Comparative Scanning Tunneling Microscopy Study on Hexaborides

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Scanning tunneling microscopy (STM) investigations on two hexaboride compounds, SmB$_6$ and EuB$_6$, are compared in an effort to provide a comprehensive picture of their surface structural properties. The latter is of particular importance for studying the nature of the surface states in SmB$_6$ by surface-sensitive tools. Beyond the often encountered atomically rough surface topographies of in situ, low-temperature cleaved samples, differentially reconstructed as well as B-terminated and, more rarely, rare-earth terminated areas can be found. With all the different surface topographies observed on both hexaborides, a reliable assignment of the surface terminations is brought forward.

1. Introduction

The hexaborides of cubic structural type CaB$_6$ (Pm$ar{3}$m) represent a very versatile class of compounds.$^{[1]}$ LaB$_6$ features a very low work function of about 2.7 eV,$^{[2]}$ whereas electron-doped CaB$_6$ is a ferromagnetic material, albeit with a low magnetic moment,$^{[3,4]}$ and CeB$_6$ exhibits quadrupolar ordering.$^{[5]}$ The hexaborides are often highly conductive. From Hall measurements, it was shown$^{[6]}$ that the majority of the hexaborides has one charge carrier per rare-earth atom, with the exceptions of divalent Eu and Yb with very low charge carrier densities and SmB$_6$ exhibiting intermediate valence.$^{[7,8]}

The material SmB$_6$ has attracted special attention recently as it was proposed to host topologically nontrivial surface states.$^{[9]}$ This material falls into the category of so-called Kondo insulators$^{[10,11]}$ in which the insulating properties are brought about by hybridization between conduction bands (here d-bands) and localized f-states. In consequence, a narrow gap opens up at sufficiently low temperatures (below the Kondo temperature $T_K$), whereas the f-electrons provide the strong spin–orbit coupling required for the development of topologically protected surface states predicted by band structure calculations.$^{[12–14]}$ Subsequently, considerable experimental effort was made to verify the topological nature of the surface states, in particular through angle-resolved photoemission spectroscopy (ARPES) with spin resolution.$^{[15,16]}$ Though there is a consensus on the existence of a conducting surface state$^{[17,18]}$ and its topological nature is a matter of ongoing debate. For instance, the surface states observed by ARPES measurements have been interpreted in terms of Rashba splitting.$^{[19]}$ One crucial aspect$^{[20,21]}$ namely a $\Gamma_8$ quartet ground state of the Sm f$^5$ configuration, has recently been observed experimentally$^{[22]}$ but is in contrast to some band structure calculations.$^{[13,23,24]}$ Here, the strong correlations of the Kondo insulator as well as its intermediate valence complicate band structure calculations.$^{[25]}$ An additional complication is the complex (001) surface of SmB$_6$ itself due to its polar nature.$^{[26]}$ Because of the cubic structure of SmB$_6$, in-situ-cleaved surfaces usually required for surface-sensitive techniques like ARPES or scanning tunneling microscopy/spectroscopy (STM/S) are often atomically rough or reconstructed.$^{[27–30]}$ But even in case of atomically flat surfaces the interpretation of the surface termination in STM is controversial.$^{[31,32]}$ In an effort to make progress in this complex situation, we here compare topographies obtained by STM on SmB$_6$ and EuB$_6$. The latter material is interesting in its own right due to its complex band structure,$^{[13]}$ ferromagnetic properties$^{[34]}$ and polaron formation.$^{[35]}$ We note that a comparative study of YbB$_6$, CeB$_6$, and SmB$_6$, primarily based on ARPES results, was recently brought forward.$^{[36]}$

2. Results

2.1. SmB$_6$

To obtain information on the nature of the surface states, the applied probe needs to be surface sensitive. One obstacle in
investigating SmB\(_6\) with highly surface-sensitive tools like ARPES or STM is the different surface terminations. Due to the cubic structure of the hexaborides, the majority of the cleaved surface areas is rough on an atomic scale.\(^{[31]}\) This may result in a modified local structure which, in turn, may influence the properties (specifically of Sm) at the surface.\(^{[37,38]}\)

Upon searching, a \((2 \times 1)\) surface reconstruction can usually be found.\(^{[28,30,39]}\) The \((2 \times 1)\) reconstruction was also observed by low-energy electron diffraction,\(^{[16,40,41]}\) as well as by STM on LaB\(_6\).\(^{[42]}\) Clearly, if we assume that the \((2 \times 1)\) reconstruction results from each second row of Sm atoms missing on top of an otherwise B-terminated surface, such a reconstruction is energetically favorable compared with an unreconstructed polar surface. Yet, other STM studies did not report this reconstruction\(^{[29]}\) or interpreted it differently.\(^{[32]}\) It should also be noted that such a reconstruction may have repercussions on the metallic surface state.\(^{[43]}\)

In Figure 1, we show such a \((2 \times 1)\) reconstructed surface area. The height scan taken along the blue line as indicated in the topography is consistent with the aforementioned idea of each second row of Sm atoms missing. This is corroborated by a change in height on and between these rows of atoms of the order 40–50 pm; yet, an order of magnitude of smaller height oscillations for the \((2 \times 1)\) reconstructed surface was also reported.\(^{[30,39]}\) The reconstruction is likely formed during the cleaving process or subsequently upon some additional diffusion of surface atoms. In both cases, one may expect domains of \((2 \times 1)\) and \((1 \times 2)\) reconstructed areas and dislocations between the Sm rows by one lattice constant, both of which can easily be recognized in the topography of Figure 1.

Rarely we also found atomically flat surface areas, as shown in Figure 2. Similar surface topographies have been presented before.\(^{[27–29,32,39,44,45]}\) It was shown, however, that the obtained topography depends on applied bias voltage \(V\), and even a contrast reversal was observed for \(V = 0.2 V\) and \(-3.0 V\).\(^{[32]}\) In the following, we make use the dual-bias mode described in Section 4, as it allows to visualize exactly the same surface area without relying on defects on top of the investigated surface (the appearance of defects may change with \(V\), see Figure 2). We have chosen values of \(V\) as small compared with the barrier height \(\Phi\) (see also below) yet larger than the hybridization gap of less than 20 meV.\(^{[29,46–50]}\) In Figure 2, dual-mode topographies for \(V = \pm 0.2 \, \text{V}\) (upper) and \(\pm 0.02 \, \text{V}\) (lower) are compared. Note that here different samples were investigated at somewhat different temperatures of \(T \approx 6 \, \text{K}\) (upper) and \(1.7 \, \text{K}\) (lower). Qualitatively, the topographies for the given temperature agree very well, i.e., there is no contrast inversion of reversed \(V\). There are subtle inhomogeneities in the background at \(T \approx 6 \, \text{K}\); we can only speculate that they result from a not fully developed conducting surface state because we so far did not observe such inhomogeneities at \(T \leq 1.7 \, \text{K}\) (see also discussion of Figure 7 below).

To investigate the surface termination in more detail, we show in Figure 3 topographies on areas exhibiting steps of less than one unit cell height \(a\).\(^{[28]}\) Such steps are perfectly suited to gain information on the different surface terminations. Again, the topographies obtained in dual mode with \(V \pm 0.2 \, \text{V}\) agree on a qualitative level. The white arrows in Figure 3 show the main crystallographic directions \((100)\) and \((010)\). Height scans taken along the blue lines, i.e., parallel to one of the main crystallographic directions and at an overall unchanged height, clearly indicate lateral distances between corrugations consistent with the lattice constant \(a\), whereas such taken along descending height (red arrows) exhibit less obvious corrugations (possibly related to crystallographic imperfections within such regions of changing overall height). Within elevated areas (bright regions), however, the corrugations appear to run along the diagonal, i.e., \((110)\) directions. This is consistent with a Sm-terminated surface where also, in addition to the Sm atoms, the apex atoms of the B-octahedra are seen, see discussion of Figure 8 below, as well as the crystal structure shown in Figure 4.

We now turn to the height scans taken along the red arrows in the topographies which, again, follow a \((100)\) direction but also...
include a height change. Atomic distances corresponding to a can be seen for $V = +0.2\,\text{V}$ but less well for $V = -0.2\,\text{V}$. Clearly, the total change in height depends to some extent on $V$. It amounts to about 130 pm for $V = +0.2\,\text{V}$ and $\approx 100\,\text{pm}$ for $-0.2\,\text{V}$. Yet, both numbers appear to be consistent with the expected step height upon going from a Sm- to a B-terminated surface considering the interoctahedron B distance of 164.6 pm. Given the fact that distances of a are observed along the main crystallographic directions on this (001) plane such a step height is difficult to interpret otherwise; a viable alternative is the opposite assignment (i.e., going from a B-terminated surface down to a Sm-terminated one) which would, however, involve breaking up of B-octahedra, i.e., intraoctahedral bond breaking. Estimates of the surface energy\cite{29,31} indicate a slight preference for interoctahedral bond breaking but impurities or sample inhomogeneities and defects may change these estimates locally. Indeed, a donut-like structure was interpreted as breaking interoctahedral bonds.\cite{27}

To gain further insight into the different terminations shown in Figure 3, tunneling spectroscopy was conducted. The STS curves shown in Figure 4 correspond in color to the areas marked in Figure 3 (right) over which the spectra were averaged. These spectra can be compared with those obtained on small areas of atomically flat surfaces but differ from those seen on larger areas in that there is no pronounced maximum in $\frac{dI}{dV}$ at around $-20\,\text{mV}$.\cite{28} The orange spectrum attained on the elevated part of the topography in Figure 3 shows a well-developed hump at $V \approx +10\,\text{mV}$.\cite{27,28,41} It is tempting to compare this hump with the conspicuous maximum observed on Sm-terminated surfaces of larger areas.\cite{27,28} Note that we did not observe (Figure 4 and the study by Rößler et al.\cite{28}) a pronounced shift in energy of features at negative $V$ as reported in previous studies.\cite{45}

The discussion earlier indicated that a $(2 \times 1)$ reconstruction is energetically favorable with respect to the polar nature of a Sm- or B-terminated surface. However, a similar effect is conceivable if the $(2 \times 1)$ reconstruction is not long ranged, but realized only locally. The lines of Sm may then meander,\cite{28,31} not giving rise to a superstructure.\cite{48} Part of such a “disordered” reconstructed surface is shown in Figure 5. In such a case, a similar change in height upon going from the topmost Sm atoms to the underlying B layer is expected, as in Figure 3. The height scan, Figure 5 (right), along the red and blue lines marked in the topography indeed support this assertion.

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**Figure 3.** SmB$_6$ topography of an area of 10 nm $\times$ 8 nm exhibiting both Sm- and B-terminated areas. The images were obtained in dual-bias mode: $V = +0.2\,\text{V}$ (left) and $V = -0.2\,\text{V}$ (right). The height scans were taken along the lines of corresponding color in the topography images. Along the direction of the red arrows the sample height decreases by about 100–130 pm. The white arrows indicate the main crystallographic directions (100) and (010), respectively. The colored rectangles indicate the areas over which the spectroscopy curves of corresponding colors in Figure 4 were averaged.

**Figure 4.** Tunneling spectroscopy averaged over the areas marked by rectangles of corresponding colors in Figure 3 (right). $V = +0.2\,\text{V}$, $I_{sp} = 0.6\,\text{nA}$, $V_{mod} = 1\,\text{mV}$. The inset exhibits two adjacent unit cells of the cubic SmB$_6$ lattice.
In one instance, we observed a topography, as shown in Figure 6. The height scan may be interpreted as every third row of atoms missing. Here, the height change between the upper and lower rows of atoms is only about 30 pm, similar to\textsuperscript{26} or slightly smaller (Figure 1) than the case of (2 × 1) reconstructions. The exact number, however, may depend on details of the tip, i.e., how well it may penetrate between the rows of atoms, and may even be much smaller.\textsuperscript{10,19}

It should be noted again that our assignment of Sm- or B-terminated surfaces depends largely on the exact cleave, i.e., whether inter- or intraoctahedral bonds are broken. Albeit the former is, as mentioned earlier, energetically favorable, the latter may also occur as suggested by the observation of so-called donuts\textsuperscript{27,31}.

In Figure 7, we show a topography over an area of 40 nm × 40 nm. Although we have certainly encountered areas showing a smaller number of defects,\textsuperscript{44} it provides an overview of the different types of defects found on a B-terminated surface. The largest protrusions, #1 (red) and #7 (dark blue) in the upper right panel, with heights well beyond 100 pm, are most likely caused by adatoms on top of the surface. The short red dashes in the height scan mark distances of \( a \), suggesting that the underlying lattice is not disturbed beyond the defects. Other defects, #5 (orange) and #6 (black) in the lower right panel, appear to be incorporated into the lattice as also the immediately adjacent lattice sites seem influenced. Albeit conceivable, there is no evidence for an exchange of B by Al in pure SmB\textsubscript{6}\textsuperscript{31} (note that this refers to substitution of individual B atoms by Al, not to Al inclusion of non-negligible size\textsuperscript{32,33}). In the Th–Pd–B system, it was found that Pd may replace two adjacent B atoms belonging to neighboring octahedra.\textsuperscript{34} Along the same line, one may speculate that a similar replacement of adjacent B atoms by impurities near the surface may result in the observed slight displacement of surface atoms. Qualitatively different are the defects #3 (light blue) and #4 (magenta). Here, the lateral position (again, the vertical dashes indicate distances of \( a \)) and the height oscillation of the protrusions appear to remain unchanged, whereas the height level is either raised (#3) or lowered (#4) by about 15–20 pm over distances of about two lattice constants from the center of the defect. We speculate that the defect itself is located in a subsurface layer, possibly on a Sm site, leaving the B-octahedra intact. It should be noted that this type of defect seems qualitatively different from the background inhomogeneity of Figure 2. Albeit a clear assignment of either one of these features to structural or electronic inhomogeneities is speculative at present, it is obvious that a clean surface is a prerequisite for their observation. It should also be noted that dents of about 80 pm have so far only been observed on Sm-terminated surfaces.\textsuperscript{26} The topography of such dents is very similar to the surface structure of La-terminated LaB\textsubscript{6} where La atoms are missing from the topmost layer.\textsuperscript{35} Therefore, it should be highly instructive to investigate Sm-deficient samples Sm\textsubscript{1−x}B\textsubscript{6} and attempt to correlate the Sm-deficiency \( x \) with the occurrence of these dents.

### 2.2. EuB\textsubscript{6}

In contrast to SmB\textsubscript{6}, the ferromagnetic semimetal EuB\textsubscript{6} has so far only scarcely been investigated by STM,\textsuperscript{35} even though its electronic structure is not fully understood, see the studies by Zhang et al. and Massidda et al.\textsuperscript{33,36} and references therein. Hence, STS—in particular using a spin-polarized tip—may provide fresh insights. In the following sections, we focus on the surface topography.

In Figure 8, we compare the topographies of rare-earth-terminated samples EuB\textsubscript{6} and SmB\textsubscript{6}. In both cases, atomically flat and clean surface areas could be found after cleaving. The blue lines in the topographies indicate where the height scans parallel to the crystallographic \((100)\) directions were taken. The corrugations of heights 30–40 pm are spaced apart by one respective lattice constant \( a \). However, at the center of the square arrangements of these main corrugations in the topography (resulting from the cubic structure), additional humps are seen, also forming a regular, square arrangement. This is evidenced by the red height scans along the diagonal \((110)\) directions, with the distances between the main and the interjacent smaller corrugations corresponding to \( a/\sqrt{2} \). Based on the distances and orientations, the higher protrusions were assigned\textsuperscript{27,28} to the rare-earth atoms and the smaller ones to the apex of the B octahedra, again assuming breaking interoctahedral bonds upon cleaving. We emphasize that the observation of interjacent
smaller corrugations along (110) is pivotal for the assignment of the surface termination, yet requires sufficiently large, atomically flat, and clean surface areas. However, the consistent observation of this type of surface topography on two different members of the hexaboride family makes a plausible case.

Based on DFT calculations, it was suggested that the work function for a Sm-terminated surface of SmB₆ is about 2 eV and at least twice as high on a B-terminated surface. We therefore started to investigate the tunneling barrier height Φ, which is related to the work functions of the sample and the tip (Φₛ and Φₜ, respectively). The tunneling current I decreases exponentially with increasing tip-sample distance Δz, i.e., \( I(z) \propto \exp(-2m_e \Phi \Delta z) \). The barrier height Φ can be calculated from \( \kappa^2 = \frac{2m_e}{I} \Phi \), where \( m_e \) is the bare electron mass. Figure 9 shows two curves \( I(\Delta z) \) obtained on a clean B-terminated EuB₆ surface shown in the inset. The barrier heights for the two exemplary curves are \( \Phi = 4.7 \) and 5.6 eV, i.e., they vary by almost 1 eV. Unfortunately, because of their highly infrequent occurrence, we were not able so far to measure Φ on a Eu-terminated surface. It therefore remains to be seen whether a measurement of the barrier height can help in identifying the termination of clean EuB₆ surfaces.

In the case of SmB₆, both the investigation of slightly Gd-substituted samples with W tunneling tips and of pristine SmB₆ with Cr tips resulted in a strong suppression of the surface state. In fact, the \( \frac{dI}{dV} \) curves in close proximity to magnetic defects and taken with magnetic tip are akin to spectra obtained with W tip on pristine SmB₆ at 20 K, a temperature high enough such that the surface states do not significantly contribute to the tunneling spectra. These observations are expected for topologically nontrivial surface states close to atoms carrying a sizable magnetic moment arising from an exchange interaction. Given this achievement in utilizing Cr tips as well as the magnetic properties of EuB₆ we also started to investigate surfaces of EuB₆ with magnetic Cr tunneling tips. One particularly intriguing example, attained in dual-bias mode for \( V = \pm 0.2 \) V, is shown in Figure 10. The dual-bias mode is important as an only partial contrast reversal for the two different \( V \) values is observed, rendering a position adjustment of subsequently obtained images based solely on defects less reliable. This partial
3. Conclusions

Investigating topographies on a large number of SmB$_6$ and EuB$_6$ samples revealed different surface terminations which show similarities between these two hexaborides. Such similarities are obvious for the rare-earth-terminated surfaces, a termination that is rather rare$^{[27,28]}$ but essential when attempting an assignment of the different terminations. In addition, utilizing a dual-bias mode allowed a comparison of topographies obtained with different bias voltages on exactly identical surface areas without relying on defects. Along with the observations of step heights less than $a$, these observations made a reliable assignment of the rare-earth and B-terminated surfaces possible. Apart from these atomically flat terminations, we observed different line structures, which may correspond to lines of rare-earth atoms on top of otherwise B-terminated surfaces. Some of these structures exhibited intriguing properties, also if probed by magnetic tips, which warrants further study.

4. Experimental Section

Single crystals of SmB$_6$ and EuB$_6$ were grown by an AI flux method$^{[60-62]}$. The orientation of the single crystals was checked by Laue diffraction. The lattice constants are $a = 4.133$ Å for SmB$_6$ and $a = 4.185$ Å for EuB$_6$

For STM investigations, two ultrahigh vacuum (UHV) systems were used$^{[63]}$. A 4He system allows for base temperatures below 5 K; if a heating stage is used, the base temperature is typically $\approx 6$ K (a temperature sensor is incorporated into the heating stage). If not stated otherwise, the STM/STS data reported in the following were obtained at $\approx 6$ K. Our 3He-based system operates down to a base temperature of $\approx 0.3$ K and allows to apply magnetic fields up to 12 T perpendicular to the investigated surface. Electrochemically etched tungsten tips were used, if not stated otherwise. Tunneling spectroscopy was conducted using a lock-in technique and adding a small alternative current (AC) modulation voltage $V_{\text{mod}}$ of 0.1 or 1.0 mV (depending on the bias voltage $V$, see respective figure caption) with a frequency of 117 Hz to the bias voltage $V$.

Some of the STM data reported in the following were obtained in a so-called dual-bias mode. In these cases, two different bias voltages $V$ were applied for the forward and backward scans of the fast scan direction. This mode of operation allows to obtain topographic images with two different $V$ at the same sample position (within the piezoelectric hysteresis of the scanner, typically giving offsets well below 1% of the total scan size of the two topographies). In doing so, drift corrections can be neglected and parameters like temperature $T$ or magnetic field, sample history, surface termination, or tip condition are identical. Even if the tip changes, it then influences the data for both $V$ at very similar sample positions.

All samples reported here were cleaved in situ along a (001) crystallographic plane at a temperature of $\approx 20$ K using identical cleaving stages in both UHV systems. After cleaving, the sample needs to be transferred into the respective STM head during which time (in the order of 10 s) the sample temperature is not controlled. We here provide results based on 24 cleaves of SmB$_6$ (on eight of which we did not find any atomically flat surface area) and five cleaves on EuB$_6$.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hexaborides, scanning tunneling microscopy and spectroscopy, surface terminations
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