Electron-tunneling studies of the hexaboride materials SmB_6, EuB_6, CeB_6, and SrB_6

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We present a series of tunneling measurements on the hexaboride materials SmB_6, EuB_6, CeB_6, and SrB_6. In this group, SmB_6, EuB_6, and CeB_6 possess magnetic moments, whereas SrB_6 is nonmagnetic. Our tunneling measurements show an asymmetric conductance, exhibiting a background that grows with energy in all four materials. We find evidence of a partial gap, but with only a small depletion in $N(E)$. Our measurements are consistent with a two-band model in which the band overlap is reduced with decreasing temperature. [S0163-1829(98)03415-8]

Hexaboride materials have attracted considerable attention for over 30 years, due to their anomalous transport and magnetic properties.[1–5] Interest in these materials arises from the fact that, although the hexaborides share the same crystal structure, there are strong qualitative differences in transport properties among these materials. SmB_6 has shown a resistivity that is activated with temperature,[6–9] possibly due to the formation of a gap at the Fermi level.[10] This scenario has been supported by optical[5,11–14] and NMR[15,16] spectroscopies which show a shifting of the carriers away from the Fermi level. In addition, no evidence of long-range order in SmB_6 has been observed down to 40 mK.[8] EuB_6 has a slightly activated resistivity at temperatures above 300 K (Ref. 17) and, upon cooling, the material becomes slightly metallic.[18,19] There is also a drop in resistivity as this material orders ferromagnetically at approximately 16 K,[18,19] and it has been suggested that EuB_6 is a degenerate semiconductor that becomes a metal as it orders.[19] The resistivity of CeB_6 possesses a Kondo-like minimum near 150 K, and exhibits semiconducting behavior down to approximately 3 K.[20,21] At 2.3 and 3.2 K, antiferromagnetic and quadrupolar ordering occur, respectively, and the resistivity is metallic at the lowest temperatures.[20–23] Finally, SrB_6 is not magnetic, since Sr does not generate a local moment, and there is work suggesting that this material, originally considered as a semiconductor,[24] may be a conventional semimetal.[25,26] It has been postulated that the formation of a hybridization gap may influence the transport properties of these materials.

Electron tunneling has been a powerful experimental tool for directly probing the density of states. We chose to fabricate planar tunnel junctions, since they are low in current density and thus are not subject to nonequilibrium heating effects. All of our tunnel junctions were made using Pb counterelectrodes, and the data presented here are representative of junctions that showed the highest quality Pb superconducting phonon and gap structure; see the inset of Fig. 1. In order to simplify the analysis, we present conductance measurements above the superconducting temperature of Pb. We have fabricated over 40 tunnel junctions for each material, except for CeB_6 where eight junctions have been studied.

The single-crystal samples, which possessed smooth surfaces, were grown from an Al flux and were tetragonal in shape, nominally $1\times1\times5$ mm^3. The magnetic properties of the materials were examined in a superconducting quantum interference device magnetometer, and the results were consistent with earlier reports by other workers. The tunnel junctions were fabricated using a variety of methods. Although the success rate was highly dependent on the particular fabrication method, the best quality junctions yielded identical conductance curves, regardless of the fabrication process. The most successful technique involved etching the crystals in a 10% Br in isopropyl alcohol solution for 10 min, followed by oxidation in a pure O_2 atmosphere. (It should be noted that mixing these two etch constituents is extremely exothermic and must be done very slowly.) The Sm compound required oxidation at 80 °C for 1 h, while room-temperature oxidation was sufficient for the other compounds. We believe the etching process removes boron from the surface of the crystal, leaving a thin metal-rich surface

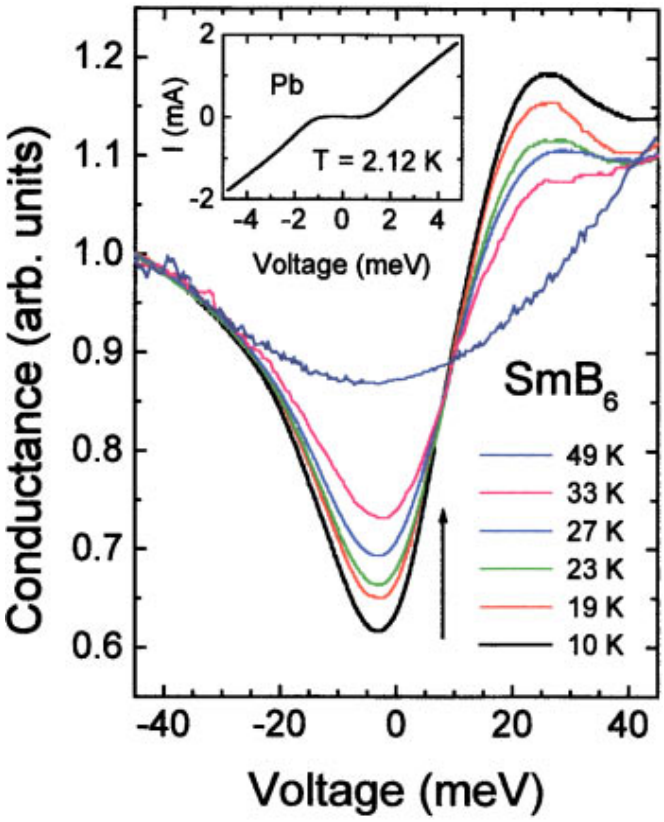

FIG. 1. (Color) The conductance $G(V,T)=dI/dV$ of SmB_6. The arrow indicates the gap, $\Delta=7$ mV. The inset shows a typical $I-V$ curve for Pb at 2.12 K.

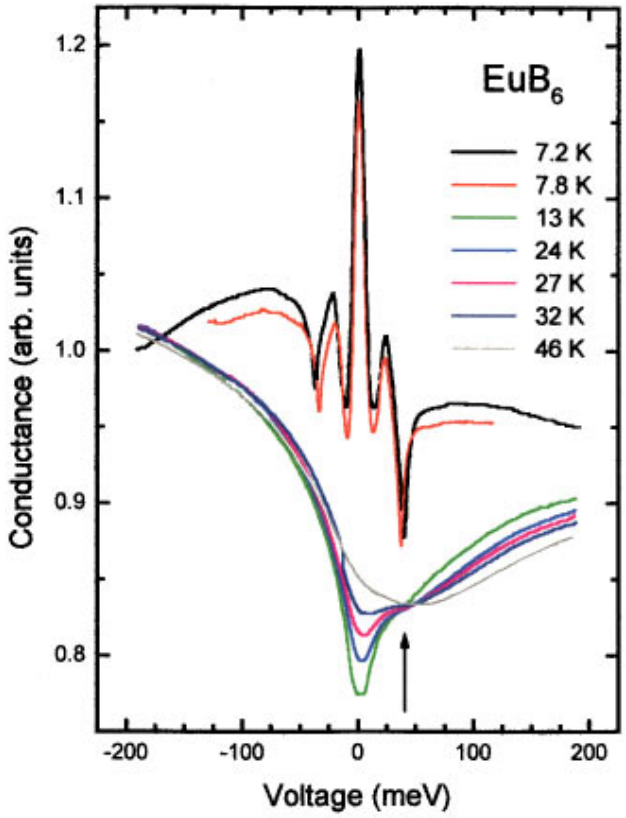

FIG. 2. (Color) The conductance $G(V,T)=dI/dV$ of EuB_6. The large zero-bias anomalies are easily detectable at the lowest temperatures. The arrow indicates the gap, $\Delta=43$ mV.

which is subsequently oxidized. Alternate etching processes in which the boron was removed and the remaining metal was oxidized produced the same results.

Figure 1 shows the conductance curves for a SmB_6 tunnel junction at various temperatures. The curves show an asymmetric conductance centered at -3 mV that grows with voltage as one moves away from the Fermi level. As the temperature is reduced, there is a depletion in the conductance below 7 mV, which we identify as the gap voltage, a value which is in good agreement with previous tunneling work on this material.[11,27,28] The missing spectral weight in this region appears above this gap, extending to a voltage of 40 mV. This reduction in the conductance is not large, corresponding to approximately a 15% suppression in zero-bias conductance between 33 to 10 K. As shown in Fig. 1, most of the change in the conductance occurs at positive bias (throughout this work, positive bias refers to positive bias on the hexaboride electrode of the tunnel junction). A good estimate of the temperature at which the gap first appears can be obtained by measuring the zero-bias conductance as a function of temperature. As the gap appears, there is a change in the slope of this curve. We estimate that the gap formation begins to occur below a temperature, which we will refer to as the ''gap temperature'' T^*, of $T^*=40\pm5$ K, yielding $\Delta\sim2k_BT^*$.

The EuB_6 conductance data at high temperature show a broad conductance minimum centered at approximately 50 mV (Fig. 2). Above its magnetic ordering temperature, EuB_6 possesses an excitation spectrum that is qualitatively similar to SmB_6. However, the EuB_6 gap value of 43 mV is significantly larger than that of SmB_6. The zero-bias conductance decreases approximately 9% between 46 and 18 K, and the missing states appear above the gap over an extended bias range. In addition, we have found that $T^*=50\pm5$ K, yielding a rather large $\Delta\sim10k_BT^*$. EuB_6 orders ferromagnetically at approximately 16 K, and about 3 K below this transition there is a dramatic change in the characteristics of the conductance curves (Fig. 2), where we see the formation of structure suggesting strong zero-bias anomalies corresponding to inelastic (magnetic) tunneling processes. The anomalies exist in all of our EuB_6 tunnel junctions, although their shape and temperature dependence vary greatly from junction to junction. They occur at bias voltages that are significantly larger than typically observed, and are accompanied by large variations in the conductance.[29] We suspect that a collective inelastic excitation may be responsible for these large anomalies. Furthermore, in all cases, the background tunnel conductance increases and becomes roughly flat and more metallic. Finally, we speculate that the temperature dependence of these anomalies is linked to the development of the ferromagnetic order parameter. Consequently, the anomalies are strongest, and approximately temperature independent below ~8 K, and this description is consistent with our experimental observations.

Our tunneling data on CeB_6 show the same background conductance as the other two materials (Fig. 3). We see evidence of a gap appearing at approximately 45 mV. The depletion in the conductance is extremely small, approximately 3.5% at zero bias between 52 and 13 K, and the gap value is not as readily observable as in the previous compounds. The gap formation temperature is $T^*=45\pm10$ K,

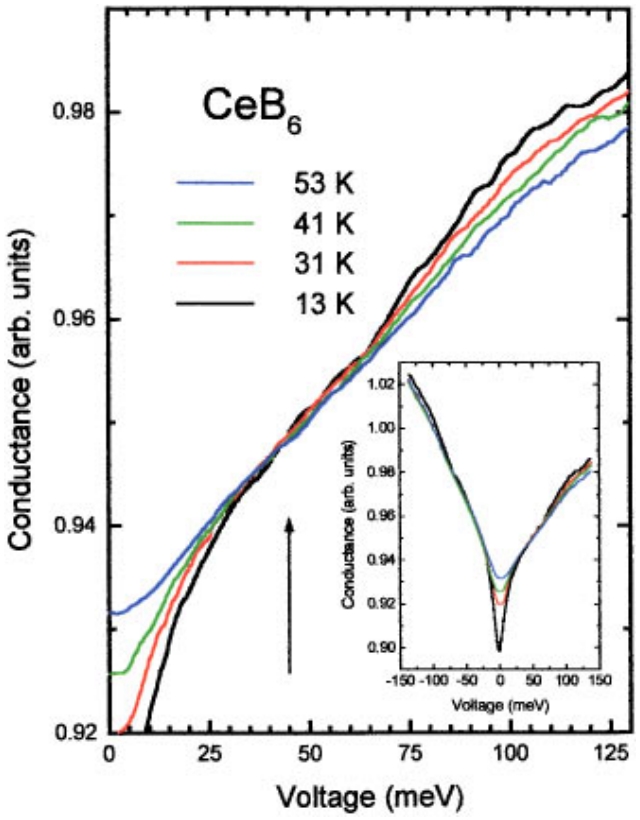

FIG. 3. (Color) The conductance $G(V,T)=dI/dV$ of CeB_6. The arrow indicates the gap, $\Delta=45$ mV.

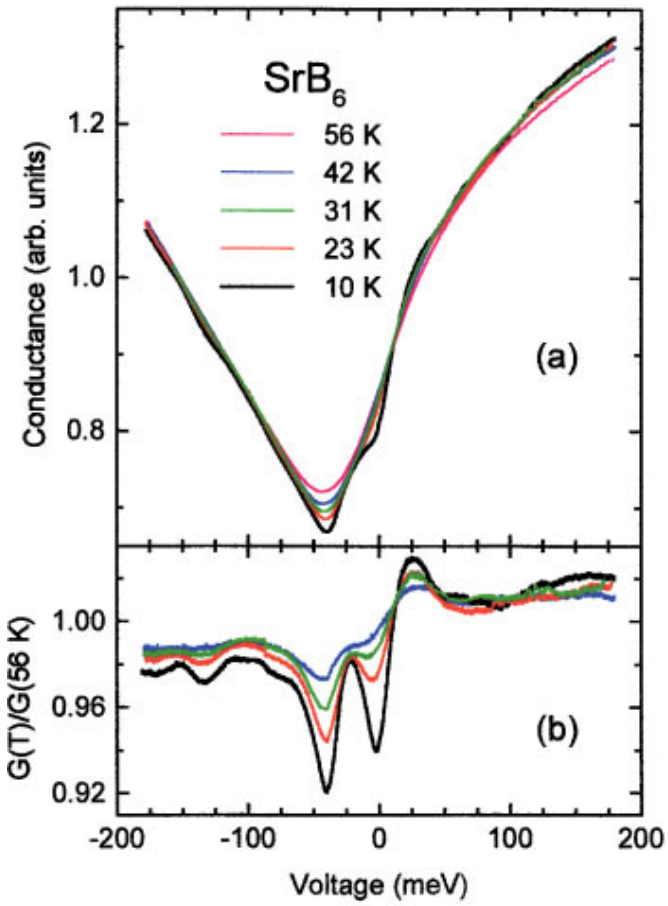

FIG. 4. (Color) (a) The conductance $G(V,T)=dI/dV$ of SrB_6. (b) The low-temperature data shown in (a) are replotted after being normalized to the results obtained at $T=56$ K.

yielding a $\Delta\sim 11k_BT^*$. Similar to EuB_6, the missing states appear over an extended range above the gap. On the other hand, in contrast to EuB_6, we see no change in the background conductance, and no evidence of zero-bias anomalies as this material orders antiferromagnetically at 2.3 K.

The most noticeable aspect of the tunnel conductance data on SrB_6 is that the conductance minimum is located at a bias of -40 mV [Fig. 4(a)]. Similar to the other materials, there is a 7% reduction in the conductance at this minimum as the temperature is lowered from 56 to 10 K. As explained below, the gap features in this data set are atop a more dominating background conductance than was observed for the previous three compounds. In order to differentiate the gap features more clearly, we have normalized the conductance curves for this material to a conductance curve taken at 56 K, which is above the gap temperature $T^*=43\pm 5$ K [Fig. 4(b)]. The data show depletions occurring in the conductance at various biases, with the most pronounced occurring at 12 mV, yielding $\Delta\sim 3.2k_BT^*$.

All four hexaborides exhibit a background conductance of the form $G\approx G_O+\alpha(V-V_O)^n$, where $n\leqslant 1$, and α increases with decreasing G_O. This conductance form results in a steep curve at high junction resistances, and increases the difficulty of measuring the gap features. This behavior is most apparent in the SrB_6 data shown in Fig. 4. Consequently, it is crucial to fabricate low-resistance junctions to accurately measure these features. The background conductances in these hexaborides is strikingly similar in shape to that arising from tunnel measurements between metals and degenerate semiconductors,[29,30] where the tunnel barrier is Schottky type. These similarities lead us to the possibility that this background conductance could be partially a barrier effect, and may not be an intrinsic feature of the density of states.

Our measurements indicate that all four materials possess strikingly similar density-of-states characteristics. It is important to note, as previously stated, that SrB_6 does not possess f bands and is nonmagnetic. The similarity between the SrB_6 data and the results for the other materials raises questions as to whether d- and f-band hybridization is responsible for the anomalous transport properties. This view is supported by recent band-structure calculations of the hexaborides, which show a small overlap at the X point between a localized d band from the metal and a broad p band from the B_6 group, with the Fermi-level crossing in this overlapping region.[25] We expect the resulting density of states to have a minimum in the energy range where the band overlap occurs. The location where the hexaboride Fermi level resides with respect to this minimum in the hexaboride density of states determines the voltage bias at which the conductance minimum occurs. This conductance minimum would occur at a bias voltage that aligns the Pb Fermi level with the minimum in the hexaboride density of states. Above the gap formation temperature, our measurements show that the EuB_6 conductance minimum occurs at a positive voltage bias, whereas, for the rest of the material studied herein, the conductance minimum is at zero or negative bias. This result leads us to believe that the Fermi level in EuB_6 resides rela-

tively higher in the band overlap region. Alternatively, for the other materials, the Fermi level must reside lower in the band overlap region.

In all of these materials, $N(E)$ does not go to zero as the gap forms. Rather, there are small depletions at the Fermi level with decreasing temperature. In addition, $N(E)$ increases roughly linearly with increasing bias within the gap region. This observation is reminiscent of the cuprate superconductors, where the conductance also grows linearly with energy,[31] possibly due to nodes in the excitation spectrum.

We propose two scenarios that lead to this partial gap forming in the density of states. One possibility is that interactions within the framework of the Falicov-Kimball model between an electronlike *d* band and a holelike *p* band lead to a reduction in the density of states, and we note that this model has been successful in explaining previous SmB_6 tunneling data.[32,33] An alternate possibility is that, at the gap formation temperature, a lattice distortion occurs, causing a change in the band structure. Since the lower band is relatively flat and nearly free of curvature,[25] we believe that this change would manifest itself mostly in the upper band. This description would be consistent with the voltage asymmetry in the conductance data since, in this picture, the density of states due to the lower band essentially remains unchanged. Such a distortion may cause these two bands to hybridize, leading to an indirect band gap near the *X* point,[34] with an enhancement of the density of states at the hybridized band edge.[2,4,5,7,10] If the curvatures of the *d* and *p* bands were similar, so that this distortion manifested itself in both bands, then there should be gap structures on both sides of the conductance minimum. This situation may occur in SrB_6, where a subtle feature is seen at approximately -130 mV (Fig. 4). Finally, we believe that the transport properties of these materials may be determined by the extent of the semimetallic band overlap and the extent to which the conduction bands become localized at the gap formation temperature,[13] and not necessarily by magnetic interactions.

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