Two-Component Analysis of the $4f$ Multiplet of Samarium Hexaboride

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Abstract

We present a detailed study on the temperature-dependence of the Sm $4f$ states in mixed-valent samarium hexaboride (SmB_6) which, as a consequence of the hybridization with the conduction band states, largely determine the physical properties of the system. By comparing soft x-ray photoemission spectra of SmB_6 with those of $\text{Sm}_{0.35}\text{La}_{0.65}\text{B}_6$, we discuss the apparent differences and similarities of the two systems. Based on our analyses we show that the $4f$ spectra of SmB_6 can be separated into two independent spectral contributions with the $4f$ peak maxima at different binding energies, representing two different electronic $4f$ configurations existing in the system.

Keywords: D.Strongly correlated electron system; D.Electronic State; D.Valence fluctuation; E.Photoelectron Spectroscopy

1. Introduction

The concept of topology [1, 2] leads to extended phase diagrams of strongly correlated systems [3, 4], whose physical properties are determined by the existence of highly localized electrons. For instance, localized $4f$ states with odd
5 parity are forming hybridization gaps with the conduction band at the Fermi energy, possibly resulting in physical phases with non-trivial $\mathbb{Z}_2$ topology [5, 6]

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and thereby giving rise to quantum spin Hall states in strongly correlated materials [3]. However, the hybridized nature of the $4f$ states can cause difficulties in estimating the $\mathbb{Z}_2$ topological indices because the hybridization may induce
10 an odd-parity character even in the electronic states predominantly assigned to the other elements [7]. When the $4f$ states are occupied with more than one single electron (or hole), the experimental investigation by photoemission spectroscopy is usually difficult because the spectral signatures of the $4f$ states appear as complicated final state multiplets [8]. Thus, further studies on com-
15 plex $4f$ multiplets hybridized with conduction bands are necessary.

Recently, samarium hexaboride (SmB_6) has drawn much attention because it exemplifies a strongly correlated system with non-trivial $\mathbb{Z}_2$ topology [7, 9, 10, 11]. Its resistivity below 5K was found to be temperature-independent, which cannot be explained by the impurity scattering mechanisms in a classical
20 metal [12, 13] and which has been interpreted as a signature of topological surface states [14, 15]. Except for the physical consequences of the topological surface states, the basic properties of SmB_6 are well explained with the electronic structure of mixed valent insulators [12, 16, 17, 18]. The Sm ion in SmB_6 shows a non-integer valence ($v_{\text{Sm}} \approx 2.6$) [19, 20], i.e., $4f^5$ ($v_{\text{Sm}} = 3$) and $4f^6$ ($v_{\text{Sm}} = 2$)
25 configurations are almost equally mixed [21, 17, 18]. The (occupied) Hubbard bands, as being measured by photoemission spectroscopy, appear near E_F and at higher binding energy $E_B \approx 7$ eV as a characteristic multiplet for the $4f^6 \rightarrow 4f^5$ and $4f^5 \rightarrow 4f^4$ transitions, respectively [8, 21, 22, 23]. Since a Hubbard band lies near E_f , SmB_6 belongs to the mixed valence regime of the Anderson model [17,
30 24] where charge fluctuations occur even in low-energy excitations [24, 25]. This gives rise to a complex thermal evolution in the electronic structure accompanied by an energy shift and a redistribution of spectral weight near E_F [10, 18, 26].

In this report we present temperature dependent changes in the spectral shape and in the energy positions of the $4f$ peaks in the photoemission spectra
35 of SmB_6 , taking strongly La-doped SmB_6 ($\text{Sm}_{1-x}\text{La}_x\text{B}_6$ at $x = 0.65$) as a reference system. For doping concentrations above $x = 0.08$, our $4f$ spectra show almost identical behavior in both the temperature dependence and the binding

energies. Since a La ion has an additional $5d$ electron but no $4f$ electron, the replacement of Sm ions with La ions gives rise to a larger effective disturbance
40 in the periodicity of $4f$ states than for the conduction band states in SmB_6 . Moreover, the heavy doping drives the system into a metallic state. By comparing the $4f$ spectra of pure SmB_6 with that of the strongly La-doped system, we discuss about the similarities and differences in the spectra as a function of the occupation numbers of f and conduction electrons, which are crucial parameters
45 in a mixed-valent system [16, 17, 27].

2. Methods

We performed soft x-ray photoemission experiments on SmB_6 and $\text{Sm}_{0.35}\text{La}_{0.65}\text{B}_6$ using the newly designed ASPHERE III endstation at the XUV beamline P04 of PETRA III (Hamburg), where the analyzer slit lies in the
50 plane of incidence. The experiments were performed in the transmission mode of the VG Scienta R4000 electron analyzer using circular polarized light. The excitation energy was $h\nu = 266 \text{ eV}$ with an energy resolution of $\sim 30 \text{ meV}$. The chosen photon energy shows higher photo-ionization cross-sections for $4f$ states than for the other states by more than two orders of magnitude [28, 29], and
55 thus is particularly suitable for the present study as compared to the UV-regime. High-quality single crystals were cleaved *in situ* at $T = 40 \text{ K}$ by use of cleaving posts glued on top of the (001) surface. The sample temperature (T) was varied in the range of $26 \text{ K} - 130 \text{ K}$ and controlled by a thermocouple.

3. Results

Fig. 1 shows the $4f$ spectra of pure SmB_6 , labeled with $S(T)$ in the following,
60 and $\text{Sm}_{0.35}\text{La}_{0.65}\text{B}_6$, $S_{La}(T)$, near E_F with the ${}^6H_{5/2}$, ${}^6H_{7/2}$, and 6F final states for the $f^6 \rightarrow f^5$ transition [8, 21, 22, 23]. The major surface $4f$ states in SmB_6 appear $0.4 - 0.7 \text{ eV}$ higher in binding energy for a cleaved surface [30] indicating that $S(T)$ and $S_{La}(T)$ sufficiently reflect bulk $4f$ states. We normalized $S(T)$
65 and $S_{La}(T)$ to unity in the range of $E_B < 2 \text{ eV}$ in order to consistently analyze

Figure 1: Temperature-dependent photoemission spectra of the Sm $4f$ multiplet states in SmB_6 and $\text{Sm}_{0.35}\text{La}_{0.65}\text{B}_6$ near the Fermi level E_F with $h\nu = 266$ eV. The spectra of SmB_6 , $S(T)$, and $\text{Sm}_{0.35}\text{La}_{0.65}\text{B}_6$, $S_{La}(T)$, are normalized to have a spectral weight of unity for binding energies $E_B < 2$ eV. (a) The ${}^6H_{5/2}$, ${}^6H_{7/2}$, and 6F peaks in $S(T)$ increase in intensity and become narrower with decreasing temperature. Above 60 K, the peaks are getting more asymmetric because of shoulders that appear at higher binding energies (red arrows). The inset shows that the peak intensity of ${}^6H_{5/2}$ gets closer to that of ${}^6H_{7/2}$ as the temperature decreases. (b) The peak positions and shapes in S_{La} at $T = 30$ K (blue-dashed line) and 110 K (red-dashed line) are identical.

the changing $4f$ line shape at various temperatures from 130 K to 26 K. With decreasing temperature, the three $4f$ peaks in $S(T)$ shift by ~ 16 meV to lower binding energy (Fig. 1 (a)) [11, 18]. It has been found previously that the Sm $4f$ states hybridize with the conduction band and thereby form an energy gap [31, 32, 33, 34]. Together with the energy shift, the $4f$ peaks gain in height and decrease in width, indicating that the temperature approaches the characteristic temperature of the system [11, 35]. While the peak intensities of both ${}^6H_{5/2}$ and ${}^6H_{7/2}$ increase with decreasing temperature, the enhancement for ${}^6H_{5/2}$ is more pronounced so that the intensity difference between the two decreases (inset). The more pronounced rise of ${}^6H_{5/2}$ cannot be explained just with the temperature-dependence of the Fermi-Dirac distribution (see also Ref. [30, 36, 37]).

In contrast, the three $4f$ peaks in the spectra S_{La} of strongly La-doped SmB_6 show neither a significant energy shift nor a change in line-shape as a function of temperature (Fig. 1 (b)). Furthermore, they appear at higher binding energies, and are broader than the main peaks in the spectra $S(T)$ of pure SmB_6 . Note that a possible phonon broadening is small below 130 K [30], i.e. unresolvable within the experimental resolution. These characteristic differences in the temperature-dependence of the $4f$ spectral features mostly originate from La-doping that disturbs the periodicity of the lattice and changes the occupation number of the Sm $4f$ and conduction states [17, 38].

In the following, we focus on the high-energy shoulders of the main peaks in $S(T)$ (arrows), which induce the asymmetric shapes at high temperatures by a change of the relative intensity compared to the main peaks. For the analysis of the data we are applying a simplified model *ansatz* in which we describe the $4f$ spectra as a linear combination of two independent spectral contributions. The temperature-dependence of the Sm valence v_{Sm} in SmB_6 suggests a relation of the $4f$ peaks in $S(T)$ and S_{La} . When the temperature increases, the number of conduction electrons in SmB_6 increases, whereas the number of f electron decreases [20]. These trends are similar to the effect of La-doping, which also increases the number of conduction electrons in the system [19, 39]. In this

approach it appears thus plausible that the spectra $S(T)$ get more and more similar to the spectra of the doped sample S_{La} when the temperature increases.

In order to demonstrate the connection between the shoulders in $S(T)$ and the $4f$ peaks of S_{La} in more detail, we subtract $S(26\text{K})$ multiplied by a constant α (black line) from $S(130\text{K})$ (red line) (Fig. 2), i.e. $S(130\text{K}) - \alpha \cdot S(26\text{K})$. We have chosen the spectra at the highest and lowest temperatures because they show the strongest difference in the shoulder intensities. The result with $\alpha = 0.65$ (gray dots) is similar to the multiplet structure for the $f^6 \rightarrow f^5$ transitions, and the peak positions in the subtracted spectrum reasonably coincide with that in S_{La} . Thus, we can use S_{La} to represent the line shape of $4f$ states responsible for the “shoulders” $B(T)$. Note that the real spectrum S_{La} is more adequate for the following analysis than the subtracted spectrum because it has no negative intensities near E_F , an artifact caused by the binding energy shift in $S(T)$ and the different thermal broadening in the Fermi-Dirac distribution. Consistent to this notion, $B(T)$ can be written as the product of the normalized temperature-independent spectrum S_{La} and a temperature-dependent factor $0 \leq \beta(T) \leq 1$ (blue-dashed line).

If $B(T)$ is assumed to show no energy shift with decreasing temperature like S_{La} in Fig. 1 (b), we can extract the main part $A(T)$ from $S(T)$ by subtracting $B(T)$, i.e., $A(T) \equiv S(T) - B(T) = S(T) - \beta(T) \cdot S_{La}$. We have chosen the weighting factor $\beta(T)$ in such a way that the resulting peak shapes in $A(T)$ are most symmetric. Thus, we extract for all temperatures from $S(T)$ two independent components, as shown in Fig. 3(a)–(b) for $T = 26\text{ K}$ and 130 K . Like the behavior of the shoulders, the spectral weight of $B(T)$ reduces as the temperature decreases, whereas the spectral weight of $A(T)$ relatively increases (Fig. 3(c)). The three peaks in $A(T)$ appear at $40 - 50\text{ meV}$ lower binding energies than that in $B(T)$.

For a comparison of the line shapes in spectra $A(T)$, we have shifted the energy and intensity axes relatively to each other so that the peak positions match. As evident from Fig. 3 (d), the peak widths of the multiplet peaks show almost no temperature-dependence except for that of the ${}^6H_{5/2}$ peak, which

Figure 2: Extracting the shoulders in $S(T)$ and comparison with S_{La} . (a) By subtracting $S(26\text{ K})$ multiplied by $\alpha=0.65$ (black line) from $S(130\text{ K})$ (red line), we obtain the shoulder structure (gray dots), i.e. $S(130\text{ K}) - \alpha \cdot S(26\text{ K})$. Note that the negative intensities in the difference near $E_B=0$ are an artifact caused by the energy shift in $S(T)$ and the different broadening of the Fermi-Dirac distribution. The peak positions in S_{La} (blue-dashed line) fairly coincide with that in the extracted spectrum. Thus, S_{La} can be used to represent the $4f$ states contributing to the shoulders.

Figure 3: Principle component analysis of SmB_6 data $S(T)$. (a)–(b) For $T = 130\text{ K}$ and 26 K , $A(T)$ (lines and circles) are obtained by taking the difference between $S(T)$ (solid line) and $B(T) \equiv \beta(T) \cdot S_{La}$ (blue-dashed line), i.e., $A(T) \equiv S(T) - B(T) = S(T) - \beta(T) \cdot S_{La}$. Thus, $A(T)$ and $B(T)$ denote the main lines in $S(T)$ and the shoulders at higher E_B , respectively. The factor $\beta(T)$ represents the ratio of $B(T)$ to $S(T)$. (c) Temperature dependence of the extracted spectra $A(T)$. (d) The ${}^6H_{7/2}$ and 6F peaks in $A(T)$ show almost the same spectral shape and width for all temperatures. (e) Intensity ratio of $A(T)$ to $B(T)$ and $\beta(T)$ are shown on the left and right axis, respectively.

is the only one that has been theoretically and experimentally studied so far [11]. Therefore, every $A(T)$ can be written as the product of a normalized spectrum S_{main} and a factor $\gamma(T)$ where $0 \leq \gamma(T) \leq 1$, if we neglect the energy shift of S_{main} . In other words, within our experimental resolution, $A(T)$ can originate from $4f$ states with constant spectral line-shape and a temperature-dependent weight $\gamma(T)$. Overall, our results suggest that $S(T)$ can be separated into the main lines and an independent shoulder part. Considering that $S(T)$, S_{La} , and S_{main} are normalized, $\gamma(T)$ is equal to $1 - \beta(T)$; therefore, $S(T) = (1 - \beta(T)) \cdot S_{main} + \beta(T) \cdot S_{La}$. Thus, the spectra $S(T)$ of SmB_6 can be described by a linear combination of two independent components whose weight $\beta(T)$ varies with the temperature (Fig. 3 (e), right axis). The ratio of $\gamma(T)$ to $\beta(T)$ is shown on the left axis in Fig. 3 (e) in order to illustrate the ratio of $A(T)$ to $B(T)$. Comparing the spectral ratios at 26 K with that at 130 K, the change in $A(T)$ is about 2 times larger than that in $B(T)$.

4. Discussion

The valence v_{Sm} of the Sm ion is an important parameter for describing the electronic state of this intermetallic hexaboride compound [40] and is even more crucial for the gap opening in the mixed valent system [17, 27]. A detailed study on doped SmB_6 has clearly indicated that Sm ions change their valence depending on the valence of a substituted metal ion rather than depending on the change in the lattice parameter [19]. Although the lattice parameter of La^{3+} , Yb^{2+} , or Sr^{2+} doped SmB_6 increases, v_{Sm} decreases for the trivalent-doping, whereas it identically increases for the divalent-doping. Large La-doping in SmB_6 , e.g. $x \geq 0.75$, gives rise to a decrease in v_{Sm} by $\approx 13\%$ and an increase in the lattice constant by $\approx 0.6\%$ maintaining the local cubic symmetry [19, 39]. v_{Sm} is crucial in pure SmB_6 because the metal-insulator transition occurs with decreasing temperature [12] while v_{Sm} changes from 2.6 to 2.5 [19, 20], whereas the lattice parameter barely changes ($< 0.04\%$) [41].

In the following, we would like to use the occupation number in the outermost

($5d6s$) shell (labeled conduction d states) of a rare-earth ion per unit cell (N_d) instead of v_{Sm} to explain the connection between the temperature and La-doping effects on SmB_6 . Since La ions do not have any $4f$ electrons, it is more
160 appropriate to use N_d to describe the change in the electronic configuration. By using v_{Sm} values obtained by x-ray absorption [19], we can estimate N_d for each doping rate. For instance, based on $v_{Sm} = 2.6$ (the occupation number of f electrons $n_f = 5.4$) for pure SmB_6 and $v_{Sm} = 2.31$ ($n_f = 5.69$) for the heavy La-doping at room temperature, N_d are 2.6 and 2.76 ($= 2.31 \times 0.35 + 3 \times 0.65$),
165 respectively. Thus, the doping with La^{3+} ions can increase N_d so that it leads to an effective electron-doping, which eventually makes the heavily doped system metallic [19, 42]. This indicates that the effect of substituting La ions has a similarity to that of rising temperature since both effects increase N_d in SmB_6 .

While N_d increases from $N_d(30\text{ K}) = 2.5$ to $N_d(300\text{ K}) = 2.6$ with increas-
170 ing temperature in SmB_6 , the complete $4f$ spectral weight in pure SmB_6 shifts to higher binding energy as shown in Fig. 1. This energy shift also intuitively follows with the change in N_d , whereas the $4f$ peak can appear at different energies because of a more complicated dependence on the valence configuration [17, 18] than in the simple rigid band model. Recent ARPES studies show that
175 the d - f hybridized band shifts from below to above E_F until SmB_6 becomes insulating, i.e., the bottom of the conduction d - f hybridized band in SmB_6 no longer lies below E_F [10, 11]. This can be explained with N_d , which decreases with decreasing temperature. Since the $4f$ peaks also shift together with the position of the Fermi level determined by N_d , it indicates that the energy posi-
180 tion of the $4f$ states in pure SmB_6 is fixed with respect to the d states so that the band structure shows an almost rigid energy shift as a function of N_d . The energy shift of the $4f$ states has already been demonstrated by recent theoretical studies, and were related to the band coherence [11, 18].

However, unlike for pure SmB_6 , neither the energy position nor the shape of
185 the $4f$ peaks changes in the La-doped system although N_d and n_f change with varying temperature [38]. This means that the $4f$ states behave differently with respect to N_d in the heavily La-doped system. Moreover, by our spectral analysis

above we show that the Sm $4f$ peaks, characteristic for the in the heavily La-doped system, appear as shoulders in the spectra of pure SmB_6 , which induce
190 the asymmetric shape at $T > 60\text{ K}$ when SmB_6 is in the metallic phase. Thus, two independent $4f$ states exist in SmB_6 that behave differently as a function of N_d and T . This observation might be related to the previous results of inelastic neutron scattering experiments, where also two components have been reported [43].

195 These two different $4f$ states with respect to N_d leave interesting questions for further investigations. Since n_f and N_d oppositely vary with temperature, the hybridization between $4f$ and d states is a characteristic feature of all $\text{Sm}_{1-x}\text{La}_x\text{B}_6$ compounds. However, it is unclear why an energy shift is observed in the strongly doped system although N_d varies. Considering that the
200 conduction d band would follow the simple one electron-picture, a rigid shift in energy is expected as a function of N_d . In order to clarify the difference in the energy shift, the importance of coherence should be investigated in both compounds. Especially, the coherent and incoherent contributions to photoemission spectra [44] should be clarified and the importance of impurities explored.

205 5. Conclusion

In summary, we have shown that one can decompose the $4f$ spectra of SmB_6 by use of a linear-combination *ansatz* to describe the characteristic temperature dependence of the spectra. With increasing temperature the $4f$ multiplet spectra become more similar to that of strongly La-doped SmB_6 , which shows
210 itself nearly no temperature dependence in the considered temperature range. Referring to the occupation number of the d states N_d , we find that the effect of increasing temperature in SmB_6 is effectively comparable to an increasing La-doping, which both increase the occupation number N_d . Following this notion, our results reveal that in pure SmB_6 two different, largely independent sets of
215 $4f$ states with a different temperature dependence exist. These two “configurations”, not to be confused with the two different valence states of the Sm ions

$v_{Sm} = 2$ and 3, might be related to an intrinsic or coherent state with a characteristically strong temperature dependence and an extrinsic state as it can be produced by La-substitution and all its consequences like defect scattering and changing electron distribution.

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