Superconductivity in the topological insulator Bi_2Te_3 under hydrostatic pressure

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We report the resistivity and ac susceptibility measurements of the topological insulator Bi_2Te_3 single crystals at pressures up to 11 GPa. Under highly hydrostatic pressure conditions generated in a multi-anvil high-pressure apparatus, a pressure-induced superconductivity only appears above a critical pressure $P_C \sim 7$ GPa, coinciding with a structural transition from a rhombohedral to a monoclinic structure. The absence of superconductivity in the rhombohedral phase at pressures below P_C, which is contrary to previous studies using the high-pressure apparatus with a solid pressure medium, suggests that the occurrence of superconductivity in the rhombohedral phase is sensitive to pressure conditions such as pressure inhomogeneity or uniaxial stress.

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Topological insulators are a new class of materials that have a topologically protected conducting surface state within a bulk band gap [1,2]. The theoretically predicted topological surface state protected by time-reversal symmetry has been confirmed experimentally in angle-resolved photoemission spectroscopy in some bismuth-based compounds, such as Bi_2Se_3 and Bi_2Te_3 [3–5]. It is fundamentally interesting to test whether the new quantum state in topological insulators can be tuned to give rise to superconductivity. In particular, the discovery of superconductivity in Cu-intercalated Bi_2Se_3 has led to an enormous number of experimental and theoretical studies for topological superconductivity [6,7]. Although the Cu intercalation does not change the crystal structure, it remains unclear whether Cooper pairs are related to the new quantum state in the parent compound.

Application of pressure provides another route to study superconductivity as experimentally observed in Bi_2Te_3 and Bi_2Se_3 [8–11]. The high-pressure superconducting phase ($P > 6.3$ GPa) in Bi_2Te_3 was already realized in the 1970s [12]; however the emergence of superconductivity at a critical pressure $P_C \sim 3$ GPa has attracted renewed interest due to the possible connection between superconductivity and a topological insulating state. This is because the P_C is much lower than the critical pressure to induce the structure transition from a rhombohedral ($R\bar{3}m$) phase to a monoclinic ($C2/m$) phase [13–15]. The rhombohedral structure supports the topological insulator phase. However, from an experimental point of view, superconductivity in Bi_2Te_3 has not been clearly demonstrated for the following reasons. First, the transport properties of Bi_2Te_3 at ambient pressure are highly sample-dependent. It is known that as-grown nominally stoichiometric Bi_2Te_3 tends to have antistructure defects with *p*-type charge carriers [16], exhibiting a metallic temperature dependence. However, by Te-vapor annealing, the defect concentrations can be varied and it is possible to achieve a bulk insulating state [17]. These differences in the transport property at ambient pressure may affect the superconducting state under pressure. Second, the critical pressure of pressure-induced superconductivity and the high-pressure phase diagram, obtained by using various high-pressure devices in different groups, remains controversial. This is probably due to the deviation from ideal hydrostatic conditions, such as pressure inhomogeneity or uniaxial stress, depending on the pressure media and the high-pressure devices used. Similar discrepancies for the pressure effect have been found in iron-pnictide compounds [18–20]. Indeed, previous studies showing the onset of superconductivity at $\sim$3 GPa were performed in a diamond anvil cell (DAC) with a solid-state pressure medium. Some significant shear stress as well as a huge pressure gradient may exist at the sample space. Therefore, it is important to carry out the study under hydrostatic pressure for comparison.

In this paper, we report on the resistivity and ac magnetic susceptibility measurements of Bi_2Te_3 single crystals with different transport properties under highly hydrostatic pressures using a multi-anvil high-pressure apparatus. In contrast to the previous report, bulk superconductivity with almost perfect diamagnetic shielding only appears above 7 GPa, which is not affected by the difference in the sample's transport properties at ambient pressure.

Bi_2Te_3 single crystals were grown by using the flux method. X-ray diffraction measurements indicate that the obtained samples crystallize in the rhombohedral structure. High-pressure experiments were performed with a cubic anvil apparatus, which is well known to generate hydrostatic pressure due to the multiple-anvil geometry [21], with glycerol as a pressure-transmitting medium. The electrical resistivity and the Hall resistivity were measured by a dc four-probe and the van der Pauw method, respectively. Here, electrical current was applied in the *ab* plane. ac magnetic susceptibility was measured at a fixed frequency of 317 Hz with a modulation field of 0.2 mT applied along the *ab* plane. The diamagnetic signal due to the superconducting transition was estimated by comparing to the diamagnetic signal of lead, which serves as a pressure manometer and has almost the same volume and shape as the sample of Bi_2Te_3.

Figure 1 shows the temperature dependence of (a) the electrical resistivity $\rho(T)$ and (b) Hall coefficient $R_H(T)$ for different samples. As reported previously, we observed the strong sample dependence of $\rho(T)$; sample no. 1 exhibits a simple metallic behavior while sample no. 2 shows a broad peak at around 100 K. The temperature dependence of the Hall coefficient $R_H(T)$ of sample no. 1 is weaker than that of

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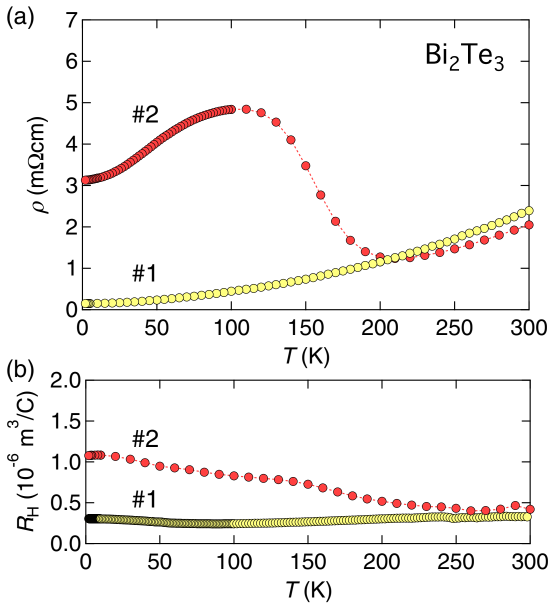

FIG. 1. (Color online) Temperature dependence of (a) the resistivity and (b) the Hall coefficient of Bi_2Te_3 single crystals with applied current in the *ab* plane.

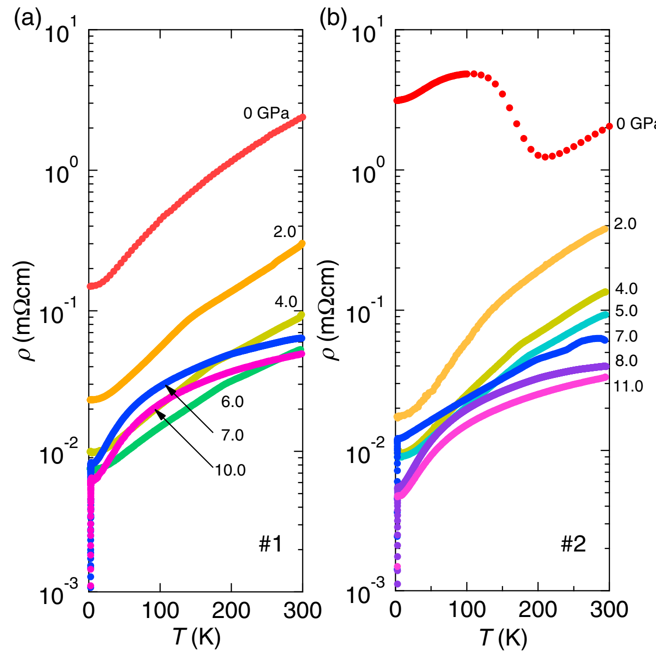

FIG. 2. (Color online) Temperature dependence of the electrical resistivity of (a) metallic (no. 1) and (b) nonmetallic (no. 2) samples of Bi_2Te_3 at selected pressures.

no. 2, whereas $R_H(T)$ of both samples is positive in the whole temperature range, indicating that the dominant carriers are holelike. As mentioned in the introduction, these differences are caused by crystal imperfections leading to a variation in the location of the Fermi level [22]. An intriguing question is whether the differences in transport properties affect the occurrence of superconductivity under pressure.

Figure 2 shows the temperature dependence of the resistivity of the metallic sample (no. 1) and the nonmetallic sample (no. 2) at selected pressures. In both cases, the resistivity at room temperature drops abruptly by more than an order of magnitude with increasing pressure. In particular, the nonmetallic behavior for sample no. 2 is suppressed, and it becomes metallic over the entire temperature range under pressure $P \geqslant 2$ GPa. For pressures exceeding ∼7 GPa, $\rho(T)$ exhibits an unusual upward curvature accompanied by an enhancement of the residual resistivity. Coinciding with these variations, superconductivity appears abruptly at low temperature, as shown in Figs. 3(a) and 3(b). Although the samples exhibit different transport properties at ambient pressure, both samples undergo a sharp superconducting transition above $P_C \sim 7$ GPa, below which there is no signature of a superconducting transition. The superconducting transition temperature reaches a maximum $T_{SC} \sim 2.7$ K near 8 GPa. Significantly, the value of T_{SC} is close to that observed in previous reports, although P_C is much higher in our case. The origin of this discrepancy will be discussed below.

To clarify whether the superconducting transition from $\rho(T)$ is a bulk property, we measured the ac magnetic susceptibility measurements under pressure. A clear drop in χ_{ac} appears above $P_C \sim 7$ GPa, while there is no apparent change in χ'_{ac} below P_C. The large diamagnetic signal corresponding to nearly 100% superconducting shielding confirms the bulk nature of the superconductivity. It is worth noting that the

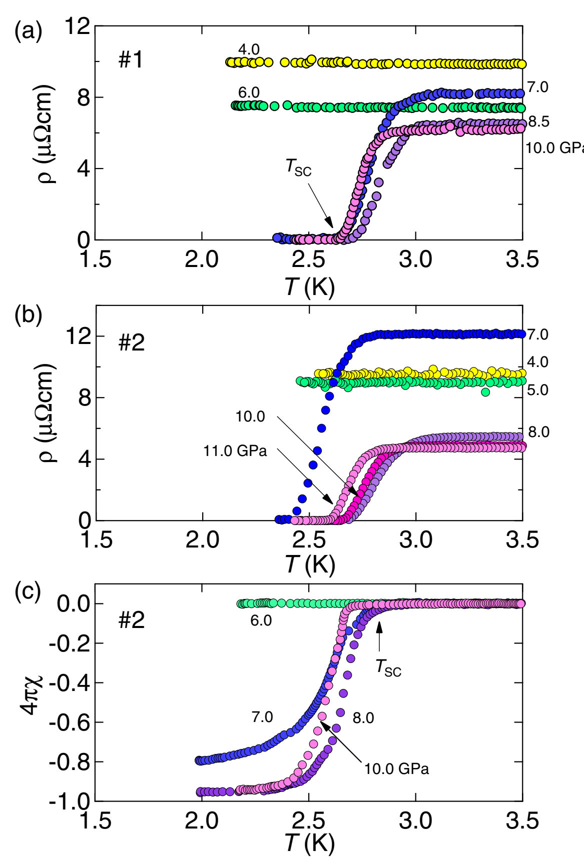

FIG. 3. (Color online) Low-temperature part of the electrical resistivity of Bi_2Te_3 for (a) metallic (no. 1) and (b) nonmetallic (no. 2) samples at selected pressures. (c) Temperature dependence of the ac magnetic susceptibility. The superconducting transition temperature T_{SC} is defined as the temperature of zero resistance and the onset of the full shielding effect.

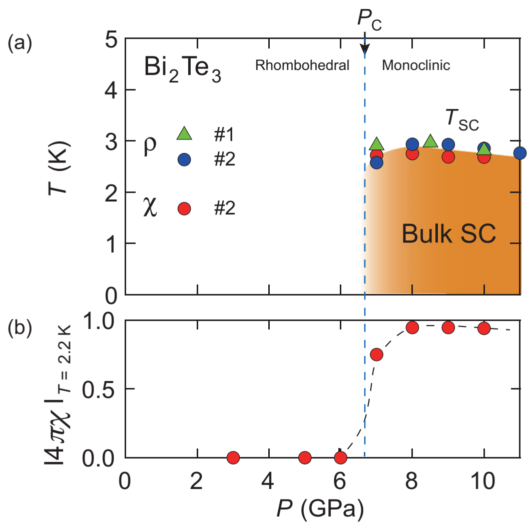

FIG. 4. (Color online) (a) Temperature pressure phase diagram of Bi_2Te_3. (b) Pressure dependence of the superconducting volume fraction $|4\pi\chi|$ taken at approximately 2.2 K. The broken line is a guide for the eye.

superconducting anomaly appears at the same temperature as that found in the resistivity measurements.

The pressure dependence of the superconducting transition temperature for Bi_2Te_3 is summarized in Fig. 4(a) together with the pressure dependence of the superconducting volume fraction, as shown in Fig. 4(b). In all high-pressure experiments, pressure-induced bulk superconductivity is observed only above $P_C \sim 7$ GPa. After peaking at $P \sim 8$ GPa, T_{SC} becomes suppressed with increasing pressure. Importantly, both T_{SC} and P_C are hardly affected by the variation of the transport properties at ambient pressure; however our experimental results contradict previous reports. We conjecture that a possible origin of this apparent contradiction is the difference of the high-pressure environment. Here we point out that a critical pressure P_C (~7 GPa) in our experiments coincides with a pressure-induced structural transition from rhombohedral to monoclinic structure, which is revealed by x-ray diffraction measurements under hydrostatic pressure using He gas or methanol-ethanol (4:1) mixture as the pressure medium in a DAC [12–14]. These features are reminiscent of those for Bi, Bi_4Te_3, and Bi_2Se_3, which exhibit successive structural phase transitions and superconducting states [11,23,24]. It is known that the first-order nature of these structural transitions induces phase separation at a phase boundary if the pressure inhomogeneity is not negligible. Generally speaking, applying pressure is known as a relatively clean tuning parameter. However, the solidification of the liquid or the use of a solid pressure-transmitting medium causes an inhomogeneous pressure distribution, especially for a pressure cell in the uniaxial geometry, such as a piston cylinder, a Bridgman anvil, or a DAC. Indeed, both high-pressure measurements on Bi_2Te_3 exhibiting superconductivity below ~7 GPa have been carried out using a DAC with a solid pressure medium [9,10]. Hence, we speculate that superconductivity appearing in the lower pressure region in the phase diagram is due to the uniaxial strain effect in the rhombohedral phase or the strain-induced rhombohedral to monoclinic phase transition. This interpretation is also supported by comparing our results with data for the aforementioned high-pressure experiment. First, the absolute value of T_{SC} and its pressure dependence in our study is comparable to those in the previous report, in spite of the crucial difference in the critical pressure for the superconducting transition. Second, the apparent superconducting volume fraction at 5.8 GPa using a DAC is approximately 50% with a large transition width [10]. This is in contrast to a much higher superconducting volume fraction in our experiment only above P_C (~7 GPa), below which no shielding signal was detected. Consequently, we ascribe the previously reported superconductivity below P_C to a combination of the nonsuperconducting rhombohedral phase and the superconducting monoclinic phase induced by the pressure inhomogeneity. The present results do not rule out the possibility that superconductivity found in the rhombohedral phase at $P \sim 3$ GPa with a DAC could be due to the shear strain effect, because the effects of hydrostatic and uniaxial pressure on crystal structures and therefore physical properties are different [25]. We believe that further investigations are warranted in order to clarify whether a topological insulator can be tuned to give rise to superconductivity under high pressure.

In conclusion, we have investigated the effect of pressure on Bi_2Te_3 single crystals under hydrostatic conditions. The obtained phase diagram is highly reproducible even for samples with different transport properties at ambient pressure, and it reveals a relationship between the structural transition and the appearance of superconductivity. In contrast to previous high-pressure studies that used a solid pressure medium with a DAC, the superconductivity is absent in a low-pressure rhombohedral phase. This result implies that the rhombohedral phase could support superconductivity only under strong uniaxial stress.

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