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Puzzle maker in SmB$_6$: accompany-type valence fluctuation state

Qi Wu$^{1,4}$ and Liling Sun$^{1,2,3,4}$

1 Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
2 University of Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
3 Collaborative Innovation Center of Quantum Matter, Beijing 100190, People’s Republic of China

E-mail: llsun@iphy.ac.cn and wq@iphy.ac.cn

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Abstract
In recent years, studying the Kondo insulator SmB$_6$, a strongly correlated electron material that has been puzzling the community for decades, has again become an attractive topic due to the discovery of its unusual metallic surface state coexisting with the bulk insulating state. Many efforts have been made to understand the microphysics in SmB$_6$, but some puzzles that have been hotly debated and argued have not been solved. In this article, based on the latest progress made in our high-pressure studies on SmB$_6$ and the accumulating results reported by other groups, we propose a notion named the ‘accompany-type valence fluctuation state’, which possibly coexists with the bulk Kondo insulating ground state of SmB$_6$. We expect that this notion could be taken as a common starting point for understanding in a unified way most of the low-temperature phenomena observed by different experimental investigations on SmB$_6$, thus promoting the deciphering of the puzzles. We also expect that this notion could attract rigorous theoretical interpretation and further experimental investigation, or stimulate better thinking on the physics in SmB$_6$.

Keywords: strongly correlated electron systems, Kondo insulator, mixed valence

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

In the decade from 1969, one of the important issues in the field of condensed matter physics was to reveal the microphysics of strongly correlated electron systems (SCESs) through studies on mixed-valence materials, among which SmB6 was a representative system. Then the attention paid to SCESs was transferred to other materials believed to be more attractive, e.g. to heavy fermion superconductors in 1979, to copper oxide superconductors in 1986 and to iron-based superconductors in 2008. However, some fundamental issues of SmB6 had not been solved thoroughly, such as the origin of the low-temperature resistance plateau (LTRP), understanding of the mixed valence behaviors (the most prominent feature of SmB6), and so on. New interest in SmB6 has been aroused by the recent discoveries of an exotic metallic surface state coexisting with the bulk insulating state and the understanding of the topological nature of the metallic surface [1–11], as well as the unusual quantum oscillation [12, 13]. All of these have pushed the studies on SmB6 back to the research frontier of SCESs. However, the convergence of the old puzzles and the new findings makes SmB6 more mysterious than ever. Therefore, a unified understanding of the abundant physical phenomena observed or discovered in SmB6 by different experimental methods or theories is urgently needed so as to reconcile the interpretations of these results.

It is known that there are two prominent low-temperature anomalies in SmB6, the resistance plateau and the unusual quantum oscillation under magnetic field. However, the real ground state responsible for these phenomena has yet to be known. Intuitively thinking, the co-emergence of these low-temperature phenomena is reminiscent of the superconducting state, in which the zero resistance and corresponding diamagnetic behaviors (Meissner effect) occur at low temperature simultaneously. The responses of the superconducting ground state to the applied electric field (current) and magnetic field lead us to raise the question as to whether all these puzzling low-temperature behaviors in SmB6 observed by applying current or magnetic fields share the same physical origin—an unknown ground state.

In this article, we propose that the ambient-pressure SmB6 is in a bulk Kondo-singlet ground state with a unique valence fluctuation, and tentatively classify this kind of valence fluctuation state as the ‘accompany-type valence fluctuation state’ (AVFS for short), the notion of which is expected to be helpful for deciphering the puzzles in SmB6.

The notion of the AVFS refers to a peculiar fashion of the valence fluctuation state in the bulk of SmB6, in which the Sm magnetic ions and d electrons increase or decrease together, as shown in figure 1(a). To our knowledge, this type of valence fluctuation can exist only in Sm- or Yb-containing hexaborides. In the other rare earth hexaborides (such as EuB6), the change in population of the magnetic ions and d electrons can be described as one falling but the other rising in valence fluctuation states, as if the f electron (determining the magnetic state of the Sm ion) and the 5d electron can transfer to each other (as shown in figure 1(b)). Therefore, we define this case as the ‘transfer-type valence fluctuation state’ (TVFS for short).

2. Lower and upper valence limits for the formation of a resistance plateau

Our motivation to clarify the ground state of SmB6 was kindled by our high-pressure studies on this hexaboride [14, 15]. It is commonly believed that pressure is a ‘clean’ way of tuning the crystal and electronic structures without introducing additional chemical complexity into the system investigated [16, 17]. The unusual effect of pressure on these two peculiar rare earth hexaborides, SmB6 and YbB6, is that the populations of the magnetic ions (Sm3+ or Yb3+) and d electrons are enhanced accordingly when the mean valence of the rare earth ions increases with pressure. Correspondingly, Sm2+ or Yb2+ changes its configuration into Sm3+ + 5d or Yb3+ + 5d. Our recent high-pressure studies on the relationship between the mean valence and low-temperature properties of SmB6 reveal that its ground state is closely connected with the instability of its mixed valence state [14, 15]. It is found that pressure can tune the onset temperature of the LTRP and the mean valence simultaneously. The resistance plateau is found to vanish at ~4 GPa, meanwhile its mean valence shows an increases from 2.52, measured at ambient pressure, to 2.62, measured at ~4 GPa. Intriguingly, the LTRP has also been discovered in pressurized YbB6, a sister compound of SmB6, at pressures above 15 GPa where its mean valence increases to 2.03 from 2.00 at ambient pressure [16]. These studies demonstrate that the most prominent difference between SmB6 and YbB6 is that SmB6 is a mixed valence compound from ambient pressure to ~10 GPa, while YbB6 is a divalent compound at ambient pressure but it can be changed into a mixed valence state by application of pressure above 15 GPa.

From the above results we know that there exist an upper valence limit and a lower valence limit for the formation of the LTRP in the rare earth hexaboride system REB6 (RE = Sm and Yb). Based on that, we can establish a combined phase diagram of pressure dependent temperatures (T°), which signifies the onset of the resistance plateau, and pressure dependent mean valence for YbB6 and SmB6, as shown in figure 2. It is seen that the upper limit (2.62°) is in the region of the pressurized SmB6, while the lower limit (2.03°) is in the region of the pressurized YbB6. In the connected part between the
two diagrams, the dome-like red line presents our prediction of the change tendency of $T^*$, either from the YbB$_6$ side (by applying positive pressure) or from the SmB$_6$ side (by applying negative pressure). Recent studies on SmB$_6$ under tensile strain found that the negative pressure can indeed increase the onset temperature ($T^*$) of the resistance plateau [18], which provides strong support for our prediction.

3. Role of temperature-induced valence change in developing the resistance plateau

Consequently, an important question as to whether an appropriate mixed valence state is a necessary condition for developing the LTRP in REB$_6$ is raised. It is known that SmB$_6$ and YbB$_6$ possess the same CsCl-type lattice structure constructed by the B$_6$ framework and the rare earth ions located in the interstitial of the framework. The interstitial space is highly symmetric and large enough to host all kinds of rare earth elements from Ce to Lu to form all corresponding rare earth hexaborides. However, it is noteworthy that the changes in the configuration of SmB$_6$ and YbB$_6$ with pressure are distinct from the other rare earth hexaborides, i.e. their configurations exhibit a balance of 4fn(NM)$\leftrightarrow$4fn$^+$1(M)5d (here NM stands for non-magnetism and M stands for magnetism, and the total angular momentum $J$ for 4fn and 4fn$^+$1 is an integer and non-integer, respectively) or Sm$^{2+}$/Yb$^{3+}\leftrightarrow$Sm$^{3+}$/Yb$^{5+}+5$d correspondingly [19], as shown in table 1. This indicates that the populations of their magnetic 4f electrons (Sm$^{3+}$/Yb$^{3+}$) and 5d electrons can increase or decrease together with the change in pressure. This pressure effect on the populations of magnetic ions and d electrons definitely impacts on the peculiar metallic surface state and the bulk insulating state differently in such a Kondo system and consequently generates some unusual physical phenomena.

The above-mentioned high-pressure studies on YbB$_6$ demonstrate a pressure-induced valence change of Yb ions from 2$^+$ (ambient pressure) to 2.09$^+$ (28 GPa), where a clear resistance plateau can be observed [16]. Does such a small change in valence really play a vital role in developing the resistance plateau in pressurized YbB$_6$? A positive answer can be drawn from the delicate valence measurements on SmB$_6$ at ambient pressure over the whole temperature range from 300 K to 2 K by Masaichiro et al [20], as shown in figure 3. It can be seen that the mean valence ($\nu$) of Sm ions decreases from 2.59 at 300 K to 2.52 at 2 K, where the resistance plateau exists. It should be noted that there exists an upturn in the mean valence value at temperatures below 10 K, indicating that the population of Sm$^{3+}$ ions increases with decreasing temperature. This may be a contributing factor for the formation of the AVFS.

The crucial importance of this temperature-induced valence change in ambient-pressure SmB$_6$ for the formation of the LTRP can be reasonably understood by comparing this ambient-pressure behavior with the high-pressure case in YbB$_6$. The variation of the temperature-induced mean valence in SmB$_6$ is $\Delta\nu = \nu_{300\,K} - \nu_{2\,K} = 0.07$, comparable with that of the pressure-induced mean valence ($\Delta\nu = 1.15$ GPa$ - \nu_{28$ GPa$ = 0.06$) for the development of the resistance plateau in YbB$_6$.

4. AVFS

Evoked by the correlation between the formation of the resistance plateau and the upper/lower valence limits, as well as the temperature-induced mean valence instability at ambient pressure and plenty of related results reported (especially the existence of magnetic fluctuation [21], charge fluctuation [22] and valence fluctuation [23–25]) from diverse experimental methods, we propose that the ambient-pressure SmB$_6$ is in a peculiar valence fluctuation state in its Kondo insulating bulk, and tentatively name this valence fluctuation state as the AVFS, the definition of which has been given in section 1. We propose that the necessary condition for developing the LTRP in the REB$_6$ (RE = Sm and Yb) systems demonstrated experimentally in figure 2 is that the compounds have an appropriate mean valence state. Therefore, a suitable mixed valence state is suggested to be a necessary condition for the formation of the AVFS, which deserves further study.

There is much evidence to support the existence of the AVFS in SmB$_6$, including (i) the existence of magnetic, charge and valence fluctuations [21–24]; (ii) the observation of a self-sustained voltage oscillation [26], which should be associated with the AVFS; (iii) different ratios of Sm$^{2+}$ and Sm$^{3+}$ (0.6–0.7/0.4–0.3) [23], as well as its valence dependence on temperature [20]. All of these seem to be intimately connected with the instability associated with the AVFS.

5. Primary analysis of the mechanism

Generally speaking, the possible mechanism of the proposed AVFS in such a Kondo system originates from the interplay between the Sm ions with the unique configuration of the f electrons (4f$^n$(NM) $\leftrightarrow$ 4fn$^+$1(M)5d) and the special lattice structure of the B$_6$ framework, which provides an appropriate environment to develop the AVFS. Here, we try to give a primary explanation for the existence of the AVFS based on our complementary analysis of the available related experimental results of SmB$_6$. We propose that the AVFS is a type of quantum oscillation between two different states, i.e. 4fn and 4fn$^{15d^1}$ states in SmB$_6$, and suggest that the Sm ion protected by the 5s
and 5p outer shells is trapped in the interstitial space of the B\textsubscript{6} framework, which has, in particular, a negative shrinkage when the temperature is decreased. In addition, the interstitial space is highly symmetric and can provide the required environment for the presence of the A VFS. Ultimately, all these factors co-create a condition that enables the Sm ions in the A VFS to maintain a dynamic balance between their intrinsic electric field and intrinsic magnetic field, which drives the oscillation between the two configurations. In-depth discussions on the possible mechanism of the A VFS are beyond the scope of this article.

As a matter of fact, we note that the concept of valence fluctuation in Sm\textsubscript{B\textsubscript{6}} was proposed previously by Kasuya et al. in 1979 [23], in which it was even pointed out that the valence is fluctuating in the time scale with a frequency between 10\textsuperscript{−9} and 10\textsuperscript{−15} s, probably around 10\textsuperscript{−13} s. However, there was no description of its ‘accompany’ character, as we present in this article. In particular, they inappropriately believed that the ratio of Sm\textsuperscript{2+} and Sm\textsuperscript{3+} is unchanged with temperature. Also, we note that most of the recent studies on Sm\textsubscript{B\textsubscript{6}} have mentioned its mixed valence feature, but lack an appropriate consideration of its A VFS.

### 6. Understanding the metallic surface state from the AVFS perspective

Currently, the most attractive issue for the study of Sm\textsubscript{B\textsubscript{6}} is the interpretation of its exotic metallic surface state. Here, let us try making a rough analysis of the origination of the metallic surface from the perspective of the AVFS notion, and also try to give a simple explanation of the different effects of the

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**Table 1.** The magnetic ground states of 4f ions for the rare earth elements with the divalence state. For each ion, by using Hund’s rules, the shell configuration and the predicted values of S (spin momentum), L (orbital momentum) and J (total angular momentum), as well as the term \(2s_1L_J\) are given. The data are derived from [19]. The electron configurations and the corresponding terms in red indicate the ion in a magnetic state. It can be seen that when the valence is increased from 2\textsuperscript{+} to 3\textsuperscript{+} the electron configuration of Sm or Yb changes from non-magnetic state to magnetic state, while the electron configuration of Eu or Tm changes from magnetic state to non-magnetic state.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Shell</th>
<th>S</th>
<th>L</th>
<th>J</th>
<th>Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm\textsuperscript{2+} (Sm\textsuperscript{3+})</td>
<td>4f\textsuperscript{5}(4f\textsuperscript{5})</td>
<td>3(5/2)</td>
<td>3(5)</td>
<td>0(5/2)</td>
<td>(7F_{0}(61_{5/2}))</td>
</tr>
<tr>
<td>Eu\textsuperscript{2+} (Eu\textsuperscript{3+})</td>
<td>4f\textsuperscript{7}(4f\textsuperscript{6})</td>
<td>7/2(3)</td>
<td>0(3)</td>
<td>7/2(0)</td>
<td>(8S_{7/2}(7F_{0}))</td>
</tr>
<tr>
<td>Tm\textsuperscript{2+} (Tm\textsuperscript{3+})</td>
<td>4f\textsuperscript{13}(4f\textsuperscript{12})</td>
<td>1/2(1)</td>
<td>3(5)</td>
<td>7/2(6)</td>
<td>(2F_{7/2}(3H_{6}))</td>
</tr>
<tr>
<td>Yb\textsuperscript{2+} (Yb\textsuperscript{3+})</td>
<td>4f\textsuperscript{14}(4f\textsuperscript{13})</td>
<td>0(1/2)</td>
<td>0(3)</td>
<td>0(7/2)</td>
<td>(1S_{0}(2F_{7/2}))</td>
</tr>
</tbody>
</table>
AVFS and the TVFS on the surface of the SmB$_6$ sample. As mentioned above, the existence of the AVFS requires that the interstitial space of the B$_6$ framework is highly symmetric to provide an appropriate environment to generate the AVFS. While on its surface, the lattice symmetry is broken and the conduction is better than the bulk due to the existence of Boron’s p dangling bonds [27], thus the populations of conduction electrons and magnetic ions are higher than that of the bulk. As a result, the AVFS cannot survive on the surface. Just as Coleman pointed out, in the ground state of SmB$_6$ the surface Kondo singlet breaks down [3]. While, the bulk Kondo singlet breakdown is revealed by our high-pressure studies on SmB$_6$. We found that at pressures above ~4 GPa the mean valence is increased to a similar level as that observed in SmB$_6$ (reproduced from [20]. © IOP Publishing Ltd. All rights reserved). The low-temperature upturn indicates that the population of the Sm ions with tri-valence state is increased as the temperature decreases, which may feature the formation of the AVFS.

In summary, we propose that SmB$_6$ is a special bulk Kondo insulator with the AVFS in its bulk, and the AVFS is prohibited from existing on its surface. As a result, the Kondo singlet on the surface breaks down and the corresponding exotic metallic surface state appears. If the notion of the AVFS is adopted as a starting point for studies on the possible topological Kondo insulator SmB$_6$, it can be optimistically expected that a more unified or precise understanding of the microphysics in SmB$_6$ can be achieved.

Acknowledgments

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Figure 3. Temperature dependence of the mean valence of Sm ions in SmB$_6$ (reproduced from [20]. © IOP Publishing Ltd. All rights reserved).


