transitions, metallization is one of the most reasonable predictions. Therefore the temperature-dependent resistance measurement was carried out on CaB_6 under various pressures to investigate its electrical properties. As shown in Fig. 3, the resistance decreases with increasing the temperature under the pressure below 6.5 GPa, which presents the electrical nature of CaB_6 in the $cP7$ structure to be of semiconductors (denoted as SP I). High-pressure and high-temperature synthesized CaB_6 single crystals have been proved to be semimetallic,[10] while polycrystalline CaB_6 presents the semiconductor behavior, indicating that the existence of grain boundaries leads to the difference of the electrical transporting properties between single crystalline and polycrystalline CaB_6 samples. In this work, we mainly focus on the analysis of the electrical properties of polycrystalline CaB_6 at high pressures. As the pressure reaches 6.5 GPa, the slope of resistance versus temperature is reversed from the negative to positive, indicating that the metallization occurs. The temperature-dependent resistance measurement has also been conducted on CaB_6 in the $oS56$ structure, confirming that its electrical nature is metallic as well.

The lowest temperature in the experiment has been decreased down to 4 K. Hereinto, a different temperature dependence of resistance is found at temperatures below 200 K, indicating that a new semiconductor phase (denoted as SP Ⅱ) emerges and it can exist even after the metallization. Figure 4 shows the transition temperature (T_c) variation as the function of pressure, where T_c for SP I↔SP Ⅱ and SP Ⅱ↔ metallic phase are defined by the kink and minimum of the temperature-dependent resistance as shown in Fig. 3. With all the results from the experiment, the electric phase diagram for CaB_6 under high pressure and temperature therefore can be obtained. It can be seen that CaB_6 is endowed with at least three different conducting features, SP I, SP Ⅱ, and metallic phase.

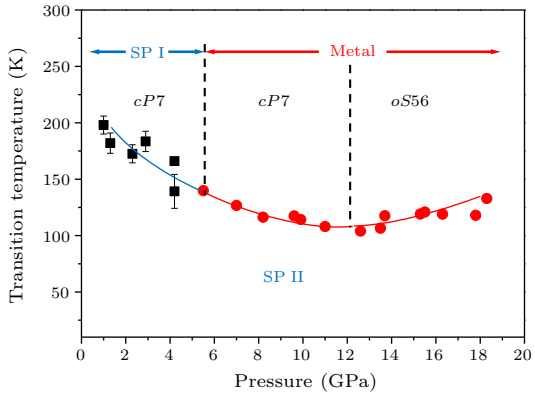

Fig. 4. The pressure dependence of T_c and the electric phase diagram for CaB_6. SP I: semiconductor phase I, and SP Ⅱ: semiconductor phase Ⅱ.

In conclusion, we have investigated the electric properties of polycrystalline CaB_6 under high pressure and low temperature. The polycrystalline CaB_6 has been proven to be a semiconductor under ambient pressure. According to the pressure-dependent resistance and temperature-dependent resistance measurements, the phase diagram for CaB_6 has been drawn. It has been found that the electric nature of CaB_6 is very sensitive to the environment and therefore in the future CaB_6 may be used to design spin-electronics-based sensors.

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