Quantum phase transition and destruction of Kondo effect in pressurized SmB$_6$

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Article info
Article history:
Received 9 October 2017
Received in revised form 16 October 2017
Accepted 16 October 2017
Available online 24 October 2017

Keywords:
Kondo insulator
Surface state
SmB$_6$
High pressure

Abstract
SmB$_6$ has been a well-known Kondo insulator for decades, but recently attracts extensive new attention as a candidate topological system. Studying SmB$_6$ under pressure provides an opportunity to acquire the much-needed understanding about the effect of electron correlations on both the metallic surface state and bulk insulating state. Here we do so by studying the evolution of two transport gaps (low temperature gap $E_l$ and high temperature gap $E_h$) associated with the Kondo effect by measuring the electrical resistivity under high pressure and low temperature (0.3 K) conditions. We associate the gaps with the bulk Kondo hybridization, and from their evolution with pressure we demonstrate an insulator-to-metal transition at $\sim$4 GPa. At the transition pressure, a large change in the Hall number and a divergence tendency of the electron-electron scattering coefficient provide evidence for a destruction of the Kondo entanglement in the ground state. Our results raise the new prospect for studying topological electronic states in quantum critical materials settings.

1. Introduction
Samarium hexaboride (SmB$_6$) is a paradigm Kondo insulator (KI) with a simple cubic structure, comprising a B$_6$ octahedral framework and Sm ions [1]. It has in common with other KIs that an insulating gap opens upon cooling due to the hybridization between the localized f-electrons and conduction electrons [2–4], but distinguishes from the other KIs by the presence of a low temperature resistance plateau which has been a puzzle for decades [5,6]. Recent theoretical studies suggest that the resistance plateau may be associated with the existence of an exotic metallic surface state, and that SmB$_6$ could be a new class of topological insulator with strong electron correlations, namely a topological Kondo insulator (TKI) [7,8]. A metallic surface state indeed has been confirmed by a variety of measurements [9–17], but whether it is protected by a non-trivial topology remains to be established [18]. Surprisingly, various energy gaps ranging from 5 to 15 meV have been observed from ambient-pressure resistivity, angle resolved photoemission spectroscopy (ARPES), and scanning tunneling spectroscopy (STS) experiments [6,19–23], but it is still unclear how these gaps relate with the bulk Kondo hybridization, and from their evolution with pressure we demonstrate an insulator-to-metal transition at $\sim$4 GPa. At the transition pressure, a large change in the Hall number and a divergence tendency of the electron-electron scattering coefficient provide evidence for a destruction of the Kondo entanglement in the ground state. Our results raise the new prospect for studying topological electronic states in quantum critical materials settings.
quantum phase transition, it is known that high pressure is a "clean" way of continuously tuning the crystal and electronic structures without introducing additional chemical complexity [28,29]. Before the proposal of topological conducting surface state [5,6,21,30–33], high-pressure phenomena of SmB6 had been extensively investigated down to 1.5 K, however a systematic understanding on the instability of the metallic surface state and Kondo hybridization bulk state is lacking. In this study we use our advanced high-pressure facilities which allow us to perform resistance measurements down to 0.3 K, and apply the complementary measurements – adopting the same high pressure cell, the same pressure transmitting medium and the same pressure gauge on the same batch of single crystal – to carry out such investigations on SmB6.

2. Methods

High quality single crystals of SmB6 were grown by the Al flux method, as described in Ref. [11]. Pressure was generated by a diamond anvil cell with two opposing anvils sitting on the Be-Cu supporting plates. Diamond anvils with 300 µm flat and non-magnetic rhenium gaskets with 100 µm diameter hole were employed for different runs of the high-pressure studies. The standard four-probe method was applied on the (0 0 1) facet of single crystal SmB6 for all high pressure transport measurements. To keep the sample in a quasi-hydrostatic pressure environment, NaCl powder was employed as a pressure transmitting medium for the high-pressure resistance and Hall coefficient measurements.

High pressure X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments were performed at room temperature at beamline 4W2 in the Beijing Synchrotron Radiation Facility and at the beamline 14W1 in the Shanghai Synchrotron Radiation Facility, respectively. Diamonds with low birefringence were selected for the experiments. A monochromatic X-ray beam with a wavelength of 0.6199 Å was adopted for all XRD measurements. To maintain the sample in a hydrostatic pressure environment, silicon oil was used as pressure transmitting medium in the high-pressure XRD and XAS measurements. Pressure was determined by the ruby fluorescence method [34].

3. Experimental results

We first performed in situ high pressure resistance measurements down to low temperatures (0.3 K) on single crystal SmB6. As demonstrated in Fig. 1a and b, the resistivity for sample A and B shows the same behavior at pressures below 4 GPa.

Fig. 1. (Color online) Resistivity-temperature data and onset temperature of resistance plateau ($T_\text{\textsuperscript{\textdegree}}$) obtained at different pressures. (a) Temperature dependence of electrical resistivity in the sample A for pressures ranging from 0.5 to 19.6 GPa. (b) Resistivity as a function of temperature in the sample B for pressures ranging from 0.2 to 4.2 GPa. The arrow in (a) and (b) specifies $T_\text{\textsuperscript{\textdegree}}$, the onset temperature for the resistance plateau. (c) Plot of $T_\text{\textsuperscript{\textdegree}}$ versus pressure extracted from the resistance measurements.
i.e. the resistivity increases continuously upon decreasing temperature and then displays a plateau below ~4 K, which is consistent with the results reported previously [5,6,21]. Upon further increasing pressure above 4 GPa, the resistivity shows a remarkable drop at low temperature, which manifests a pressure-induced insulator-metal transition (MIT). It is noteworthy that the different pressure transmitting medium can give rise to different pressure environments for the sample. This pressure medium effect on sample is particularly serious in SmB6, as reported by Derr et al. in Ref [35]. The MIT of the SmB6 in a hydrostatic pressure environment (using an argon gas as pressure medium) is pushed up to 10 GPa, while in a quasi-hydrostatic pressure environment (using steatite [35–37] or NaCl in this study as pressure medium) the MIT occurs at ~4 GPa.

Interestingly, the onset temperature ($T^*$) of the resistance plateau exhibits a downward trend with increasing pressure, and disappears at ~4 GPa (Fig. 1c). Above 4 GPa, while the resistivity vs. temperature becomes metallic-like at low temperatures ($T<\sim 20$ K), it still exhibits insulating-like behavior at higher temperatures ($T>\sim 20$ K). This is so for pressures below ~10 GPa; only at even higher pressures (>10 GPa) does the system change to metallic-like behavior over the entire measured temperature range (Fig. S1, Supplementary Information). In the pressure range investigated, no crystal structural phase transition is observed (Fig. S2, Supplementary Information), in agreement with the results reported [32,33,38]. This indicates that the pressure-induced resistance evolution stems from purely electronic physics.

To determine the nature of the ground state at 4 GPa and above, we fitted the resistivity-temperature ($R$-$T$) data from 0.3 to 4 K with the power law, $\rho(T) = \rho_0 + AT^n$ (where $\rho_0$ is the residual resistivity, $A$ the electron-electron scattering coefficient and $n$ the exponent), we find that below 0.7 K the $R$-$T$ curve at 4 GPa clearly follows a Fermi liquid (FL) behavior with $n=2$ (Fig. 2a). A linear $R$-$T$ behavior at 4 GPa presents only in the temperature range of 1.5–4 K (Fig. 2a), in agreement with previous measurements at higher temperatures (>1.5 K) [21]. Within the temperature range of 0.7–1.5 K, $n$ lies between 1 and 2. Our results reveal that the real ground state of SmB6 at 4 GPa is a FL state, instead of a non-FL state. Our investigations reveal that the real ground state of SmB6 at 4 GPa is a FL state, instead of a non-FL state.

We made fits to our resistivity data by the Arrhenius equation (Fig. S8, Supplementary Information), and extracted the energy gap at each pressure value. In line with the multiplicity of the gaps, we identify two energy gaps $E_h$ (low temperature gap) and $E_l$ (high temperature gap), respectively. As shown in the inset of Fig. 3a, their ambient-pressure values are very consistent with the reported results determined by previous resistance measurements [6,21,22]. It is seen that both $E_h$ and $E_l$ decrease monotonically upon increasing pressure. As pressure is increased towards 4 GPa, the $E_l$ decreases to zero. Simultaneously, the onset temperature ($T^*$) of the resistivity plateau that features the existence of the metallic surface state decreases with increasing pressure and vanishes at the critical pressure ~4 GPa (Fig. 1a and b). Thus our high-pressure results reveal the intimate connection between $T^*$ and $E_l$ which supports that the ground state (the resistivity plateau) at $T< T^*$ is protected by the energy gap $E_l$. Our results also suggest that the $E_l$ gap reflects the hybridization gap developed upon the formation of a static Kondo-singlet in the ground state. While, the $E_h$ gap remains finite across 4 GPa and gradually decreases upon further increasing the pressure towards ~10 GPa. We therefore interpret the $E_l$ as a signifying for the onset of the dynamical Kondo hybridization, which exists at higher temperature.

For SmB6, the unusual phenomena occur in a mixed valence state with $f$ electron configuration between $4f^0$ and $4f^{5+5d^1}$. To understand the pressure-induced resistance behavior, the corresponding evolution of the two energy gaps and the ground state of the phases in the intermediate-pressure and high-pressure regions, we performed in situ high pressure synchrotron X-ray absorption measurements. Representative $L_3$-edge spectra collected at different pressures are presented in Fig. S9 (Supplementary Information). The mean valance ($\nu$) as a function of pressure is plotted in Fig. 3b. It can be seen that $\nu$ increases with pressure. Particularly across 4 GPa, the mean $\nu$ shows an increase from 2.55 to 2.62. The pressure-induced valence change leads us to suggest that an appropriate mixed valence state is crucial for the low temperature behavior in SmB6. In the high pressure region above 10 GPa, we found that the mean valence is closed to $3+$, i.e. the concentration of magnetic Sm$^{3+}$ ions is dominant, which should promote the development of long-ranged magnetic order [40,41]. It is noted that the high-pressure valence measurements on SmB6 were also carried out by Butch et al. as reported in Ref. [38], the tendency of the pressure-induced valence changes of Sm ions between our measurements and Butch’s measurements is the same, i.e. both increase with pressure, though their value shows
(Color online) Electrical resistivity as a function of temperature measured down to 0.3 K. (a) The blue solid are the plot of resistivity versus temperature obtained at 4 GPa. The data can be fitted by $\rho = \rho_0 + A T^2$ in the range below 0.7 K (red line) and by $\rho = \rho_0 + B T$ in the temperature range of 1.5–4 K (light blue), respectively. The low temperature part is zoomed in for a clear view (inset), indicating a Fermi-liquid ground state. (b) and (c) Electrical resistivity versus $T^2$ at 5.7 and 13.2 GPa, respectively. The highest temperature of the quadratic behavior is defined as the onset temperature ($T_{FL}$) of the Fermi-liquid state. (d) Pressure dependence of the $A$ coefficient, showing a divergence tendency as the pressure approaches ∼4 GPa.
a deviation from ours. We attribute the deviation to the difference of the pressure transmitting mediums used in these two experiments. Our high-pressure X-ray absorption results are consistent with the previous nuclear forward scattering and specific heat measurements, in which a magnetic order phase is observed at pressure above 7 GPa [30,31]. The corresponding pressure dependence of the magnetic transition temperature ($T_M$), taken from Refs. [30,31], are also shown in the phase diagram (Fig. 3a). How this transition line evolves as the pressure is further decreased is an important issue that needs to be clarified by future experiments.

In summary, we have studied the exotic high pressure behavior of SmB$_6$ through comprehensive in situ high pressure measurements of resistance, Hall coefficient and synchrotron X-ray diffraction and absorption. From these measurements, we are able to establish the pressure dependences of two energy gaps (the low temperature gap $E_l$ and the high temperature gap $E_h$), the onset temperature of resistance plateau, the Fermi liquid temperature, the Hall coefficient and valence change of Sm ions, all up to 20 GPa. The real ground state of SmB$_6$ at 4 GPa is uncovered using our advanced high-pressure and low-temperature (0.3 K) cryostat, and an ultra-low-temperature (0.03 K) cryostat, to be Fermi-liquid state, instead of non-Fermi liquid state known before. We find a pressure-induced quantum phase transition from the ambient-pressure state of a possibly topological Kondo insulator to a Fermi-liquid state with a divergence tendency of the effective mass at ~4 GPa, which occurs in the background of mixed valence state, and we provide direct evidence for the destruction of the bulk Kondo hybridization state at this quantum phase transition. In addition, we find that the $E_l$ gradually decreases with pressure and reaches zero at 4 GPa, which is accompanied by the suppression of the resistance plateau, suggesting that the metallic surface state is protected by the existence of the $E_l$ gap. Our findings point towards an exciting prospect for studying topological electronic states in quantum critical materials settings.

Fig. 3. (Color online) Summary of pressure dependence of temperature, inverse Hall coefficient and mean valence of SmB$_6$. (a) Phase diagram depicted by the pressure dependence of the onset temperature of the resistance plateau ($T^*$) and Fermi liquid ($T_{FL}$), respectively. Here P-TKI and FL represent the putative topological Kondo insulating state and Fermi liquid state, respectively. $T_M$ stands for the magnetic transition temperature taken from Refs. [30,31]. The filled green square represents the $T_{FL}$ determined from the resistance measurements down to 0.3 K and the filled green circle represents the $T_{FL}$ determined from the resistance measurements down to 0.03 K. The inset displays pressure dependence of the two activation gaps $E_l$ (low temperature gap) and $E_h$ (high temperature gap), respectively. (b) Plots of inverse Hall coefficient ($R_H$) and mean valence of Sm ions versus pressure. The inset displays the inverse $R_H$ as a function of pressure at different temperatures.
Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

The work in China was supported by the National Key Research and Development Program of China (2017YFA0302900, 2016YFA0300300 and 2015CB921303), the National Natural Science Foundation of China (91321027, 11427805, 11404384, U1532267 and 11522435) and the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB07020300 and XDB07020200). R.Y. was supported by the National Natural Science Foundation of China (1374361), the National Key Research and Development Program of China (2016YFA0300300), and the Fundamental Research Funds for the Central Universities and the Research Funds of Renmin University of China (14XNLF08). Work at Los Alamos was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences and Engineering. P. F. S. Rosa acknowledges the support of a Director's Postdoctoral Fellowship that is funded by the Los Alamos LDRD program and the FAPESP Grant 2013/2018-0. Work at Rice University was supported by the ARO Grant No. W911NF-14-1-0525 and the Robert A. Welch Foundation Grant No. C-1411.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.scib.2017.10.008.

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