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Pressure-induced exotic states in rare earth hexaborides

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1. Introduction

All hexaborides possess the same crystal structure that is simply constructed with a framework of \( B_6 \) octahedrons and the rare-earth ions isolated in the interstitials of the framework [1], as shown in figure 1. Experimental measurements demonstrate that the \( RB_6 \) structure is quite sturdy, and the interstitial spaces of the \( B_6 \) framework are rather large to host a variety of rare earth ions in a broad range of sizes. This is the reason why all rare earth hexaborides, including...
the ones with Y, La and the elements from Ce to Lu with $4f$-electrons in the periodic table can be formed. It is suggested that this structural peculiarity should be taken as one of the basic starting points to explain some of the anomalies in the $RB_6$ systems.

The compounds $RB_6$ are typical strongly correlated electron systems (SCESs). Since their electron structure is featured by incompletely filled $d$- or $f$-electron shells with narrow energy bands, the behavior of the electrons in $RB_6$ cannot be described effectively in terms of the non-interacting entities [2]. In the vicinity of the Fermi level, the rare-earth hexaborides generally have three types of electronic bands [3], namely, the R 5$d$ band, the R 4$f$ band and the B 2$p$ band. The physical behavior of $RB_6$ is cooperatively determined by the relative energy levels to the Fermi level and the width of these bands, which is mainly governed by the delicate interplays among the spin, orbital, charge and lattice degrees of freedom. As containing $f$-electrons in their configurations, these hexaborides may exhibit a variety of exotic electron correlation behaviors [4]. In particular, theorists predict that they may host the novel topological electronic states that are different from the usual topological insulators (TIs) without $f$-electrons [5–7], which needs to be further confirmed by more convicive experimental results [8–11].

In past years, a lot of progress has been made on hexaboride studies, including the discovery of superconductivity in YB$_6$ [12], very low work functions used as a thermionic emitter in monovalent metal LaB$_6$ [13], dense Kondo system behavior and electric quadrupole ordering in CeB$_6$ [14, 15], low-carrier-density magnetism with a narrow semiconducting gap in EuB$_6$ [16] and nonmagnetic narrow gap in YbB$_6$ [17], mixed valence and Kondo insulating property in SmB$_6$ [18, 19]. Particularly, a new electronic state with a possibly nontrivial metallic surface and insulating bulk has been found in SmB$_6$ [20], which brings new excitement in the condensed matter physics community and consequently attracts considerable attention from theoretical and experimental scientists to revisit the subgroup of $RB_6$ ($R = $ Sm, Yb, Eu, Ce).

Figure 1. Schematic crystal structure of $RB_6$. In crystallographic description, $RB_6$ takes the body center cubic structure in space group Pm3m, in which rare earth ion $R$ (dark pink) and B$_6$ octahedron (green) are arranged in a CsCl-like packing.
QPT by controlling these external parameters can yield great opportunities to find novel properties, which may be different from those connecting with the QPT induced by chemical doping at ambient pressure.

Some exotic states of the $RB_6$ can be induced by pressure via generating volumetric compression, in turn to give rise to a change of the electron structure accordingly. In general, pressure can tune the mean valence of rare earth ions between di-valence (without magnetism) and tri-valence (with magnetism) in $SmB_6$ or $YbB_6$ because pressure can shrink the volume of the $f$-electron shell to change the configurations from $f^6$ (with larger volume) to $f^2$ (with a smaller volume) for Sm ions and from $f^{14}$ (with a larger volume) to $f^{13}$ (with a smaller volume) for Yb ions, respectively [24]. Therefore, we can know that the populations of their magnetic ions and $d$-electrons can be enhanced simultaneously with increasing pressure, which is different from the other rare earth hexaborides. For example, the pressure-induced valence changes from tri-valence (with a larger-volume) to tetra-valence (with a smaller-volume) for Ce ions in CeB$_6$ and from di-valence to tri-valence for Eu ions in EuB$_6$ take place due to the changes of $f^1$-to-$f^0$ and $f^2$-to-$f^6$, respectively. These changes are accompanied by the alternation from magnetic ions to non-magnetic ions [24]. As a result, upon increasing pressure, the population of the magnetic ions is reduced while the population of $d$-electrons is increased. It is seen that the pressure-induced changes in the populations of magnetic ions and $d$-electrons are quite different between $SmB_6$ (or $YbB_6$) and $CeB_6$ (or $EuB_6$). Thus, the diverse contributions of the valence states in determining the electronic structure and the corresponding properties in the pressurized $RB_6$ systems with different $f$-electron configurations are understood basically. However, there is still a lack of reports on high pressure experimental investigations on the valence state in $RB_6$ above 10 GPa [25]. The recent progress reported by Zhou et al [26] demonstrates the pressure-induced valence increase in $YbB_6$ up to 28 GPa by x-ray absorption measurements.

2. Related high pressure methods

Advanced high pressure techniques can provide a tunable pressure range from ambient pressure to more than 300 GPa ($1\text{ GPa} = 10^9 \text{ Pa}$) for high pressure studies on matters. The high pressure techniques commonly adopted in the related studies of the hexoborides mainly include the in situ high-pressure measurements of resistance, Hall coefficient, synchrotron radiation x-ray diffraction (XRD) and x-ray absorption. Some aspects of these techniques are described as follows.

2.1. High-pressure transport measurements at low temperature

A few types of high pressure apparatus have been developed and employed for low temperature transport measurements. A piston-cylinder tungsten anvil cell is commonly used for high pressure studies below ~3 GPa [27] and a toroid tungsten anvil cell can reach up to 8 GPa [28]. However, the diamond anvil cell (DAC) can be used in a vast pressure range up to 240–250 GPa for transport measurements [29–32] and above 300 GPa for optical measurements [33–36], because diamond is such a material which is the hardest and chemically inert to most of the matters. Moreover, due to its light and compact body, DAC has good integratability with the cryostat like 3He/4He dilution refrigerators.

The main consideration for reaching a higher pressure regime lies in the quality and alignment of the diamond anvils. Therefore, the single crystal diamonds without inclusion should be selected as the anvils, and a perfect alignment for the two culets of the anvils is required in order to achieve a higher pressure in the DAC [37–40]. Diamond anvils sitting atop of a supporting plate is shown in figure 2.

One of the difficulties for the high-pressure transport measurements is the preparation for the four electrodes on the tiny culet of a diamond anvil. The development of a microfabrication technique allows us to prepare the fine electrodes as...
shown in figure 3. It demonstrates the typical arrangements of four electrodes on the culet with a diameter as small as 80 μm, the size similar to the diameter of a human being’s hair, for resistance measurement and Hall coefficient measurement, respectively.

2.2. High pressure XRD and absorption measurements

Diamond is transparent for the electromagnetic wave with a wide range of energy, therefore the DAC has the great advantage to be adopted to many types of spectroscopic measurements, such as the synchrotron XRD and x-ray absorption spectroscopy measurements, which can help us to know the information about the crystal structure and valence state of the system investigated. In the recent decades, the developments in a variety of high pressure techniques have resulted in a wealth of new information about the unexpected behaviors of the RB₆ systems [24, 26, 41–43].

3. High pressure studies on the hexaborides

One of the recent remarkable advances in the field of strongly correlated electron physics is the finding of the coexistence of an insulating bulk and a metallic surface in the rare-earth hexaboride SmB₆ [44–48], which is one of the common features for a non-trivial topological state [49]. Consequently, these hexaborides are expected to bridge the physics between strongly correlated electron materials and TIs. As one of the powerful tools, the high pressure method is frequently applied in the other most famous strongly correlated systems to find new phenomena (such as heavy Fermion behavior and high-\(T_c\) superconductivity) and to help understanding their physics. Naturally, the high pressure studies on these hexaborides are specially needed for establishing this link. Generally, the ambient-pressure information of the system investigated is fundamentally important to reveal its pressure-induced phenomena, therefore, in each subtopic of this section, we will first introduce some related results obtained at ambient pressure, and then the results achieved at high pressure together with simple discussions accordingly.

3.1. Pressure-induced exotic insulator–metal transition in SmB₆

After discovery more than 40 years ago [50, 51], SmB₆, as a prototypical Kondo insulator with strongly correlated \(f\)-electrons, is found to have an exotic metallic surface state connected with an insulating bulk state by measurements of angle-resolved photoemission spectroscopy (ARPES) [44, 45, 52, 53], scanning tunneling microscopy (STM) [10, 47, 54], thickness tuning transport [20, 55–57], field dependence of magnetoresistance [58–61], ionic irradiation surface [62] and neutron scattering [63]. In particular, the discoveries of the unconventional Fermi surfaces revealed by the quantum oscillation patterns for the SmB₆ in a strong magnetic field [64, 65] provide a new perspective to help understand the physics of this unique hexaboride.

The temperature dependence of the ambient-pressure electrical resistance of SmB₆ can be described as transforming from a poor metallic state at room temperature to a Kondo insulating state with a small energy gap (14–20 meV) due to the hybridization of localized \(f\)-electrons with conduction electrons at temperature below \~100 K, and then to a saturated resistance state (featured by the puzzling resistance plateau) below the temperature 3–5 K [9, 44, 66, 67]. This resistance plateau has been suggested to be originated from the existence of an in-gap state [67–69]. This in-gap state with a scale of 3–5 meV has been identified by experimental measurements, which is ascribed to reside in the hybridization gap [70, 71].

In recent studies, the phenomena of bulk quantum oscillations with characteristics of an unconventional Fermi liquid are observed in SmB₆ [64, 65]. Li et al revealed two Fermi surfaces on the (100) surface plane and one Fermi surface on the (101) surface plane by means of torque magnetometry, and demonstrated the 2D nature of the conducting electronic states of SmB₆. Tan et al found that the quantum oscillation amplitude of SmB₆ strongly increased at low temperatures, although its quantum oscillation frequency characteristic of a large 3D conduction electron Fermi surface was similar to another two metallic rare earth hexaborides such as LaB₆ and PrB₆ [65]. These findings yield a new puzzle. As emerging in the same low temperature range, the quantum oscillation anomaly (the new puzzle) and the resistance plateau (the old puzzle) possibly share the same origination. Recent investigations propose that the surface Kondo breakdown is responsible for the metallic surface state [72, 73], which may be associated to these two puzzling behaviors.
Many high-pressure studies on SmB$_6$ have been carried out [41, 42, 74–79] before the prediction that SmB$_6$ is a candidate of topological Kondo insulator. Several high-pressure electrical resistivity measurements found the same phenomena of an existing resistance plateau at temperature below 3–5 K, a narrow-gap in the temperature range below 15 K and a hybridization gap at temperature below 100 K at pressure below 4 GPa [74–77]. However, the resistance plateau can be fully suppressed at pressure ~4 GPa, meanwhile a remarkable resistance drop appears, as shown in figure 4. The resistance drop at 4 GPa suggests that SmB$_6$ undergoes an insulator–metal transition. From the resistivity data, Gabini et al estimated the pressure dependence of activation energy, demonstrating pressure-induced simultaneous changes of the two energy scales [76]. The coexistence of the two gaps in the ambient-pressure SmB$_6$ is supported by the results obtained recently from ARPES studies [44, 45, 52, 53], i.e., the hybridization gap lies in 10–20 meV and the in-gap state is at 3–5 meV below the Fermi surface.

Related efforts indicated that the metallic phase emerging at ~4 GPa showed a non-Fermi-liquid behavior in the temperature range 1.5 K–4 K [76]. At pressure above 6 GPa, a Fermi-liquid state clearly presents. However, it is noteworthy that there exists a continuous change tendency for its $R$–$T$ curves above 4 GPa, which leads us to propose that the ground state of the metallic phase near 4 GPa probably is also in a Fermi liquid state. To prove this, the high-pressure resistance measurements in a Helium-3 refrigerator are needed.

High-pressure $^{149}$Sm nuclear forward scattering of synchrotron radiation measurements were performed by Barla et al [78]. The results showed that SmB$_6$ undergoes a transition from a paramagnetic state to an ordered magnetic state at ~6 GPa. The ordered state was found to persist up to ~25 GPa, as shown in figure 5. This magnetic ordered state in pressurized SmB$_6$ was supported by high pressure specific heat measurements, and a homogeneous magnetic state occurring only at pressure above 10 GPa was suggested [80]. To clarify whether the pressure-induced insulator–metal and the nonmagnetic–magnetic transitions are related to a structure phase transition, high-pressure synchrotron XRD measurements were performed by Nishiyama et al [41]. They found that the ambient-pressure crystal structure of SmB$_6$ is stable up to 10 GPa. Extended high-pressure measurements by Paraskevas et al revealed that no first-order phase transition was observed up to 39 GPa at 300 K and 16 GPa at 10 K, but lattice modifications were observed at a critical pressure of ~7 GPa in both cases [42]. Based on these results, they concluded that the pressure-induced metallization and lattice modifications in SmB$_6$ are associated with the emergence of a long-range ordered magnetic phase. However, it should be emphasized that SmB$_6$ is a mixed valence compound and the valence state of the Sm ions is sensitive to pressure, temperature or doping. The extrapolation from the high pressure results suggested that the trivalent state of the Sm ions in SmB$_6$ may show up at the pressure as high as above 20 GPa [25, 81]. More importantly, it was also found that the mean valence of SmB$_6$ is reduced from 2.59 at 300 K to 2.53 at ~2 K, which matches up with its temperature dependence of resistivity [82]. The recent high pressure x-ray absorption results measured by the authors’ group indicate that, upon increasing pressure, the mean valence of SmB$_6$ enhances from 2.56 at ambient pressure to nearly 3 at ~10 GPa [83]. All these results consistently indicate that the valence state plays a vital role in developing the exotic phenomenon of SmB$_6$. As the connections among the pressure-induced valence change, evolution of two energy gaps and magnetic ordering are still not clear, further experimental and theoretical studies with more attention on the valence state are urgently needed.

3.2. Pressure-induced exotic states in YbB$_6$

As a sister compound of SmB$_6$, YbB$_6$ crystallizes in the same crystal structure of SmB$_6$ and possesses the same sets of low-energy bands (Yb 5$d$, Yb 4$f$ and B 2$p$), but presents very different electronic structures due to the fact that Yb has a fully filled 4$f$ shell while Sm has a nearly half-filled 4$f$-shell. The crucial factor that makes the divergence between YbB$_6$ and SmB$_6$ stems from the difference of their electronic structures. On the (001) natural cleavage surface of the YbB$_6$ sample, the lowest 4$f$ flat band is about 1 eV below the Fermi energy ($E_F$), while that of SmB$_6$ is only 15 meV below the $E_F$. As a result, the ambient pressure YbB$_6$ exhibits semiconductor behavior [84], in stark contrast to that showed in
the Kondo insulator SmB$_6$. Theorists predicted that YbB$_6$ and SmB$_6$ are all candidate materials for the new class of TIs with $f$-electrons. However, measurements of ARPES on YbB$_6$ suggest that its electronic state should originate from the hybridization between Yb $d$-orbitals and B $p$-orbitals [3, 85–87]. Remarkably, very recent results from theoretical and ARPES studies on the (1 1 0) surface termination argue that the ambient-pressure YbB$_6$ is a non-Kondo and non-TI [88].

The obtained ambient pressure results give rise to a new interest on whether the semiconductor-like YbB$_6$ can be pressurized into a possibly topological non-trivial Kondo insulator as SmB$_6$. Recently, the authors’ group reports their investigations of a comprehensive in situ high pressure measurements of transport, XRD and x-ray absorption [26] on the high quality single crystal YbB$_6$ provided by Fisk’s lab at the University of California (Irvine) [20, 55]. They find two pressure-induced QPTs (figure 6), i.e. from a topologically trivial semiconducting state and the possibly topological non-trivial high-pressure gapped phase, respectively. SM stands for the topologically trivial semiconducting state and the overlap SM with small Yb mixed $p$-orbitals overlaps with TNT-HP phase.

The authors observe an insulating phase and the low-temperature resistance measurements performed by the same group indicated that no pressure gapped state. These results reveal the sensitive response of the electron state to the valence change in YbB$_6$, and more significantly the formation of its resistance plateau is intimately connected to the valence state, similar to that of SmB$_6$. Therefore, the phase evolution in the pressurized YbB$_6$ may be resulted not only from the interplay of all the three electron orbitals [89] but also from the complicated interactions involving the pressure-induced valence instability.

Recent theoretical studies on the electronic structure for pressurized YbB$_6$ propose that the YbB$_6$ subjected to pressure above 15 GPa may be a $p$–$d$ overlap SM with small Yb mixed valency [88]. This interesting high-pressure gapped phase with the famous feature of the resistance plateau deserves further investigations.

3.3. Unexpected valence stability of rare earth ions in CeB$_6$ and EuB$_6$

As one of the typical dense Kondo compounds, CeB$_6$ at ambient-pressure displays a magnetic order which is considered to stem from the 4$f$$^1$ configuration of Ce$^{3+}$ ions. In general, application of external pressure can alter the valence of Ce ions with the tendency from Ce$^{3+}$ to Ce$^{4+}$. This change can drive the system converting from a state with higher population of magnetic ions toward a state with lower ones. Therefore, according to the Doniach diagram [90], the primary effect of high pressure on the CeB$_6$ is that the $f$–$d$ hybridization is enhanced [91]. It is conceivable that sufficient high pressure may succeed in transforming CeB$_6$ into a possibly topological Kondo insulating state similar to that of SmB$_6$. Motivated by whether the CeB$_6$ can be pushed into a possibly topological insulating state under pressure, Shilling’s group performed high-pressure resistance measurements on single crystal CeB$_6$ over the temperature range 1.3–295 K [43]. They did not observe an insulating phase and the low-temperature resistance plateau at pressure up to 122 GPa. Synchrotron XRD measurements performed by the same group indicated that no
pressure-induced structure phase transition is found in CeB$_6$ up to 85 GPa. These diffraction results provide very important information on the structural stability against pressure, which may help to understand the puzzling physics in SmB$_6$.

Another interesting hexaboride EuB$_6$, with divalent Eu ions, behaves like a semi-metal and it is the only rare-earth hexaboride with ferromagnetic order [92]. Electron paramagnetic resonance (EPR) experiments reveal that the dominant interaction in EuB$_6$ is Ruderman–Kittel–Kasuya–Yosida (RKKY)-like [93, 94]. In 1997, Cooley et al. measured the electrical resistivity for single crystal EuB$_6$ in the temperature range from 1.2 to 300 K at high pressure (0–16.9 GPa) [95]. They found that the room temperature resistivity is dramatically reduced with increasing pressure, meanwhile the transition temperature of the ferromagnetic order is strongly enhanced. As a result, they argued that the magnetic order is driven by the RKKY interaction between the localized Eu moments and the very dilute conduction electrons. With increasing pressure, the band overlap is enhanced, leading to an increase in carriers at the Fermi surface.

For the question of why no resistance plateau behavior was found in pressurized CeB$_6$ or EuB$_6$, some rough analysis combined with our most recent experimental results are given here. In fact, the pressure-induced valence change is frequently observed in Ce or Eu-containing compounds, which yields many interesting phenomena [96–98]. However the most recent high pressure x-ray absorption measurements performed by the authors’ group at Shanghai Synchrotron Radiation Facilities demonstrate that the valence state of the rare earth ions in CeB$_6$ or EuB$_6$ is highly stable [99]. In this study, they found that the valence of Ce$^{3+}$ or Eu$^{2+}$ remains unchanged up to 25 GPa, while at the same beamline this group found the pressure-induced valence change of the rare earth ions in EuFe$_2$As$_2$ and CeFeAsO$_{1-x}F_x$. Their results showed that the mean valence of Eu ions in EuFe$_2$As$_2$ alters from 2 to 2.3 at ~10 GPa [96], and that of Ce ions in CeFeAsO$_{1-x}F_x$ changes from 3 to 3.1 at ~11 GPa [97]. Therefore, it can be learnt that the valence state of Ce ions in pressurized CeB$_6$ or Eu ions in pressurized EuB$_6$ is protected by the rigid B$_6$ framework. In addition to the stable valence state, the configuration of the $f$ electrons for Ce ions in CeB$_6$ or Eu ions in EuB$_6$, as described in the introduction, may be one of the reasons why the resistance plateau phenomenon cannot emerge in these two hexaborides at high pressure.

4. Conclusions and perspectives

The family of rare earth hexaborides is one of the fascinating SCEs and has versatile abilities to host a plethora of interesting physical phenomena that attract considerable attention from scientists. In this family, RB$_6$ ($R =$ Sm, Yb, Eu and Ce) show interesting behaviors. In particular for SmB$_6$, the most remarkable low-temperature phenomena include its resistance plateau and anomaly quantum oscillation, named as the twin puzzles of SmB$_6$. Now, the concept of the ‘surface state of TT’ is expected to be applied in deciphering these puzzles. Exploring how the ambient-pressure crystal/electronic structure and the corresponding properties evolve with external pressure and analyzing them in a comprehensive fashion are always helpful in understanding the physics behind, and also can provide opportunities to find new phenomena. Through this brief review on both the high-pressure induced phenomena and the ambient-pressure behaviors in the RB$_6$s, some main points and related perspectives are given below.

(i) The unusual behaviors of the mixed-valence compound RB$_6$ ($R =$ Sm, Yb) are governed by their unstable valence state, because the valence state tightly connects with almost all the factors controlling the electronic structure of the system, including the $f$-electron configuration, the densities of magnetic ions and conduction electrons, the hybridization strength of $f$–$d$ orbital electrons (Kondo effect) and the corresponding energy gap, etc. Therefore, we propose that a deeper analysis on the relations between the valence state and the transport/spectroscopy properties may be a pathway to uncover the twin puzzles in SmB$_6$.

(ii) After disappearance of the resistance plateau and occurrence of insulator–metal transition in SmB$_6$ at ~4 GPa, its $R$–$T$ curve exhibits a linear behavior in the temperature range 1.5–4 K. However, considering that the change tendency of the $R$–$T$ curves measured at pressure above 4 GPa is in a continuous way, we propose that the ground state of the metallic phase near 4 GPa probably is also in a Fermi liquid state.

(iii) For the resistance plateau observed in pressurized YbB$_6$, it will be of great significance to confirm whether it shares the same origin as that of SmB$_6$, if yes, what is the difference between them. Further investigations are needed to clarify this issue.

(iv) The sturdy structure of the B$_6$ framework provides a unique environment for the rare earth ions. It is noteworthy that the pressure-induced change of the valence state with a general tendency from 2+ to 3+ in SmB$_6$ or YbB$_6$ yields more magnetic rare earth ions (Sm$^{3+}$ with 4$f^5$ configuration and Yb$^{3+}$ with 4$f^{13}$ configuration respectively) and more 5$d$ conduction electrons simultaneously. While for CeB$_6$ or EuB$_6$, the pressure-induced valence change results in more 4$f^0$ nonmagnetic ions (Ce$^{4+}$ in CeB$_6$ or 4$f^6$ (Eu$^{3+}$) in EuB$_6$ and the 5$d$ conduction electrons. These facts may help to understand the diverse behaviors of SmB$_6$ (or YbB$_6$) and CeB$_6$ (or EuB$_6$). Therefore, it can be proposed that the B$_6$ framework prevents the valence state of the rare earth ions in CeB$_6$ and EuB$_6$ from the effect of pressure. This may lead to the unexpected stability of the valence state in CeB$_6$ and EuB$_6$.

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