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Phase diagram of a pressure-induced superconducting state and its relation to the Hall coefficient of Bi_2Te_3 single crystals

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Pressure-induced superconductivity and its relation to the corresponding Hall coefficient (R_H) have been investigated for Bi_2Te_3, a known topological insulator, through *in situ* measurements of magnetoresistance and ac susceptibility with diamond anvil cells. A full phase diagram is presented which shows a complex dependence of the superconducting transition temperature as a function of pressure over an extensive range. High-pressure R_H measurements reveal a close relation to these complex behaviors; in particular, an abrupt change of dR_H/dP is observed in crossing from the nonsuperconducting to the superconducting ambient-pressure phase.

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The topological insulators represent an unusual state of quantum matter, the bulk state of which is characterized by a full insulating gap while the edge state or surface state is gapless.[1] This state has attracted much attention because of its potential applications in topological quantum computing.[2] Recent theoretical predictions[3,4] and experimental observations[5–8] have successfully discovered a number of topological insulator systems.[9] It has been proposed that electronic excitations like Majorana states may be realized when topological insulators are combined with magnetic or superconducting materials.[10,11] In particular, topological superconductors analogous to topological insulators have been proposed, which have a fully gapped pairing state in the bulk but with a gapless surface state consisting of Majorana fermions.[12] It has been reported that Cu intercalation in Bi_2Se_3 gave rise to superconductivity with $T_c = 3.8$ K although whether a topological superconducting state was realized remains to be established.[13] There has been a great impetus to induce superconductivity in topological insulators or to search for clear topological superconductors.

In this study, we report an investigation of pressure-induced superconductivity over an extensive pressure range and its relation to the Hall coefficient (R_H) in bismuth telluride (Bi_2Te_3), which is a prototypical topological insulator in its rhombohedral phase at ambient pressure (AP), through *in situ* measurements of magnetoresistance and ac susceptibility in diamond anvil cells. We find that the pressure-induced superconductivity exhibits nonmonotonic behaviors with pressure, i.e., a distinct pressure dependence is observed in different phases [AP phase (<8 GPa), high-pressure phase I (8–14 GPa), and high-pressure phase II (>14 GPa) denoted as HP I and HP II phases, respectively, hereafter] induced by high pressure. In particular, even at low pressure where the crystal structure remains the same as at ambient pressure (AP phase), a nonmonotonic pressure dependence of the superconducting transition temperature (T_c) is observed. Furthermore, ac susceptibility data obtained at 5.8 GPa demonstrate that the pressure-induced superconductivity in Bi_2Te_3 has bulk nature. High-pressure Hall coefficient measurements reveal an interesting correlation with the pressure-induced nonsuperconducting to superconducting transition in the AP phase, which indicates that the superconducting transition is related to a clear electronic structure change. From the AP to the HP phase, R_H changes sign from positive to negative, giving clear evidence for a crossover in the electron structure. In the HP phases, T_c also displays nonmonotonic behaviors with pressure.

Single crystals of Bi_2Te_3 were grown by the self-flux method. Bismuth and tellurium powders were weighed according to the stoichiometric Bi_2Te_3 composition. After mixing thoroughly, the powder was placed in alumina crucibles and sealed in a quartz tube under vacuum. The materials were heated to 1000 °C, held for 12 h to obtain a high degree of mixing, and then slowly cooled down to 500 °C over 100 h before cooling to room temperature. Bi_2Te_3 single crystals of several millimeters in size were obtained. The quality of the resulting crystals was confirmed by use of a single-crystal x-ray diffraction instrument (SMART, APEXII) at room temperature.

High-pressure electrical resistance measurements were performed using the standard four-probe technique in a nonmagnetic diamond anvil cell (DAC) made of BeCu alloy. The Bi_2Te_3 single crystal assembled with platinum wires was loaded into the DAC. Nonmagnetic rhenium metal was employed as the gasket, which was insulated with a fine powder of cubic boron nitride. The pressure-induced superconducting transition in the Bi_2Te_3 single crystal was confirmed using two compensating primary and secondary coil systems. The excitation field for the ac susceptibility studies is 4 Oe at 478 Hz. The Be-Cu gasket was used for ac susceptibility measurements. By means of the van der Pauw technique, the high-pressure Hall resistivity was measured by sweeping the magnetic field at a fixed temperature for each pressure point. The pressure media used for the resistance and ac susceptibility measurements are NaCl powder and glycerin, respectively. The DAC was set in a closed-cycle refrigerator equipped with a superconducting magnet. Pressure was determined by ruby fluorescence.[14]

Figure 1 shows the resistance-temperature dependence of Bi_2Te_3 at different pressures over an extensive range. No superconducting transition is detected down to 1.5 K when the applied pressure is below 3 GPa [Fig. 1(a)]. As the pressure approaches 3.2 GPa, a clear resistive drop appears with an onset temperature at 2.6 K. The resistive drop gets more pronounced with increasing pressure, and zero resistance

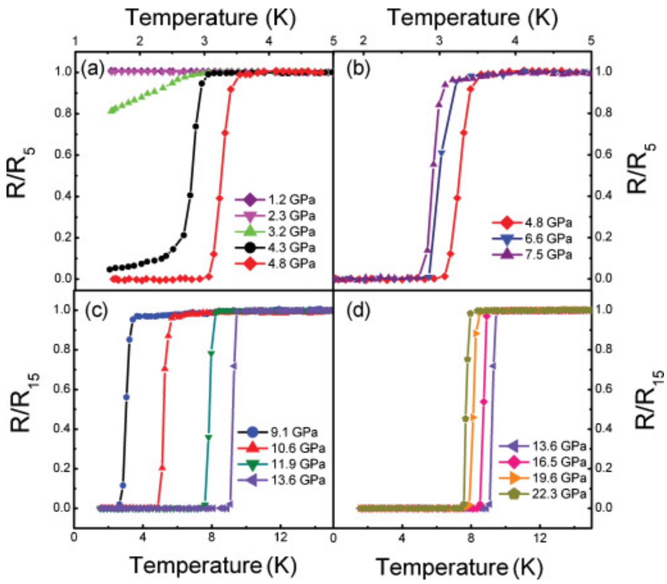

FIG. 1. (Color online) Electrical resistance of Bi_2Te_3 as a function of temperature at different pressures.

is fully realized at 4.8 GPa. This zero resistance persists all the way to 22.3 GPa which is the highest pressure we applied in the present studies (Fig. 1). The pressure-induced superconductivity exhibits clear nonmonotonic behaviors over the pressure range investigated. In the pressure range between 3.2 and 4.8 GPa [Fig. 1(a)], the onset temperature of the resistive drop increases with increasing pressure. However, in the pressure range of 4.8–7.5 GPa [Fig. 1(b)], the onset temperature decreases with increasing pressure. This trend is reversed again in the pressure range of 9.1–22.3 GPa where the onset temperature of the resistive drop goes up [Fig. 1(c)] and then goes down with increasing pressure [Fig. 1(d)].

To characterize whether the resistive drop is related to a superconducting transition, we applied magnetic fields on the compressed Bi_2Te_3. As shown in Figs. 2(a) and 2(b), the resistive drops, in different phases, at 3.5 and 9.5 K for 4.8 and 13.6 GPa shift toward lower temperature, and finally the zero resistance is lost at higher magnetic field, indicating that the resistive drops are truly caused by a superconducting transition. The pressure-induced superconducting transition is also detected using a side-by-side coil system in a DAC, as displayed in the inset of Fig. 2(c). In the ac susceptibility measurements, none is observed above 1.5 K at pressures below 1.5 GPa. However, at 5.8 GPa a superconducting transition does appear with T_c about 3.3 K, as seen in Fig. 2(c). By a comparison with MgB_2 (100%) measured in the same refrigerator, the superconducting volume fraction of Bi_2Te_3 at 5.8 GPa is estimated to be about ~50% from the magnitude of its superconducting transition (170 nV). This result indicates that the pressure-induced superconductivity of Bi_2Te_3 in its AP phase has bulk properties, eliminating the concern that superconductivity occurs only at the dislocations caused by pressure. The superconducting transition temperature T_c (onset T_c) as a function of applied field is displayed in Fig. 2(d).

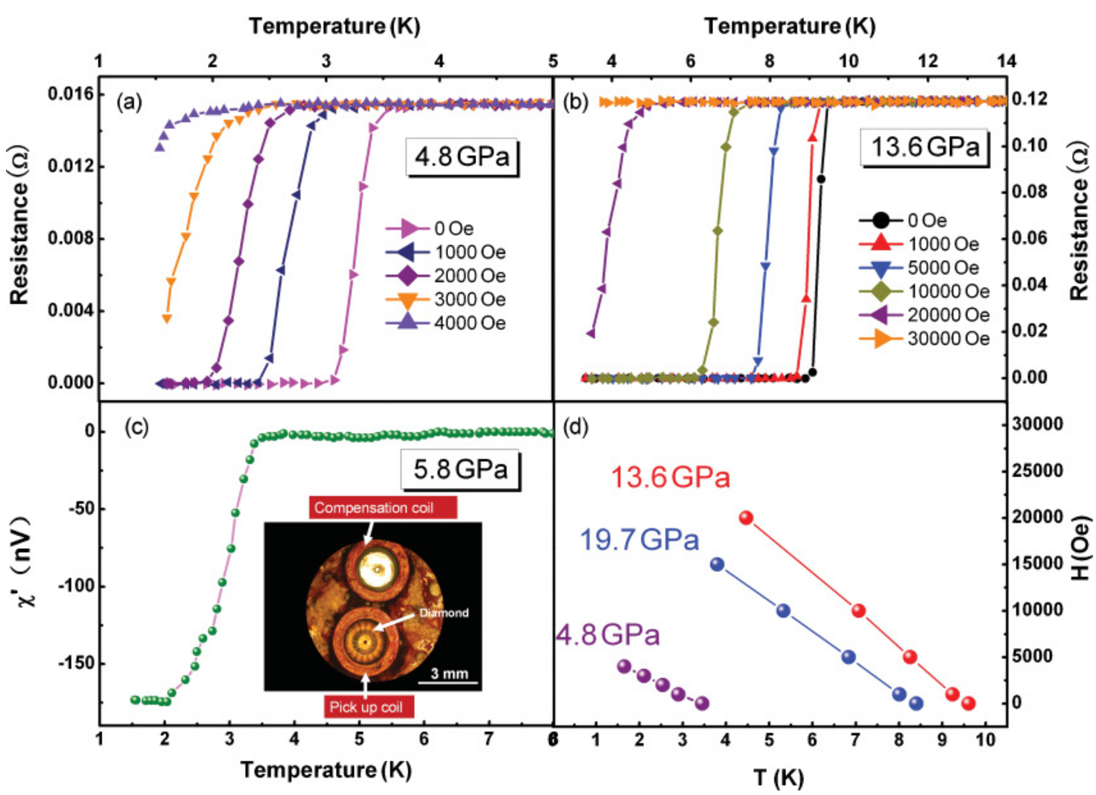

FIG. 2. (Color online) (a) Magnetic-field dependence of the resistive drop of Bi_2Te_3 under different magnetic fields of (a) 4.8 and (b) 13.6 GPa. The real part of the ac susceptibility of the sample at 5.8 GPa is shown in (c). The T_c dependence of the magnetic field is displayed in (d).

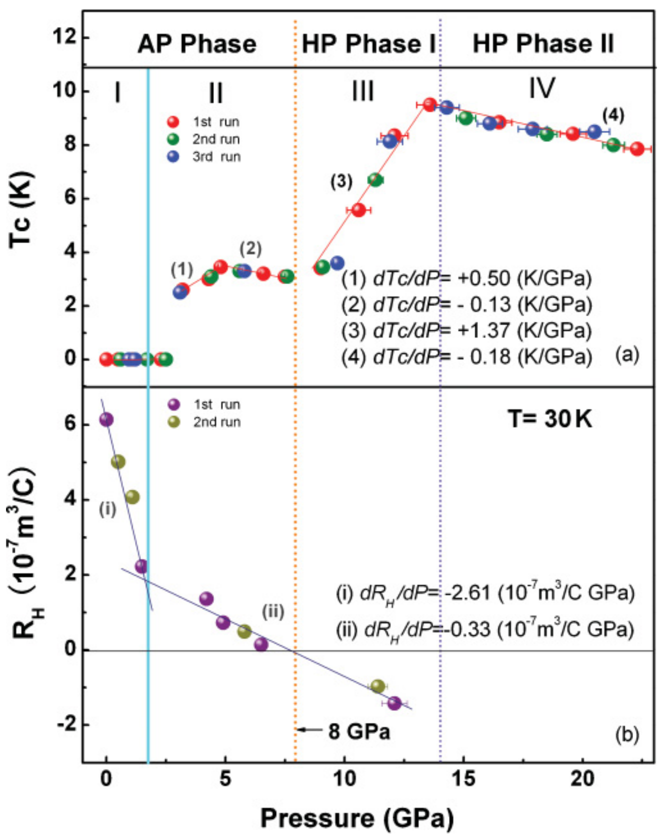

FIG. 3. (Color online) (a) Pressure dependence of superconducting transition temperature in three different phases of Bi_2Te_3 crystal structure. (b) Corresponding pressure dependence of Hall coefficient R_H. The lines are guides to the eye.

We have repeated high-pressure measurements on Bi_2Te_3 for seven independent runs using different samples and the results are highly reproducible. In order to demonstrate the results more clearly, we present the experimental data for the pressure dependence of the onset T_c derived from only three runs of these measurements in Fig. 3(a). It is known that there are phase transitions occurring at around 8 GPa between the AP and HP I phases and 14 GPa between the HP I and HP II phases.[15] The distinct pressure dependence of T_c is clearly related to these three phases because the change of crystal structure influences the symmetry of the Fermi surface, which is tightly related to the superconductivity.

It is interesting to note that a superconducting transition temperature up to 9.5 K is realized at 13.6 GPa near the boundary between the HP I and HP II phases [Fig. 3(a)]. High-pressure studies of possible superconductivity in Bi_2Te_3 have been reported by several groups;[16–21] however, no diamagnetization experiments or complete superconducting phase diagram with different phases of crystal structure over such a large pressure range have reported to our knowledge.

To understand the complex pressure dependence of T_c [$T_c(P)$] in Bi_2Te_3, particularly the emergence of superconductivity and the nonmonotonic $T_c(P)$ in the AP phase, we performed Hall coefficient measurements on Bi_2Te_3 at high pressure, with a magnetic field perpendicular to the *ab* plane of the sample up to 5 T, by sweeping the magnetic field at a fixed temperature for each given pressure. Figure 3(b) shows the pressure dependence of the Hall coefficient $R_H = \rho_{xy}/\mu_0 H$ $(B = \mu_0 H)$ at 30 K. To discuss detailed features in Figs. 3(a) and 3(b) more clearly, we divide the diagram of the superconducting phase and the pressure dependence of the Hall coefficient into four regions. Particularly interesting regions in the phase diagram of Fig. 3(a) are regions I and II. First, these are the regions in which the crystal structure remains the same as in the AP phase where the topological insulator is well established. Second, at 3.2 GPa, there is a pressure-induced superconducting transition. Third, even after the sample becomes a superconductor above 3.2 GPa, the superconducting temperature exhibits nonmonotonic variation with pressure, showing a maximum of 3.5 K at 4.8 GPa where dT_c/dP changes sign. The Hall coefficients in these two regions show quite different behaviors. The initial value of R_H at ambient pressure is positive, indicating that hole carriers are dominant in Bi_2Te_3. R_H decreases rapidly with increasing pressure at the rate $dR_H/dP = -2.61 \times 10^{-7}$ m^3/C GPa in region I where the sample is not superconducting; for pressures above 1.5 GPa in region II, where superconductivity is induced, R_H decreases at a much lower rate $dR_H/dP = -0.33 \times 10^{-7}$ m^3/C GPa. The abrupt slope change in R_H in the AP phase is closely related to a pronounced change of band structure. However, no anomaly is observed in the R_H-P curve in region II where the sample is superconducting and $T_c(P)$ shows a bell shape under pressure [Fig. 3(a)], the origin of which needs further investigation. As the pressure increases further in region III, T_c increases again at the rate $dT_c/dP = +1.37$ K/GPa after the structural phase transition as indicated in Fig. 3(a), indicating that the HP phase I favors higher T_c. The maximum value of T_c in Bi_2Te_3 reaches nearly 9.5 K at 13.6 GPa. However, R_H changes from positive to negative sign at a pressure between regions II and III, suggesting that pressure induces a crossover of the electron structure in Bi_2Te_3, probably turning the sample into an electron-dominated conventional superconductor. T_c passes through a maximum and then decreases in region IV after the second phase transition. Since Bi_2Te_3 is an exotic material in the sense of topological insulators, its superconducting mechanism, particularly the dramatic pressure-induced change of dR_H/dP in the AP phase and the crossover of R_H from the AP to the HP phase, deserves further experimental and theoretical efforts.

In summary, we have provided a complete phase diagram to show the complex dependence of the superconducting transition temperature on pressure and its relation to the Hall coefficient over an extensive pressure range in Bi_2Te_3, a typical topological insulator at ambient pressure. Distinct behaviors are observed in different phases in the pressure range investigated. We found that the initial value of R_H decreases rapidly with increasing pressure up to 1.5 GPa in region I, where the sample is not superconducting; afterward it decreases very slowly as pressure increases further in region II, where superconductivity is discovered from *in situ* resistance and ac susceptibility measurements under high pressure. These results suggested that the dramatic change in dR_H/dP reflects a pronounced change in band structure. In region II, $T_c(P)$ exhibited rising and falling behavior, while R_H changed linearly. With increasing pressure, the AP phase transforms to the HP phase in region III and the T_c rises again. The corresponding Hall coefficient changes from positive to negative after the transition, demonstrating that pressure induces a crossover of the electron state from the hole-dominated to electron-dominated type in Bi_2Te_3. In addition, we found that the value of T_c in the Bi_2Te_3 superconductor with electron carriers is higher than that with hole carriers. We believe that our present work may stimulate further experimental and theoretical investigations to understand the origin of these observations and to clarify whether a topological superconductor could be realized in Bi_2Te_3 at high pressure.

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