Phase diagram of a pressure-induced superconducting state and its relation to the Hall coefficient of Bi_{2}Te_{3} single crystals

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Phase Diagram of Pressure-induced Superconductivity and its Relation to Hall Coefficient in Bi_2Te_3 Single Crystal

Chao Zhang, Liling Sun*, Zhaoyu Chen, Xingjiang Zhou, Qi Wu,
Wei Yi, Jing Guo, Xiaoli Dong and Zhongxian Zhao*

Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China;

Pressure-induced superconductivity and its relation to corresponding Hall coefficient (R_H) have been reported for Bi_2Te_3, one of known topological insulators, 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 with these complex behaviors, particularly, an abrupt change of dR_H/dP is observed in crossing from the non-superconducting ambient pressure phase to the superconducting ambient pressure phase.

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*Corresponding authors:
llsun@aphy.iphy.ac.cn
zhxzhao@aphy.iphy.ac.cn

The topological insulators represent a new 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]. It 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 novel electronic excitations like Majorana states may be realized when combining topological insulators with magnetic or superconducting materials [10-11]. Particularly, analogous to topological insulators, topological superconductors have been proposed which have a fully gapped pairing state in the bulk but its gapless surface state consisting of Majorana Fermions [12]. It was reported that Cu intercalation in Bi_2Se_3 gave rise to superconductivity with Tc= 3.8 K although whether topological superconducting state is realized remains to be established [13]. There has been a great impetus in inducing superconductivity into topological insulators or searching for clear topological superconductors.

In this study, we report pressure-induced superconductivity over an extensive pressure range and its relation to Hall coefficient (R_H) in bismuth telluride (Bi_2Te_3), which is a prototypical topological insulator in its rhombohedral phase at ambient pressure (denoted as AP phase hereafter), through *in-situ* measurements of magnetoresistance and ac susceptibility in diamond anvil cells. We find that pressure-induced superconductivity exhibits non-monotonic behaviors with pressure, i.e. 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 ambient pressure (AP phase), non-monotonic pressure dependence of superconducting transition temperature (*Tc*) is observed. Furthermore, ac susceptibility data obtained at 5.8 GPa demonstrates that the pressure-induced superconductivity in Bi_2Te_3 has bulk nature. High-pressure Hall coefficient measurement reveals an interesting correlation between the pressure-induced non-superconducting and superconducting transition in AP phase, which indicates that the superconducting transition is related with a clear electronic structure change. From AP phase to HP phase, R_H changes the sign from positive to negative, giving a clear evidence for a crossover of electron structure. In HP phases, *Tc* also displays non-monotonic behaviors with pressure.

Single crystals of Bi_2Te_3 were grown by self-flux method. Bismuth and tellurium powders were weighted 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 hours for high degree of mixing, and then slowly cooled down to 500°C over 100 hours before cooling to room temperature. Bi_2Te_3 single crystals with several millimeters in size were obtained. The quality of the resulting crystals was confirmed by using 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 the platinum wires was loaded into the DAC. A nonmagnetic rhenium metal was employed as the gasket which was insulated by fine powder of cubic boron nitride. The pressure-induced superconducting transition in Bi_2Te_3 single crystal was confirmed using two compensating primary/secondary coil system. 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 van der Pauw technique, high-pressure Hall resistivity was measured by sweeping the magnetic field at a fixed temperature for each pressure point. The pressure mediums used for the resistance and ac susceptibility measurements are NaCl powder and Glycerin, respectively. The DAC was set in a close cycle refrigerator equipped with a superconducting magnet. Pressure was determined by ruby fluorescence [14].

Figure 1 shows 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. 1a). 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 is fully realized at 4.8 GPa. This zero resistance persists all the way to 22.3 GPa that is the highest pressure we applied in the present studies (Fig. 1). The pressure-induced superconductivity exhibits clear non-monotonic behaviors over the pressure range investigated. In the pressure range between 3.2 and 4.8 GPa (Fig. 1a), the onset temperature of the resistive drop increases with increasing pressure. However, in the pressure range of 4.8~7.5 GPa (Fig. 1b), 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. 1c) and then goes down with increasing pressure (Fig. 1d).

To characterize whether the resistive drop is related to superconducting transition, we applied magnetic fields for the compressed Bi_2Te_3. As shown in Fig.2 (a-b), the resistive drops, in different phases, at 3.5 K and 9.5 K for 4.8 GPa and 13.6 GPa are seen to shift towards lower temperature and finally the zero resistance loses at higher magnetic field, indicating that the resistive drops are truly caused by superconducting transition. The pressure-induced superconducting transition is also detected using 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 pressure below 1.5 GPa. However, at 5.8 GPa superconducting transition does appear where the Tc is about 3.3 K, as seen in Fig.2(c). By comparing 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 its magnitude of superconducting transition (170 nV). This result indicates that pressure-induced superconductivity of Bi_2Te_3 in its AP phase has a bulk property, eliminating the concern that superconductivity occurs only at the dislocations caused by pressure. The superconducting transition temperature *Tc* (onset *Tc*) as a function of applied field is displayed in Fig.2 (d).

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 on pressure dependence of onset *Tc* derived from only three runs of these measurements in Fig. 3a. It is known that there are phase transitions occurring at around 8 GPa between the AP phase and HP I phase and 14 GPa between HP I phase and HP II phase [15]. The distinct pressure dependence of *Tc* is clearly related with these three phases because the change of crystal structure influences symmetry of Fermi surface which is tightly related to the superconductivity.

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

To understand the complex pressure dependence of *Tc* (*Tc(P)*) in Bi_2Te_3, particularly the emergence of superconductivity and the non-monotonic *Tc(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. Fig.3b shows the pressure dependence of Hall coefficient $R_H=\rho_{xy}/\mu_0H$ ($B=\mu_0H$) at 30 K. To discuss detailed features in Fig.3 (a) and (b) more clearly, we divide the diagram of superconducting phase and pressure dependence of Hall coefficient into four regions. Particularly interesting regions in the phase diagram of Fig. 3a are region I and II.

First, these are the regions that the crystal structure keeps the same as 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 non-monotonic variation with pressure, showing a maximum of 3.5 K at 4.8 GPa where the *dTc/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. The R_H decreases rapidly with increasing pressure at the rate dR_H/dP= -2.61 ($10^{-7}m^3$/C GPa) in region I where the sample is not superconducting, for the pressure above 1.5 GPa in region II the R_H decreases at a much lower rate dR_H/dP= -0.33($10^{-7}m^3$/C GPa) where superconductivity is induced. 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 R_H-*P* curve in range II where the sample is superconducting and the *Tc(P)* shows a bell-shape under pressure (Fig. 3a), the origin of which needs further investigation. As the pressure increases further in region III, *Tc* increases again at the rate *dTc/dP*= +1.37 K/GPa after the structural phase transition as indicated in Fig.3 (a), indicating that the HP phase I favors higher *Tc*. The maximum value of *Tc* in Bi_2Te_3 reaches nearly 9.5 K at 13.6 GPa. However, the R_H changes from positive to negative sign at pressure between region II and III, suggesting that pressure induces a crossover of electron structure in Bi_2Te_3, probably turning the sample to be an electron-dominated conventional superconductor. The *Tc* passes through the maximum and then decreases in region IV after the second phase transition. Since Bi_2Te_3 is a 'new' material in a sense of topological insulators, its superconducting mechanism, particularly pressure-induced dramatic change of dR_H/dP in the AP phase and the crossover of R_H from AP phase to the HP phase, deserves further experimental and theoretical efforts.

In summary, we have provided a complete phase diagram to show a complex dependence of the superconducting transition temperature with pressure and its relation to 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 initial value of R_H decreases rapidly with pressure up to 1.5 GPa in region I where the sample is not superconducting, afterward decreases very slowly as pressure increasing further in the region II where the 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, the $Tc(P)$ exhibited rising and falling behavior, while the R_H changed linearly. As increasing pressure, AP phase transforms to HP phase in region III and the Tc rises again. Corresponding Hall coefficient changes from the positive to the negative after the transition, demonstrating that pressure induces a crossover of electron state from hole-dominated type to electron-dominated one in Bi_2Te_3. In addition, we found that the value of Tc in 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 topological superconductor could be realized in the Bi_2Te_3 at high pressure.

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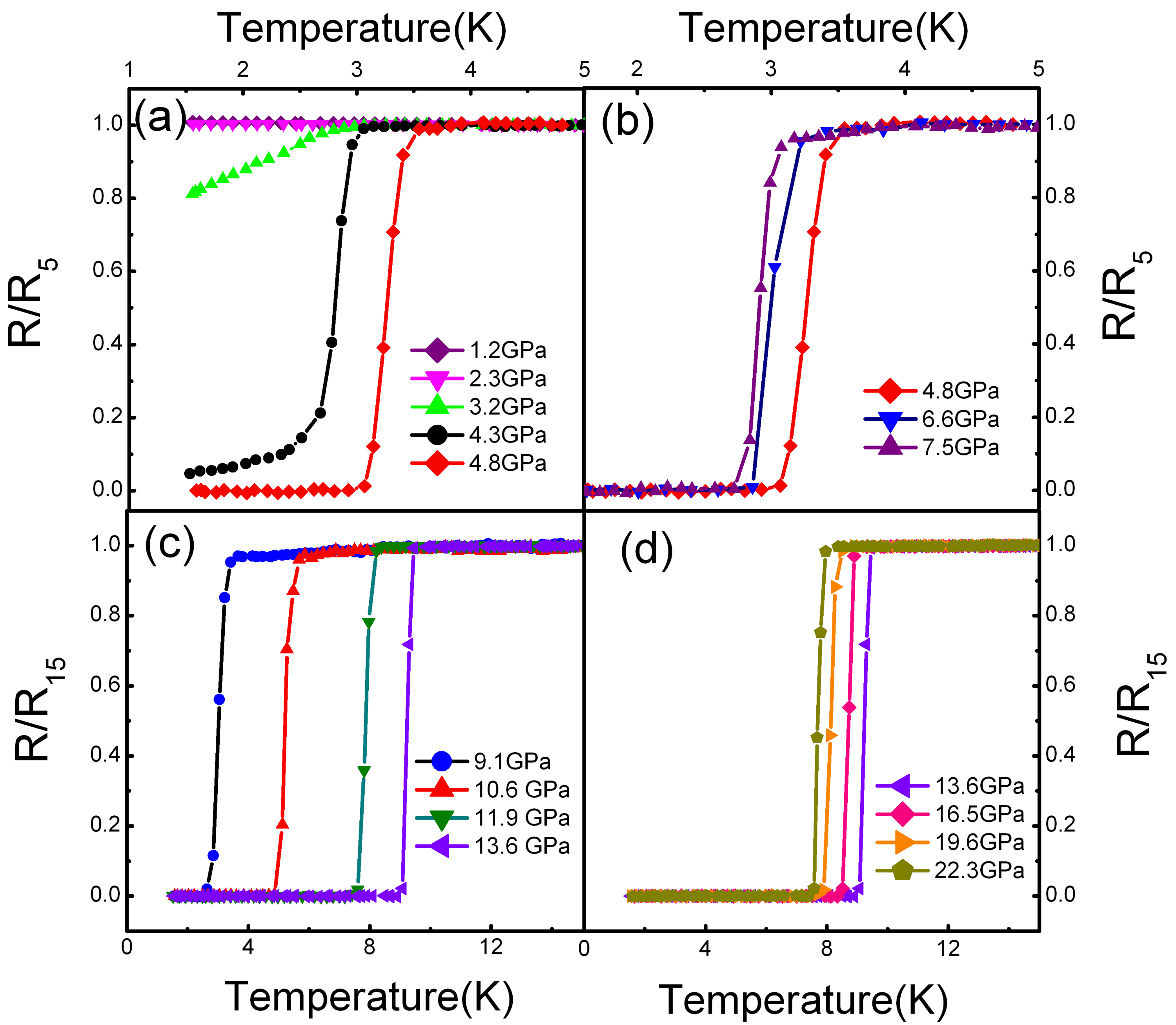
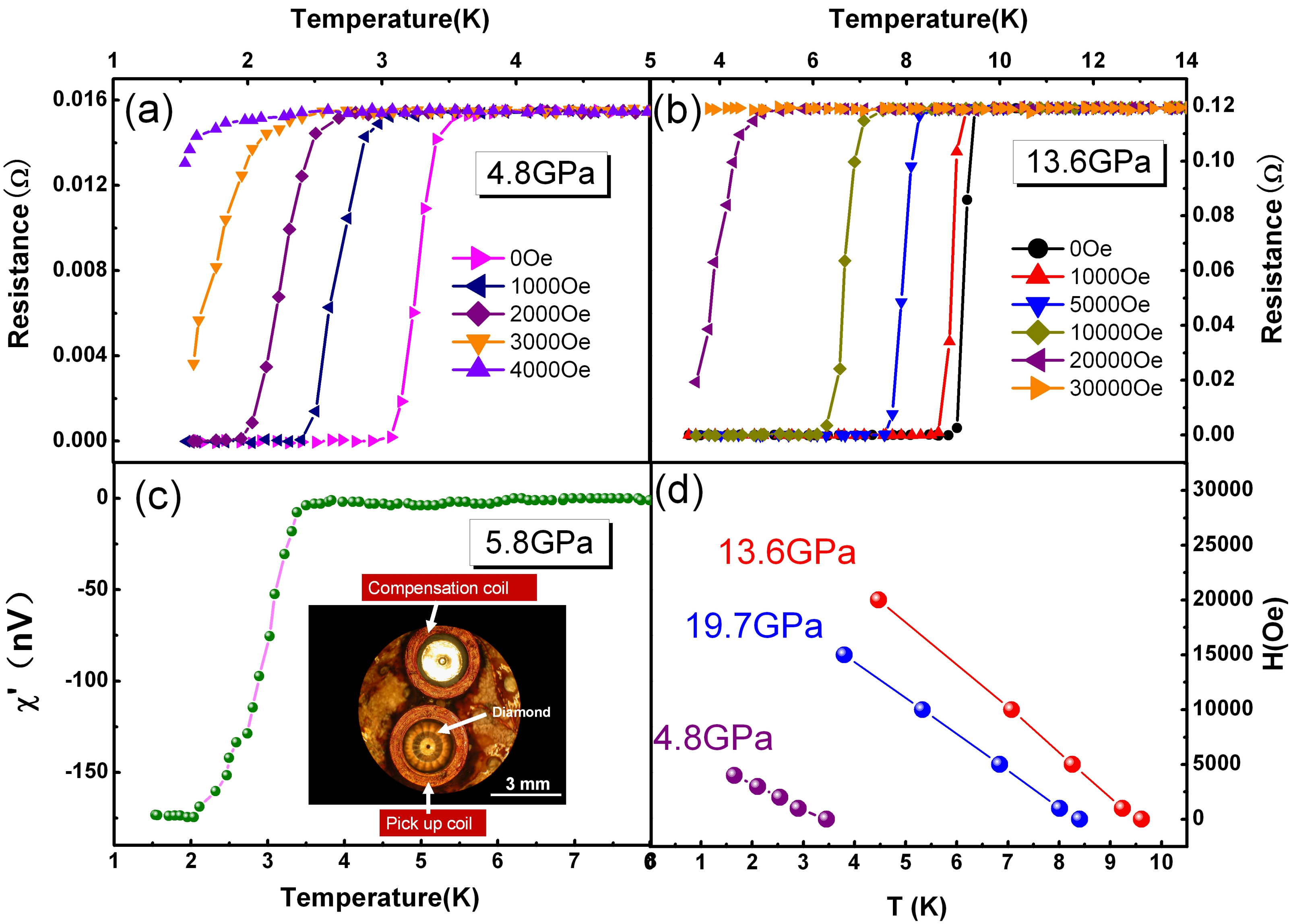
Figure captions:

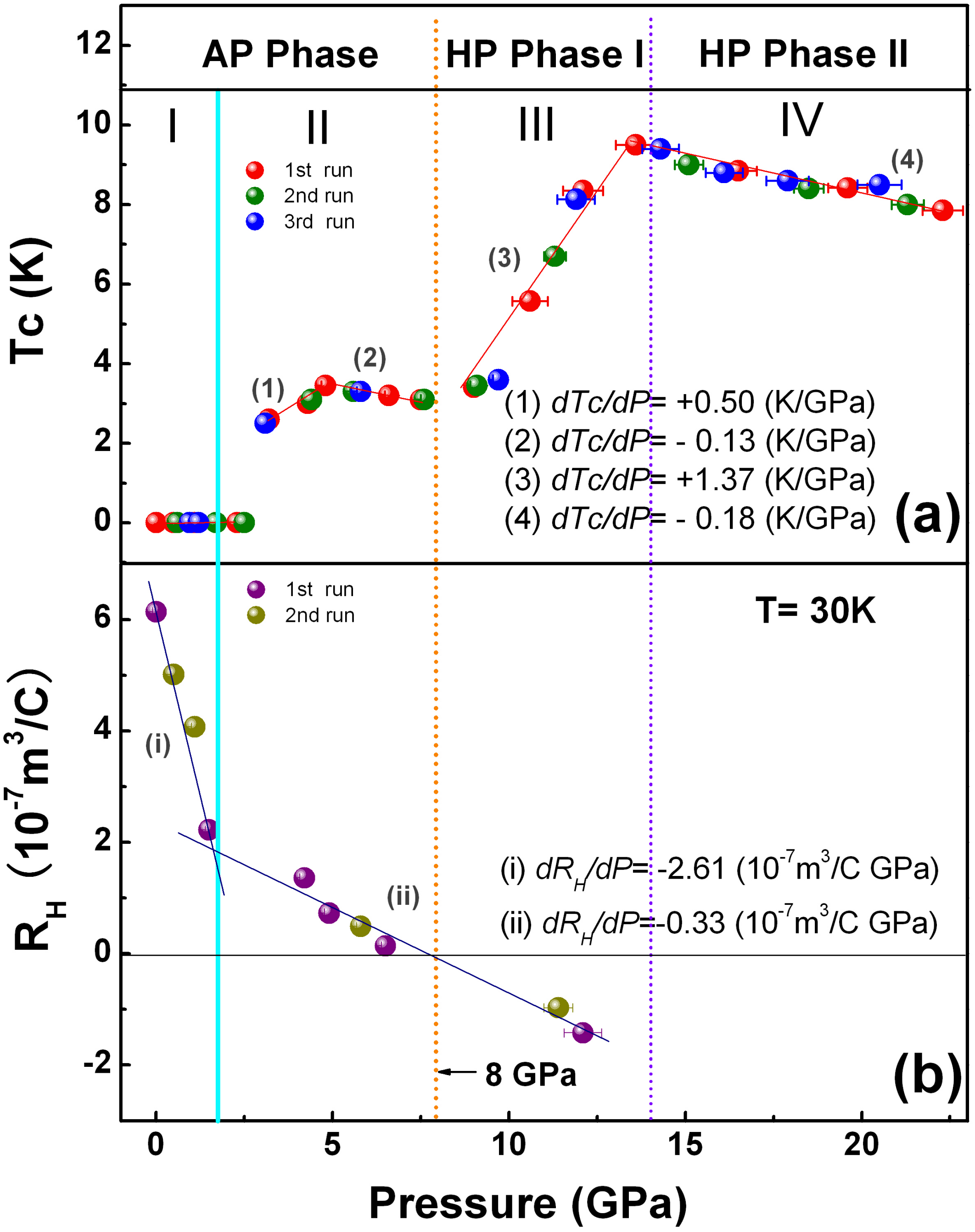
Fig. 1 (Color online) Electrical resistance of Bi_2Te_3 as a function of temperature at different pressures.

Fig. 2 (Color online) (a) Magnetic-field dependence of the resistive drop of Bi_2Te_3 under different magnetic fields at (a) 4.8 GPa, (b) 13.6 GPa. The real part of ac susceptibility of the sample at 5.8 GPa is shown in (c). The Tc dependence of 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 guided to the eye.


Temperature(K)
1
2
3
4
5
Temperature(K)
2
3
4
5
(a)
(b)
R/R_5
1.0
0.8
0.6
0.4
0.2
0.0
1.2GPa
2.3GPa
3.2GPa
4.3GPa
4.8GPa
4.8GPa
6.6GPa
7.5GPa
R/R_5
(c)
(d)
R/R_{15}
9.1GPa
10.6 GPa
11.9 GPa
13.6 GPa
13.6GPa
16.5GPa
19.6GPa
22.3GPa
R/R_{15}
0
4
8
12
Temperature(K)
Temperature(K)


Temperature(K)
1
2
3
4
5
Resistance (Ω)
0.016
0.012
0.008
0.004
0.000
(a)
4.8GPa
0Oe
1000Oe
2000Oe
3000Oe
4000Oe
Temperature(K)
4
6
8
10
12
14
(b)
13.6GPa
0Oe
1000Oe
5000Oe
10000Oe
20000Oe
30000Oe
Resistance (Ω)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
(c)
5.8GPa
χ' (nV)
0
-50
-100
-150
Compensation coil
Diamond
3 mm
Pick up coil
1
2
3
4
5
6
7
8
Temperature(K)
(d)
13.6GPa
19.7GPa
4.8GPa
30000
25000
20000
15000
10000
5000
0
H(Oe)
0
1
2
3
4
5
6
7
8
9
10
T (K)


AP Phase
HP Phase I
HP Phase II
I
II
III
IV
1st run
2nd run
3rd run
(1)
(2)
(3)
(4)
(1) dTc/dP= +0.50 (K/GPa)
(2) dTc/dP= - 0.13 (K/GPa)
(3) dTc/dP= +1.37 (K/GPa)
(4) dTc/dP= - 0.18 (K/GPa)
(a)
Tc (K)
12
10
8
6
4
2
0
1st run
2nd run
T= 30K
(i)
(ii)
(i) dR_H/dP= -2.61 (10^-7 m^3/C GPa)
(ii) dR_H/dP=-0.33 (10^-7 m^3/C GPa)
8 GPa
(b)
R_H (10^-7 m^3/C)
6
4
2
0
-2
0
5
10
15
20
Pressure (GPa)