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Report on Progress

Pressure-induced exotic states in rare earth hexaborides

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Abstract

Finding the exotic phenomena in strongly correlated electron systems (SCESs) and understanding the corresponding microphysics have long been the research frontiers of condensed matter physics. The remarkable examples for the intriguing phenomena discovered in past years include unconventional superconductivity, heavy Fermion behaviors, giant magneto-resistance and so on. A fascinating type of rare earth hexaboride RB_6 ($R = \text{Sm}, \text{Yb}, \text{Eu}$ and Ce) belongs to a strongly correlated electron system (SCES), but shows unusual ambient-pressure and high-pressure behaviors beyond the phenomena mentioned above. Particularly, the recent discovery of the coexistence of an unusual metallic surface state and an insulating bulk state in SmB_6 , known to be a Kondo insulator decades ago, by theoretical calculations and many experimental measurements creates new interest for the investigation of the RB_6 . This significant progress encourages people to revisit the RB_6 with an attempt to establish a new physics that links the SCES and the unusual metallic surface state which is a common feature of a topological insulator (TI). It is well known that pressure has the capability of tuning the electronic structure and modifying the ground state of solids, or even inducing a quantum phase transition which is one of the kernel issues in studies of SCESs. In this brief review, we will describe the progress in high pressure studies on the RB_6 based on our knowledge and research interests, mainly focusing on the pressure-induced phenomena in YbB_6 and SmB_6 , especially on the quantum phase transitions and their connections with the valence state of the rare earth ions. Moreover, some related high-pressure results obtained from CeB_6 and EuB_6 are also included. Finally, a summary is given in the conclusions and perspectives section.

Keywords: strongly correlated electron systems, topological insulator, rare earth hexaboride, high pressure, valence state

(Some figures may appear in colour only in the online journal)

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

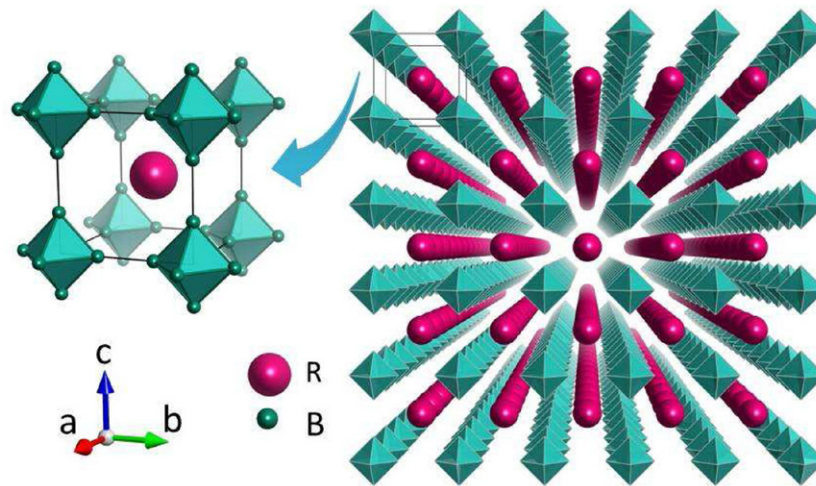


Figure 1. Schematic crystal structure of RB_6 . In crystallographic description, RB_6 takes the body center cubic structure in space group $Pm\bar{3}m$, in which rare earth ion R (dark pink) and B_6 octahedron (green) are arranged in a CsCl-like packing.

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 $5d$ band, the R $4f$ band and the B $2p$ 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 convictive 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 ($R = Sm, Yb, Eu, Ce$).

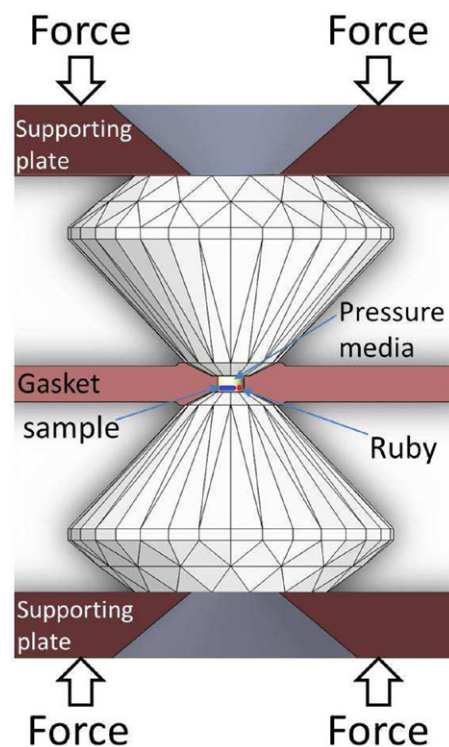


Figure 2. A sketch of the diamond anvil cell used for high pressure studies. Two diamond anvils are glued on the supporting plates oppositely. The sample is located in the hole of a gasket which is placed between the culets of the anvils. A tiny ruby ball is put next to the sample to determine the pressure applied.

A remarkable feature of these RB_6 is that their valence states are usually unstable in different temperature ranges at ambient pressure or in different pressure ranges at fixed temperature [21]. This leads people to consider that the unstable valence state in RB_6 intimately connects to their exotic behaviors observed in different experimental investigations. Usually, external control parameters, such as pressure or magnetic field, can tune the ground state of a correlated electron system from one to another, which is known as the quantum phase transition (QPT) [22, 23]. Studies on the

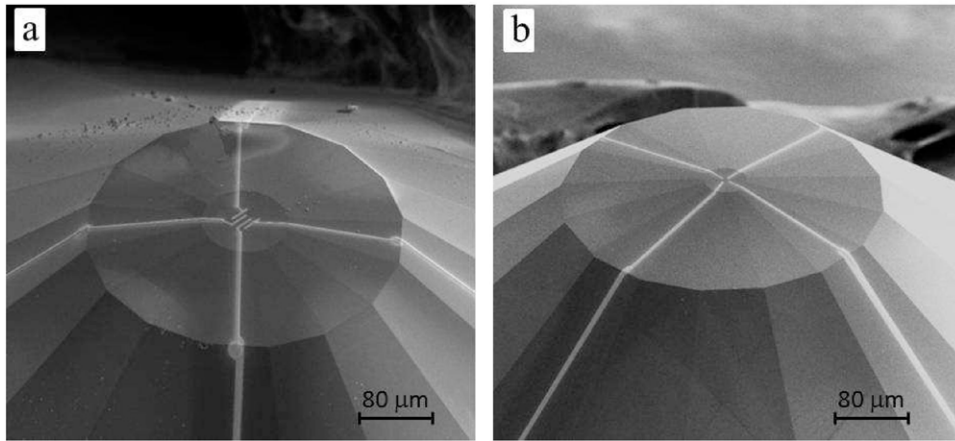


Figure 3. (a) Photograph showing arrangement of four standard electrodes fabricated on the culet of the diamond anvil for *in situ* high pressure resistance measurements. (b) Configuration of Van der Pau type of four electrodes on the culet of the diamond anvil, adopted for *in situ* high pressure Hall coefficient measurements.

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^5 (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^7 -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 hexaborides 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 $\sim 3 \text{ GPa}$ [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 $3\text{He}/4\text{He}$ 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 micro-fabrication 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 $80\ \mu\text{m}$, 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 RB_6 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 SmB_6 [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 SmB_6

After discovery more than 40 years ago [50, 51], SmB_6 , 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 SmB_6 in a strong magnetic field [64, 65] provide a new perspective to help understand the physics of this unique hexaboride.

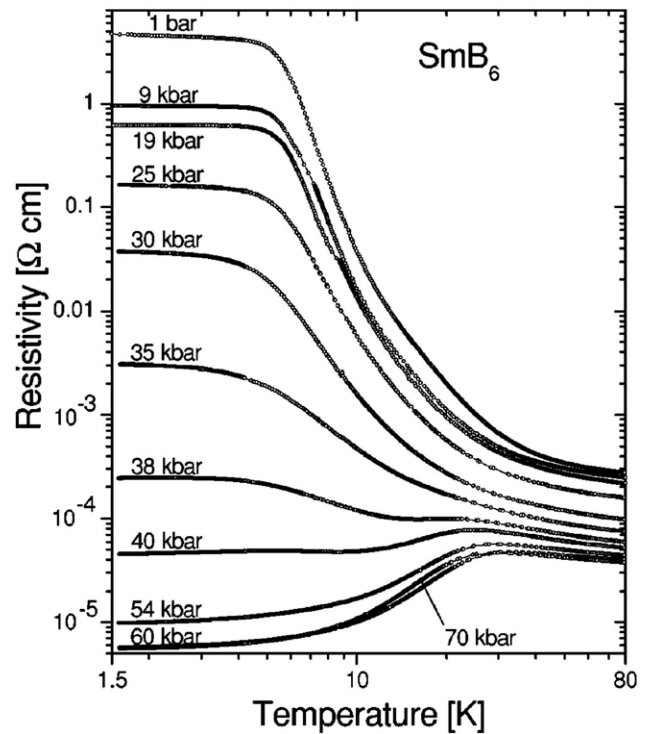


Figure 4. Temperature dependence of resistivity at different pressures in SmB_6 , demonstrating an insulator–metal transition at 4 GPa. Reproduced with permission from [76]. Copyright 2003 American Physical Society.

The temperature dependence of the ambient-pressure electrical resistance of SmB_6 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 $4f$ -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 SmB_6 [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 SmB_6 . Tan *et al* found that the quantum oscillation amplitude of SmB_6 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 LaB_6 and PrB_6 [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.

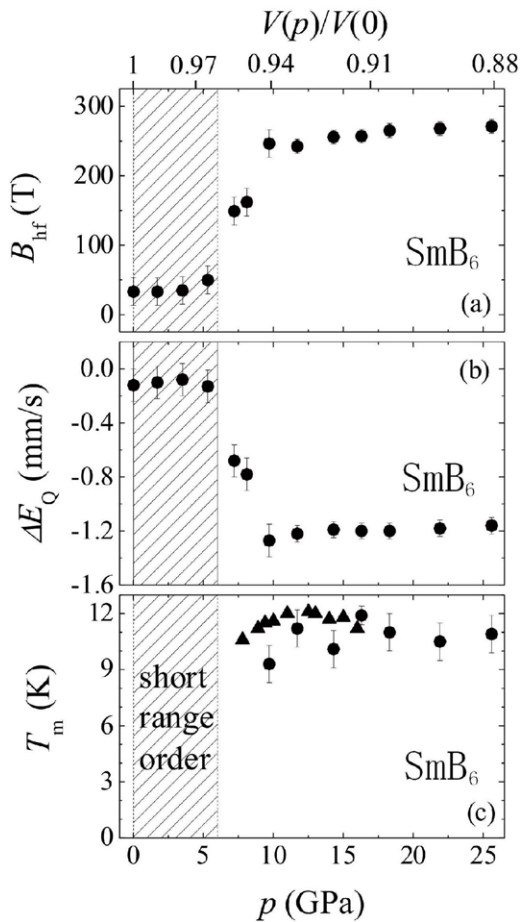


Figure 5. Pressure and volume dependences of (a) the average magnetic hyperfine field B_{hf} at 3 K, of (b) the average electric quadrupole interaction ΔE_Q at 3 K, and of (c) the magnetic transition temperature T_m (circles) and specific heat (triangles). Reproduced with permission from [78]. Copyright 2005 American Physical Society.

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, Gabáni *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 $5d$, Yb $4f$ and B $2p$), but presents very different electronic structures due to the fact that Yb has a fully filled $4f$ shell while Sm has a nearly half-filled $4f$ -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 $4f$ 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

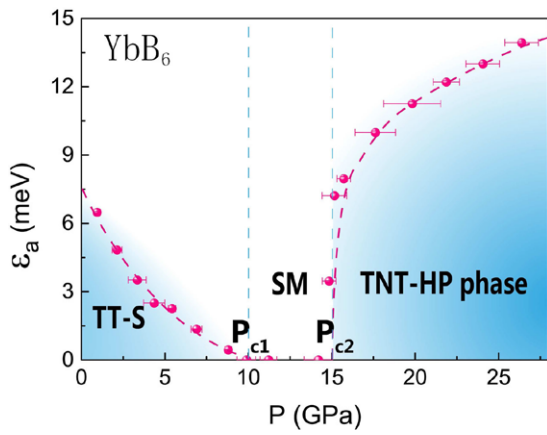


Figure 6. Phase diagram of the pressure dependence of activation energy gap (ϵ_a) for YbB_6 . The acronyms TT-S and TNT-HP phases stand for the topologically trivial semiconducting state and the possibly topological non-trivial high-pressure gapped phase, respectively. SM represents the semimetallic state. The data are derived from [26].

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 by 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 semiconductor (TT-S) to an intermediate semimetal (SM) at ~10 GPa and then from the SM to a possible topologically non-trivial high-pressure (TNT-HP) gapped phase above 15 GPa. In the high pressure gapped phase, YbB_6 significantly displays a resistance plateau at low temperature, similar to what has been seen in the possibly topological Kondo insulator SmB_6 . Importantly, the resistance plateau observed in YbB_6 shows the same positive magnetoresistance behavior as SmB_6 , suggesting that the resistance plateau phenomenon in pressurized YbB_6 may also originate from the surface [20].

XRD experiments rule out the possibility of a pressure-induced structural transition in YbB_6 , thus the authors propose that the new gapped state emerged at high pressure in YbB_6 stems from electron–electron interactions. The data reported also show that the onset temperature (T^*) of the resistance plateau varies with pressure and shifts to higher temperatures upon increasing pressure, which is in contrast to the behavior of SmB_6 [67].

To further clarify the underlying mechanism for the pressure-induced QPTs and the nature of the two gapped phases, they performed high-pressure x-ray absorption measurements

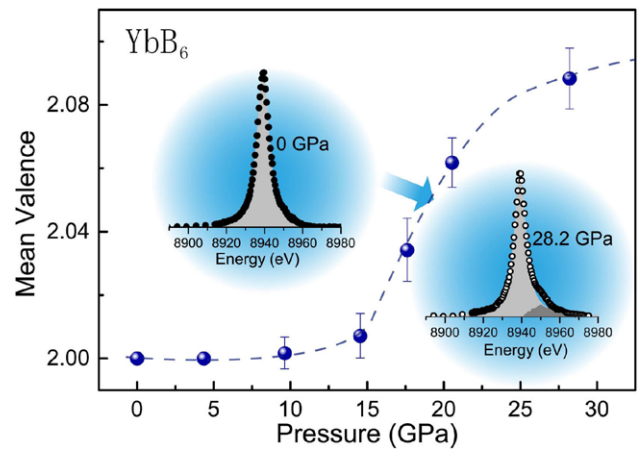


Figure 7. Pressure dependence of mean valence determined from XAS data. The insets display XAS of Yb measured at ambient pressure and 28.2 GPa, respectively. The data are derived from [26].

(figure 7) and find that the mean valence (ν) remains nearly unchanged below 10 GPa, but it increases remarkably at pressure greater than 15 GPa where the YbB_6 enters the high 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 $4f^1$ 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 CeB₆ 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 SmB₆.

Another interesting hexaboride EuB₆, 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 EuB₆ is Ruderman–Kittel–Kasuya–Yosida (RKKY)-like [93, 94]. In 1997, Cooley *et al* measured the electrical resistivity for single crystal EuB₆ 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 CeB₆ or EuB₆, 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 CeB₆ or EuB₆ is highly stable [99]. In this study, they found that the valence of Ce³⁺ or Eu²⁺ 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 EuFe₂As₂ and CeFeAsO_{1-x}F_x. Their results showed that the mean valence of Eu ions in EuFe₂As₂ 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 CeB₆ or Eu ions in pressurized EuB₆ is protected by the rigid B₆ framework. In addition to the stable valence state, the configuration of the *f* electrons for Ce ions in CeB₆ or for Eu ions in EuB₆, 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 SCESs and has versatile abilities to host a plethora of interesting physical phenomena that attract considerable attention from scientists. In this family, RB₆ (*R* = Sm, Yb, Eu and Ce) show interesting behaviors. In particular for SmB₆, the most remarkable low-temperature phenomena include its resistance plateau and anomaly quantum oscillation, named as the twin puzzles of SmB₆. Now, the concept of the 'surface state of TI' 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 RB₆, some main points and related perspectives are given below.

- (i) The unusual behaviors of the mixed-valence compound RB₆ (*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 SmB₆.
- (ii) After disappearance of the resistance plateau and occurrence of insulator–metal transition in SmB₆ 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 YbB₆, it will be of great significance to confirm whether it shares the same origination as that of SmB₆, if yes, what is the difference between them. Further investigations are needed to clarify this issue.
- (iv) The sturdy structure of the B₆ 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 SmB₆ or YbB₆ yields more magnetic rare earth ions (Sm³⁺ with 4*f*⁵ configuration and Yb³⁺ with 4*f*¹³ configuration respectively) and more 5*d* conduction electrons simultaneously. While for CeB₆ or EuB₆, the pressure-induced valence change results in more 4*f*⁰ nonmagnetic ions (Ce⁴⁺) in CeB₆ or 4*f*⁶ (Eu³⁺) in EuB₆ and the 5*d* conduction electrons. These facts may help to understand the diverse behaviors of SmB₆ (or YbB₆) and CeB₆ (or EuB₆). Therefore, it can be proposed that the B₆ framework prevents the valence state of the rare earth ions in CeB₆ and EuB₆ from the effect of pressure. This may lead to the unexpected stability of the valence state in CeB₆ and EuB₆.

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References

- [1] Young D P *et al* 1999 High-temperature weak ferromagnetism in a low-density free-electron gas *Nature* **397** 412
- [2] Jorge Q and Chris H 2009 The strong-correlations puzzle *Phys. World* **22** 32
- [3] Neupane M *et al* 2015 Non-Kondo-like electronic structure in the correlated rare-earth hexaboride YbB₆ *Phys. Rev. Lett.* **114** 016403
- [4] Varma C 1976 Mixed-valence compounds *Rev. Mod. Phys.* **48** 219
- [5] Lu F, Zhao J, Weng H, Fang Z and Dai X 2013 Correlated topological insulators with mixed valence *Phys. Rev. Lett.* **110** 096401
- [6] Feng X Y, Dai J, Chung C H and Si Q 2013 Competing topological and Kondo insulator phases on a honeycomb lattice *Phys. Rev. Lett.* **111** 016402
- [7] Weng H M, Zhao J Z, Wang Z J, Fang Z and Dai X 2014 Topological crystalline Kondo insulator in mixed valence ytterbium borides *Phys. Rev. Lett.* **112** 5
- [8] Hlawenka P *et al* 2015 Samarium hexaboride: a trivial surface conductor (arXiv:1502.01542)
- [9] Zhu Z H *et al* 2013 Polarity-driven surface metallicity in SmB₆ *Phys. Rev. Lett.* **111** 216402
- [10] Ruan W, Ye C, Guo M, Chen F, Chen X, Zhang G-M and Wang Y 2014 Emergence of a coherent in-gap state in the SmB₆ Kondo insulator revealed by scanning tunneling spectroscopy *Phys. Rev. Lett.* **112** 136401
- [11] Wolgast S, Kurdak Ç, Sun K, Allen J W, Kim D-J and Fisk Z 2013 Low-temperature surface conduction in the Kondo insulator SmB₆ *Phys. Rev. B* **88** 180405
- [12] Lortz R *et al* 2006 Superconductivity mediated by a soft phonon mode: specific heat, resistivity, thermal expansion, and magnetization of YB₆ *Phys. Rev. B* **73** 024512
- [13] Yamauchi H, Takagi K, Yuito I and Kawabe U 1976 Work function of LaB₆ *Appl. Phys. Lett.* **29** 638
- [14] Nakamura S, Goto T and Kunii S 1995 Magnetic phase diagrams of the dense kondo compounds CeB₆ and Ce_{0.5}La_{0.5}B₆ *J. Phys. Soc. Japan* **64** 3941
- [15] Nakao H, Magishi K-i, Wakabayashi Y, Murakami Y, Koyama K, Hirota K, Endoh Y and Kunii S 2001 Antiferro-quadrupole ordering of CeB₆ studied by resonant x-ray scattering *J. Phys. Soc. Japan* **70** 1857
- [16] Süllow S, Prasad I, Aronson M C, Bogdanovich S, Sarrao J L and Fisk Z 2000 Metallization and magnetic order in EuB₆ *Phys. Rev. B* **62** 11626
- [17] Kim J Y, Sung N H and Cho B K 2007 Weak ferromagnetism in single crystalline YbB_{6-δ} *J. Appl. Phys.* **101** 09D512
- [18] Chazalviel J N, Campagna M, Wertheim G K and Schmidt P H 1976 Study of valence mixing in SmB₆ by x-ray photoelectron spectroscopy *Phys. Rev. B* **14** 4586
- [19] Dzero M, Sun K, Galitski V and Coleman P 2010 Topological Kondo insulators *Phys. Rev. Lett.* **104** 106408
- [20] Kim D J, Xia J and Fisk Z 2014 Topological surface state in the Kondo insulator samarium hexaboride *Nat. Mater.* **13** 466
- [21] Chandran L, Krishna-murthy H R and Ramakrishnan T V 1992 Pressure-induced valence changes in mixed-valent systems *J. Phys.: Condens. Matter* **4** 7067
- [22] Si Q and Steglich F 2010 Heavy fermions and quantum phase transitions *Science* **329** 1161
- [23] Gegenwart P, Si Q and Steglich F 2008 Quantum criticality in heavy-fermion metals *Nat. Phys.* **4** 186
- [24] Röhler J 1987 *Handbook on the Physics and Chemistry of Rare Earths* vol 10 (New York: Elsevier)
- [25] Beaurepaire E, Kappeler J P and Krill G 1990 X-ray-absorption near-edge structure study in mixed-valent samarium systems *Phys. Rev. B* **41** 6768
- [26] Zhou Y *et al* 2015 Pressure-induced quantum phase transitions in a YbB₆ single crystal *Phys. Rev. B* **92** 241118
- [27] Walker I R 1999 Nonmagnetic piston-cylinder pressure cell for use at 35 kbar and above *Rev. Sci. Instr.* **70** 3402
- [28] Petrova A E, Sidorov V A and Stishov S M 2005 High-pressure helium gas apparatus and hydrostatic toroid cell for low-temperatures applications *Phys. B: Condens. Matter* **359-61** 1463
- [29] Eremets M I and Troyan I A 2011 Conductive dense hydrogen *Nat. Mater.* **10** 927
- [30] Sakata M, Nakamoto Y, Shimizu K, Matsuoka T and Ohishi Y 2011 Superconducting state of Ca-VII below a critical temperature of 29 K at a pressure of 216 GPa *Phys. Rev. B* **83** 220512
- [31] Sun L *et al* 2009 Pressure-induced superconducting state in crystalline boron nanowires *Phys. Rev. B* **79** 140505
- [32] Eremets M I, Struzhkin V V, Mao H-k and Hemley R J 2001 Superconductivity in boron *Science* **293** 272
- [33] Loubeyre P, Occelli F and LeToullec R 2002 Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen *Nature* **416** 613
- [34] Narayana C, Luo H, Orloff J and Ruoff A L 1998 Solid hydrogen at 342 GPa: no evidence for an alkali metal *Nature* **393** 46
- [35] Ma Y, Eremets M, Oganov A R, Xie Y, Trojan I, Medvedev S, Lyakhov A O, Valle M and Prakapenka V 2009 Transparent dense sodium *Nature* **458** 182
- [36] Zha C-S, Liu Z and Hemley R J 2012 Synchrotron infrared measurements of dense hydrogen to 360 GPa *Phys. Rev. Lett.* **108** 146402
- [37] Hamlin J J and Schilling J S 2007 Pressure-induced superconductivity in Sc to 74 GPa *Phys. Rev. B* **76** 012505
- [38] Matsuoka T, Debessai M, Hamlin J J, Gangopadhyay A K, Schilling J S and Shimizu K 2008 Pressure-induced superconductivity in CaLi₂ *Phys. Rev. Lett.* **100** 197003
- [39] Hamlin J J, Tissen V G and Schilling J S 2006 Superconductivity at 17 K in yttrium metal under nearly hydrostatic pressures up to 89 GPa *Phys. Rev. B* **73** 094522
- [40] Eremets M I 1996 *High Pressure Experimental Methods* (Oxford: Oxford University Press)
- [41] Nishiyama K *et al* 2013 Pressure-induced localization of 4f electrons in the intermediate valence compound SmB₆ *J. Phys. Soc. Japan* **82** 123707
- [42] Paraskevas P, Martin B and Mohamed M 2015 High-pressure structural anomalies and electronic transitions in the topological Kondo insulator SmB₆ *Europhys. Lett.* **110** 66002
- [43] Foroozani N, Lim J, Fabbris G, Rosa P F S, Fisk Z and Schilling J S 2015 Suppression of dense Kondo state in CeB₆ under pressure *Phys. B: Condens. Matter* **457** 12
- [44] Xu N *et al* 2014 Direct observation of the spin texture in SmB₆ as evidence of the topological Kondo insulator *Nat. Commun.* **5** 5
- [45] Neupane M *et al* 2013 Surface electronic structure of the topological Kondo-insulator candidate correlated electron system SmB₆ *Nat. Commun.* **4** 7
- [46] Phelan W A, Koohpayeh S M, Cottingham P, Freeland J W, Leiner J C, Broholm C L and McQueen T M 2014 Correlation between bulk thermodynamic measurements and the low-temperature-resistance plateau in SmB₆ *Phys. Rev. X* **4** 031012
- [47] Min C-H, Lutz P, Fiedler S, Kang B Y, Cho B K, Kim H D, Bentmann H and Reinert F 2014 Importance of charge fluctuations for the topological phase in SmB₆ *Phys. Rev. Lett.* **112** 226402
- [48] Hasan M Z and Kane C L 2010 Colloquium: topological insulators *Rev. Mod. Phys.* **82** 3045
- [49] Qi X L and Zhang S C 2011 Topological insulators and superconductors *Rev. Mod. Phys.* **83** 1057
- [50] Menth A, Buehler E and Geballe T H 1969 Magnetic and semiconducting properties of SmB₆ *Phys. Rev. Lett.* **22** 295

- [51] Vainshtein E E, Blokhin S M and Paderno Y B 1965 X-ray absorption studies on SmB_6 *Sov. Phys.—Solid State* **6** 2318
- [52] Jiang J *et al* 2013 Observation of possible topological in-gap surface states in the Kondo insulator SmB_6 by photoemission *Nat. Commun.* **4** 3010
- [53] Xu N *et al* 2014 Exotic Kondo crossover in a wide temperature region in the topological Kondo insulator SmB_6 revealed by high-resolution ARPES *Phys. Rev. B* **90** 085148
- [54] Rößler S, Jang T-H, Kim D-J, Tjeng L H, Fisk Z, Steglich F and Wirth S 2014 Hybridization gap and Fano resonance in SmB_6 *Proc. Natl Acad. Sci.* **111** 4798
- [55] Kim D J, Thomas S, Grant T, Botimer J, Fisk Z and Xia J 2013 Surface hall effect and nonlocal transport in SmB_6 : evidence for surface conduction *Sci. Rep.* **3** 3150
- [56] Yong J *et al* 2014 Robust topological surface state in Kondo insulator SmB_6 thin films *Appl. Phys. Lett.* **105** 222403
- [57] Syers P, Kim D, Fuhrer M S and Paglione J 2015 Tuning bulk and surface conduction in the proposed topological Kondo insulator SmB_6 *Phys. Rev. Lett.* **114** 096601
- [58] Chen F *et al* 2015 Magnetoresistance evidence of a surface state and a field-dependent insulating state in the Kondo insulator SmB_6 *Phys. Rev. B* **91** 205133
- [59] Luo Y, Chen H, Dai J, Xu Z-a and Thompson J D 2015 Heavy surface state in a possible topological Kondo insulator: magnetothermoelectric transport on the (011) plane of SmB_6 *Phys. Rev. B* **91** 075130
- [60] Yue Z, Wang X, Wang D, Wang J, Culcer D and Dou S 2015 Crossover of magnetoresistance from fourfold to twofold symmetry in SmB_6 single crystal, a topological Kondo insulator *J. Phys. Soc. Japan* **84** 044717
- [61] Nakajima Y, Syers P, Wang X, Wang R and Paglione J 2016 One-dimensional edge state transport in a topological Kondo insulator *Nat. Phys.* **12** 213
- [62] Wakeham N, Wang Y Q, Fisk Z, Ronning F and Thompson J D 2015 Surface state reconstruction in ion-damaged SmB_6 *Phys. Rev. B* **91** 085107
- [63] Fuhrman W T *et al* 2015 Interaction driven subgap spin exciton in the Kondo insulator SmB_6 *Phys. Rev. Lett.* **114** 036401
- [64] Li G *et al* 2014 Two-dimensional Fermi surfaces in Kondo insulator SmB_6 *Science* **346** 1208
- [65] Tan B S *et al* 2015 Unconventional Fermi surface in an insulating state *Science* **349** 287
- [66] Aeppli G and Fisk Z 1992 Kondo insulators *Comments Condens. Matter Phys.* **16** 155
- [67] Cooley J C, Aronson M C, Fisk Z and Canfield P C 1995 SmB_6 : Kondo insulator or exotic metal? *Phys. Rev. Lett.* **74** 1629
- [68] Gorshunov B, Sluchanko N, Volkov A, Dressel M, Knebel G, Loidl A and Kunii S 1999 Low-energy electro-dynamics of SmB_6 *Phys. Rev. B* **59** 1808
- [69] Sluchanko N E *et al* 2000 Intragap states in SmB_6 *Phys. Rev. B* **61** 9906
- [70] Allen J W, Batlogg B and Wachter P 1979 Large low-temperature Hall effect and resistivity in mixed-valent SmB_6 *Phys. Rev. B* **20** 4807
- [71] Kronmüller H and Parkin S S P 2007 *Handbook of Magnetism and Advanced Magnetic Materials* (Hoboken, NJ: Wiley)
- [72] Alexandrov V, Coleman P and Erten O 2015 Kondo breakdown in topological Kondo insulators *Phys. Rev. Lett.* **114** 177202
- [73] Erten O, Ghaemi P and Coleman P 2016 Kondo breakdown and quantum oscillations in SmB_6 *Phys. Rev. Lett.* **116** 046403
- [74] Beille J, Maple M B, Wittig J, Fisk Z and DeLong L E 1983 Suppression of the energy gap in SmB_6 under pressure *Phys. Rev. B* **28** 7397
- [75] Cooley J C, Aronson M C, Fisk Z and Canfield P C 1994 High pressure insulator–metal transition in SmB_6 *Phys. B: Condens. Matter* **199** 486
- [76] Gabáni S, Bauer E, Berger S, Flachbart K, Paderno Y, Paul C, Pavlík V and Shitsevalova N 2003 Pressure-induced Fermi-liquid behavior in the Kondo insulator SmB_6 : possible transition through a quantum critical point *Phys. Rev. B* **67** 172406
- [77] Gabáni S, Bauer E, Della Mea M, Flachbart K, Paderno Y, Pavlík V and Shitsevalova N 2004 Insulator–metal phase transition in SmB_6 under pressure *J. Magn. Magn. Mater.* **272–6** 397
- [78] Barla A *et al* 2005 High-pressure ground state of SmB_6 : electronic conduction and long range magnetic order *Phys. Rev. Lett.* **94** 166401
- [79] Nishiyama K *et al* 2013 Effect of pressure on the intermediate-valence semiconductor SmB_6 : ^{11}B -NMR *J. Korean Phys. Soc.* **62** 2024
- [80] Derr J, Knebel G, Lapertot G, Salce B, Méasson M A and Flouquet J 2006 Valence and magnetic ordering in intermediate valence compounds: TmSe versus SmB_6 *J. Phys.: Condens. Matter* **18** 2089
- [81] Ogita N, Nagai S, Udagawa M, Iga F, Sera M, Oguchi T, Akimitsu J and Kunii S 2005 Raman scattering study of rare-earth hexaboride *Phys. B: Condens. Matter* **359–61** 941
- [82] Masaichiro M, Satoshi T and Fumitoshi I 2009 Temperature dependence of Sm valence in SmB_6 studied by x-ray absorption spectroscopy *J. Phys.: Conf. Ser.* **176** 012034
- [83] Zhou Y *et al* High pressure studies on SmB_6 , submitted
- [84] Tarascon J M, Etourneau J, Dordor P, Hagenmuller P, Kasaya M and Coey J M D 1980 Magnetic and transport properties of pure and carbon-doped divalent RE hexaboride single crystals *J. Appl. Phys.* **51** 574
- [85] Frantzeskakis E *et al* 2014 Insights from angle-resolved photoemission spectroscopy on the metallic states of $\text{YbB}_6(001)$: $E(k)$ dispersion, temporal changes, and spatial variation *Phys. Rev. B* **90** 235116
- [86] Xia M *et al* 2014 Angle-resolved photoemission spectroscopy study on the surface states of the correlated topological insulator YbB_6 *Sci. Rep.* **4** 5999
- [87] Xu N *et al* 2014 Surface versus bulk electronic structures of a moderately correlated topological insulator YbB_6 revealed by ARPES (arXiv:1405.0165)
- [88] Kang C-J *et al* 2016 Electronic structure of YbB_6 : is it a topological insulator or not? *Phys. Rev. Lett.* **116** 116401
- [89] Witczak-Krempla W, Chen G, Kim Y B and Balents L 2014 Correlated quantum phenomena in the strong spin–orbit regime *Annu. Rev. Condens. Matter Phys.* **5** 57
- [90] Doniach S 1977 *Valence Instabilities and Related Narrow Band Phenomena* ed R D Parks (New York: Plenum) p 169
- [91] Kobayashi T C, Hashimoto K, Eda S, Shimizu K, Amaya K and Onuki Y 2000 Pressure dependence of quadrupole ordering temperature TQ in CeB_6 *Phys. B: Condens. Matter* **281–2** 553
- [92] Süllo S *et al* 1998 Structure and magnetic order of EuB_6 *Phys. Rev. B* **57** 5860
- [93] Glaunsinger W S 1975 Indirect exchange interactions in EuB_6 *Phys. Status Solidi b* **70** K151
- [94] Glaunsinger W S 1976 ERP study of the RKKY interaction in metallic $\text{Eu}_x\text{Gd}_{1-x}\text{B}_6$ *J. Phys. Chem. Solids* **37** 51
- [95] Cooley J C, Aronson M C, Sarrao J L and Fisk Z 1997 High pressures and ferromagnetic order in EuB_6 *Phys. Rev. B* **56** 14541
- [96] Sun L *et al* 2010 Valence change of europium in $\text{EuFe}_2\text{As}_{1.4}\text{P}_{0.6}$ and compressed EuFe_2As_2 and its relation to superconductivity *Phys. Rev. B* **82** 134509
- [97] Sun L *et al* 2010 Pressure-induced competition between superconductivity and Kondo effect in $\text{CeFeAsO}_{1-x}\text{F}_x$ ($x = 0.16$ and 0.3) *Europhys. Lett.* **91** 57008
- [98] Jing G *et al* 2015 Correlation between intercalated magnetic layers and superconductivity in pressurized $\text{EuFe}_2(\text{As}_{0.81}\text{P}_{0.19})_2$ *Europhys. Lett.* **111** 57007
- [99] Zhou Y Z *et al* X-ray absorption measurements on EuB_6 and CeB_6 under pressure, submitted