Low-temperature conducting state in two candidate topological Kondo insulators: SmB_6 and $Ce_3Bi_4Pt_3$

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We have investigated the low-temperature conducting state of two Kondo insulators, SmB_6 and $Ce_3Bi_4Pt_3$, which have been theoretically predicted to host topological surface states. Through comparison of the specific heat of as-grown and powdered single crystals of SmB_6, we show that the residual term that is linear in temperature is not dominated by any surface state contribution, but rather is a bulk property. In $Ce_3Bi_4Pt_3$, we find that the Hall coefficient is independent of sample thickness, which indicates that conduction at low temperatures is dominated by the bulk of the sample, and not by a surface state. The low-temperature resistivity of $Ce_3Bi_4Pt_3$ is found to monotonically decrease with low concentrations of disorder introduced through ion irradiation. This is in contrast to SmB_6, which is again indicative of the contrasting origins of the low-temperature conduction. In SmB_6, we also show that the effect of low concentrations of irradiation damage of the surface with Fe^+ ions is qualitatively consistent with damage with nonmagnetic ions.

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I. INTRODUCTION

The study of three-dimensional topological insulators (TIs) has been an area of intense interest since their existence was first predicted [1]. This has been fueled by the fundamental interest in the consequences of topologically nontrivial band structures, as well as possible technological applications of their physical properties [2]. More recently, attention has turned to topological Kondo insulators (TKIs). In Kondo insulators, the insulating behavior is a strong correlation effect arising from the interaction between localized *f* and conduction electrons. It was predicted that some Kondo insulators may also be topological and display a topologically protected conductive surface state analogous to conventional TIs [3]. The existence of a conductive surface state in the Kondo insulator SmB_6 is now firmly established [4–6], and, although not conclusively proven, there is mounting evidence that it may indeed be topologically protected [7–11]. However, there remain many open questions about the surface and bulk properties of SmB_6, and TKIs in general [11]. More work is required to study the intrinsic properties of SmB_6, but, in addition, it is important to search for further examples of TKIs to help expand our understanding of these important materials.

We report on the study of SmB_6 and a second Kondo insulator that has been theoretically predicted to be topologically nontrivial, $Ce_3Bi_4Pt_3$ [3,12]. This has involved three experiments. First, an important question in SmB_6 is the origin of the low-temperature contribution to the specific heat that is linear in temperature [13,14]. In a conventional insulator without impurity states or magnetic excitations, the only contribution to the specific heat is from phonons, and therefore there would not be any T-linear term from the bulk. A metallic state would be expected to give a T-linear contribution to the specific heat. However, the contribution to the total specific heat from the thin conductive surface state would be expected to be negligible. Hence, the most fundamental question about this term is whether it originates from the bulk or surface of the crystal. Through measurement of the specific heat in single crystals and a ground powder of SmB_6 we show that there is no significant contribution from the surface state. Next, we have studied the thickness dependence of the Hall effect in $Ce_3Bi_4Pt_3$. $Ce_3Bi_4Pt_3$ is predicted to be a topological insulator, and shows a saturation of the resistivity at low temperatures similar to SmB_6. From Hall effect measurements we can conclude that the dominant conduction at low temperatures in this material is through the bulk of the crystal and not from a conductive surface state, in contrast to SmB_6. Finally, through measurement of the resistivity of SmB_6 and $Ce_3Bi_4Pt_3$ before and after ion irradiation, we show a striking difference between the response of these two materials, and attribute this to the different origins of the low-temperature resistance plateau observed in each material. In addition, we find that in agreement with previous ion damage [7,15] and magnetoresistance measurements [16], the surface state of SmB_6 is robust against weak time reversal symmetry breaking perturbations.

II. EXPERIMENTAL TECHNIQUES

Single crystals of SmB_6 and $Ce_3Bi_4Pt_3$ were grown using aluminum and bismuth fluxes, respectively [17]. Specific heat measurements were performed using the time-relaxation method with a Quantum Design physical property measurement system (PPMS). Unpolished single crystals of SmB_6 were measured and a single crystal was powdered using a pestle and mortar and sieved to isolate grains between 38–53 μm. The powdered sample was measured encased in GE varnish.

Resistivity measurements were performed on crystals polished to a platelike geometry with approximate dimensions of the length, width, and thickness of 300 μm, 180 μm, and 35 μm, respectively. Contacts were made to SmB_6 using spot-welded contacts of 25-μm Pt wires. In $Ce_3Bi_4Pt_3$ the Pt wires were attached using silver epoxy. These contacts remained in place during all of the measurements and ion irradiation. The resistance R of the samples as a function of temperature T was measured with a PPMS, using a conventional four-probe

TABLE I. The ion and acceleration energy used in the ion-irradiation of each material to induce damage to the stated depth.

Material	Depth (nm)	Ion	Energy (keV)
$Ce_3Bi_4Pt_3$	12	Ar^+	30
SmB_6	17	Fe^+	10

geometry and a low-frequency ac resistance bridge. The ion irradiation was performed using accelerated Fe^+ and Ar^+ to ion-irradiate the samples with magnetic and nonmagnetic ions, respectively. The ion used on each material and the acceleration energy to produce damage of the crystal surface to a given depth are shown in Table I. The concentration of damage was controlled by the exposure time. This concentration is given in units of displacements per atom (DPA), and the damage depth is defined as the depth at which there is half of the maximum damage, as discussed in detail elsewhere [7]. The damage parameters were calculated using the SRIM Monte Carlo code in the full cascade mode with default threshold displacement energies used in SRIM-2011 [18].

Hall effect measurements of $Ce_3Bi_4Pt_3$ were performed on a wedge-shaped sample to investigate the thickness dependence. Current flowed from the thick end to the thin end of the wedge, and voltage was measured perpendicular to the current at two points along the wedge. A magnetic field was applied perpendicular to both the current and voltage directions.

III. RESULTS AND DISCUSSION

A. Origin of the residual T-linear specific heat in SmB_6

An interesting experimental observation in SmB_6 is the significant finite T-linear term in the low-temperature specific heat C [13,14,19]. This residual γ has been consistently observed over the long history of the study of the material. However, the temperature dependence of C/T and the absolute magnitude of γ do vary between samples. One important question is whether the origin of this term is from a bulk property, such as impurity states, or is intrinsic to the conductive surface state. To resolve this question we have performed specific heat measurements on two pristine single crystals of SmB_6 as well as another crystal from the same batch that was ground to a fine powder. By powdering the crystal we have substantially increased the surface area. The grains of the powder were sieved to produce sizes in the range of 38–53 μm, and the pristine single crystals of SmB_6 had approximate dimensions of $500\times500\times300$ μm^3. Therefore, if we assume an average powder grain was spherical with a diameter of 45.5 μm, we estimate that powdering the sample increased the surface area by a factor of 9. If the surface state gave a significant contribution to the residual γ, we would observe an associated increase in γ in the powdered sample from the increased surface area, provided that powdering did not destroy the surface state. As we have shown from ion irradiation studies [7] and discuss later, the surface state of SmB_6 is remarkably robust, and therefore, we do not expect powdering to degrade the surface state significantly.

Figure 1 shows C/T as a function of T for the two single crystals and the powdered single crystal encased in GE varnish. The varnish contribution is negligible below 5 K and therefore does not affect our measurement of γ [20]. As seen in this figure, the low-temperature C/T values of the powder and single crystals are very comparable. From these data we conclude that γ is not significantly increased by an approximately 9-fold increase in the surface area, and therefore the dominant contribution to γ comes from the bulk of the material. Ascertaining the origin of γ from the bulk will require further investigation, but given some variability between sample growths and the doping dependence, it is likely there is a large extrinsic contribution [13]. Indeed, studies of C/T in samples with varying purity were suggestive of an extrinsic origin [14]. However, in SmB_6 we cannot exclude theoretical suggestions that charge neutral excitations in the bulk may give rise to a residual linear term in C [21,22].

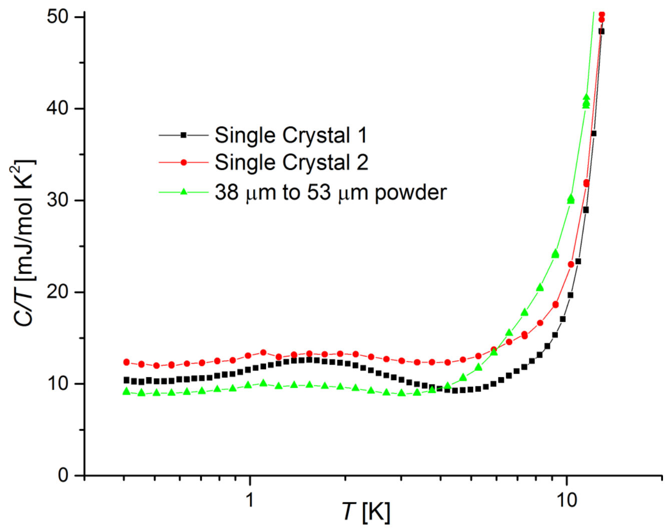

FIG. 1. Specific heat divided by temperature C/T as a function of T for three crystals of SmB_6 from the same batch. Two are pristine single crystals; one was ground to a powder and sieved to leave grain sizes in the stated range. The data for the ground powder include the contribution of the GE varnish which is negligible at low T.

B. Thickness dependence of the Hall effect in $Ce_3Bi_4Pt_3$

$Ce_3Bi_4Pt_3$ has been theoretically predicted to be a TKI with a conductive surface state dominating the low-temperature transport properties, as seen in SmB_6 [3,12]. Indeed, the resistivity of $Ce_3Bi_4Pt_3$ has been consistently observed to saturate at temperatures below about 2 K [23,24], indicating that a conductive state shorts out the bulk intrinsic energy gap. However, it has not been established whether this saturation behavior is due to a surface state or bulk conduction from impurity bands, for example. To address this question we have performed Hall effect measurements at two points along a wedge-shaped single crystal. In this way, it is possible to measure the thickness dependence of the Hall coefficient R_H. If the conduction occurs through the bulk of the material, the Hall coefficient should be independent of the thickness of the sample at the point along the wedge where the Hall voltage contacts are placed. However, if the dominant conduction in $Ce_3Bi_4Pt_3$ occurs through the surface of the crystal, then R_H should be proportional to the thickness of the sample at each

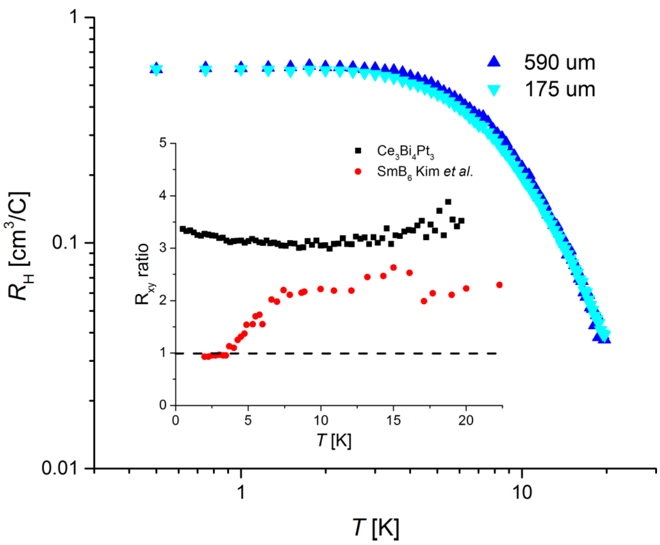

FIG. 2. Temperature dependence of the Hall coefficient of $Ce_3Bi_4Pt_3$ at two points along a wedge-shaped sample to demonstrate thickness dependence. Inset shows the ratio of the Hall resistivity R_{xy} at the two points, and the same ratio for previous measurements on SmB_6 [6].

point. Figure 2 shows R_H as a function of temperature with the Hall voltage measured along the wedge at two thicknesses. These measurements clearly show that R_H is independent of the thickness. The inset shows the ratio of the Hall resistance R_{xy} for the two different thicknesses. For comparison, previous data from the same experiment on SmB_6 are shown [6]. The relative change in thickness in SmB_6 was 2.6, and therefore comparable to our measurements. The decrease in the ratio of R_{xy} in SmB_6 at low temperatures is a signature of a crossover from bulk to surface conduction. The independence of that ratio in $Ce_3Bi_4Pt_3$ is evidence that there is no such crossover, and the conduction is through the bulk because of in-gap states.

It is interesting to note that in $Ce_3Bi_4Pt_3$ a significant residual T-linear term is observed in C, as it is in SmB_6 [25]. It seems plausible that the origin of this residual γ may be common to both $Ce_3Bi_4Pt_3$ and SmB_6, despite the observation that surface states dominate electron transport in SmB_6, but not in $Ce_3Bi_4Pt_3$.

C. Ion irradiation of $Ce_3Bi_4Pt_3$ and SmB_6

In the previous section it was shown that the low-temperature conduction in $Ce_3Bi_4Pt_3$ occurs through bulk states, in contrast to the surface state conduction observed in SmB_6. Therefore, it is interesting now to compare the response of the two systems to the introduction of disorder in a very thin layer of the crystals' surface, and to compare that response to varying degrees of disorder produced at greater depths. To study the effects of controlled disorder, we have measured the change in resistance of individual crystals as a function of ion-irradiation damage.

The dependence of the resistance of $Ce_3Bi_4Pt_3$ and SmB_6 on varying concentrations of ion irradiation is shown Fig. 3. Figure 3(a) shows the resistivity ρ of $Ce_3Bi_4Pt_3$ as a function of temperature for weak to strong disorder produced by Ar^+ irradiation to a depth of 17 nm. The undamaged sample

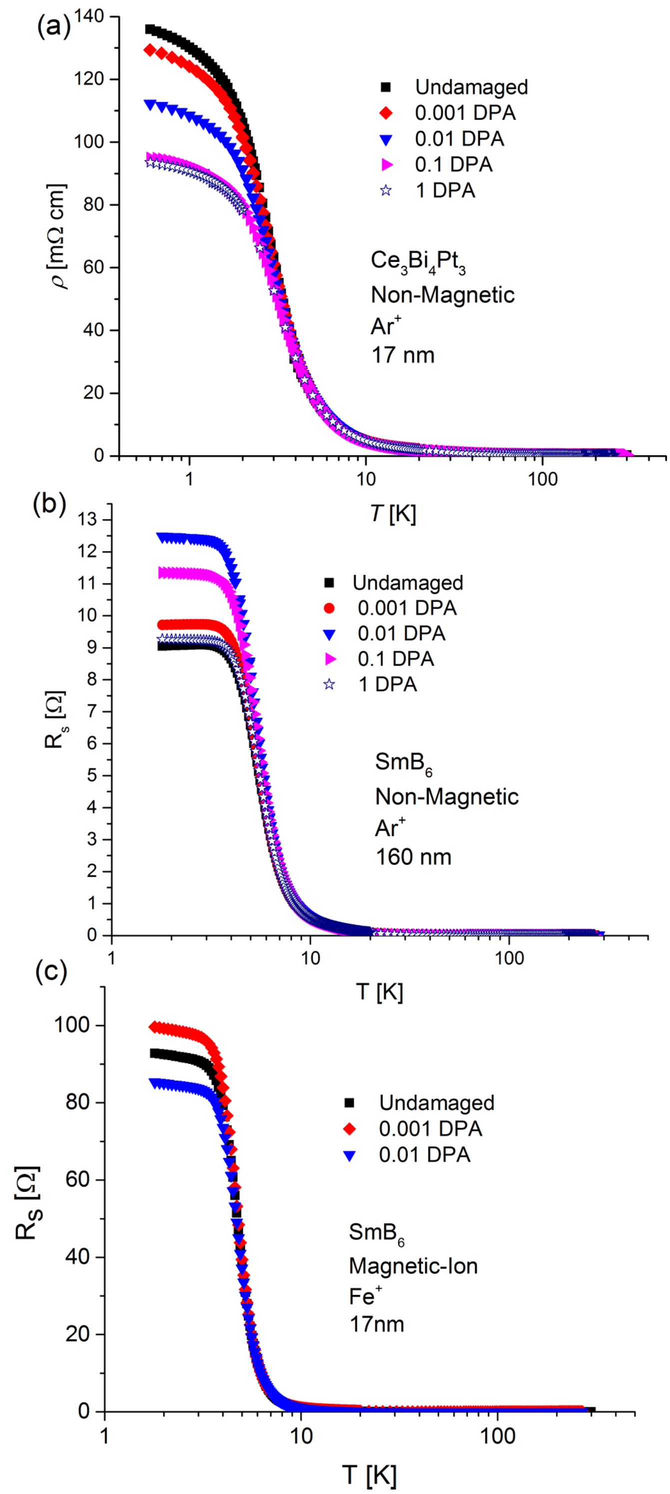

FIG. 3. Temperature dependence of the resistance of (a) $Ce_3Bi_4Pt_3$ and (b), (c) SmB_6 after differing concentrations of ion-irradiation damage to the top and bottom face to the stated depth using the stated ion. Panel (b) is reproduced from a previous study [7].

shows the saturation of the resistivity at low temperatures, discussed above, that we now attribute to bulk states. The damage-dependent resistivity of $Ce_3Bi_4Pt_3$ shows a monotonic decrease with increasing concentration of damage, with the decrease saturating between 0.1 and 1 DPA. This reduction of resistivity through disorder in the damaged region is likely to be the result of a decrease in the Kondo gap through a loss of periodicity and therefore coherence, and/or the introduction of in-gap states [13,29,30]. Indeed, such a decrease in resistivity has been observed in SmB_6 when a small concentration of dopants is added to the *bulk*, or the *bulk* is disordered by neutron irradiation, even at concentrations as low as 0.001 DPA [26–28].

However, the monotonic decrease in resistivity of $Ce_3Bi_4Pt_3$ from surface disorder is in stark contrast with previous surface damage experiments on SmB_6 [15]. In that work, SmB_6 was damaged with Ar^+ to 160 nm. The data are reproduced in Fig. 3(b). The low-temperature sheet resistivity R_S has a nonmonotonic dependence on damage concentration. Initially, the low-temperature resistivity increases at low damage concentrations and then decreases at higher concentrations.

The significantly different responses of $Ce_3Bi_4Pt_3$ and SmB_6 to low concentrations of nonmagnetic ion damage to the surface are likely related to the different origins of the low-temperature saturation of the resistivity. In $Ce_3Bi_4Pt_3$, the dominant contribution to the low-temperature conduction is through bulk impurity states, and therefore disorder of these bulk states is the only channel by which the resistivity is altered, leading to a monotonic decrease with increasing damage. In the case of SmB_6 there are two channels by which the disorder in the damaged region can affect the resistivity. Initially, increased disorder scattering in the intrinsic metallic surface state leads to an increase of the resistance with low levels of damage. Then, at higher concentrations of damage, the introduction of in-gap states and/or reduction of the Kondo gap in the damaged layer, as discussed for $Ce_3Bi_4Pt_3$, dominates the resistivity and a decrease is therefore observed. This may be consistent with theoretical predictions and experimental observations that impurities and/or disorder produce scattering in a topological surface state [31–34].

In SmB_6 it has been shown that when the surface is damaged to very high concentrations, of order 1 DPA, the intrinsic surface state reconstructs below the conductive damaged layer [7], in qualitative agreement with theoretical predictions [35]. At these high concentrations there was no significant difference resulting from whether this damage was caused by irradiation with magnetic or nonmagnetic ions [15]. This result suggested an insensitivity of the surface state conductivity to these kinds of time reversal symmetry breaking perturbations, which may be consistent with the surface state being robust to applied fields of 60 T [16]. However, the damage in those experiments was sufficient to cause a reconstruction of the intrinsic surface state beneath the damaged layer. As discussed above, low concentrations of nonmagnetic ion damage may affect the resistance of the intrinsic surface state, and hence, it is now interesting to consider the effect of a low concentration of damage from irradiation by magnetic ions on the resistivity of SmB_6. These data are shown in Fig. 3(c). There is again a modest increase in the low-temperature resistivity with 0.001 DPA of damage. This small increase of 10% is comparable to the increase from 0.001 DPA caused by nonmagnetic ions, reproduced in Fig. 3(b).

Detailed quantitative comparison of the low-concentration damage from magnetic and nonmagnetic ions is difficult because of the different sheet resistances of the two samples. However, the comparable relative increase in resistance at 0.001 DPA in the two cases again suggests that the surface state is insensitive to whether the damage was caused by magnetic or nonmagnetic ions. We do not observe a significantly larger increase in the low-temperature resistance as a result of introducing time reversal symmetry breaking perturbations. In addition, we do not observe a significant change in the slope of $R_S(T)$ after irradiation. This is in contrast to the reported effect of doping magnetic Gd ions into the bulk of SmB_6 single crystals, where dR/dT became large and negative at low T [28]. This suggests that the nature of the perturbation in each case may be different.

IV. CONCLUSION

We are able to draw several conclusions from the work discussed above. First, the thickness independence of the Hall coefficient in $Ce_3Bi_4Pt_3$ has demonstrated that the dominant contribution to conduction at low temperatures in $Ce_3Bi_4Pt_3$ comes from bulk states, not from the surface. The contrasting response of SmB_6 and $Ce_3Bi_4Pt_3$ to light irradiation damage by nonmagnetic ions further confirmed this, and suggested that this kind of light irradiation can perturb the surface state of SmB_6. The observation of no qualitative difference between the effect of light irradiation using magnetic and nonmagnetic ions suggests that this time reversal symmetry breaking perturbation is too weak to destroy the conductive surface state. Finally, we have shown that the residual linear term in the low-temperature specific heat of SmB_6 is predominantly a bulk property and does not originate from the conductive surface state.

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