Pressure-induced superconductivity in Bi single crystals

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Measurements on resistivity and magnetic susceptibility have been carried out for Bi single crystals under pressures up to 10.5 GPa. The temperature dependent resistivity shows a semimetallic behavior at ambient and low pressures (below about 1.6 GPa). This is followed by an upturn of resistivity in the low temperature region when the pressure is increased, which is explained as a semiconductor behavior. This feature gradually gets enhanced up to a pressure of about 2.52 GPa. Then a nonmonotonic temperature dependent resistivity appears upon further increasing pressure, which is accompanied by a strong suppression to the low temperature resistivity upturn. Simultaneously, a superconducting transition occurs at about 3.92 K under a pressure of about 2.63 GPa. With further increasing pressure, a second superconducting transition emerges at about 7 K under about 2.8 GPa. For these two superconducting states, the superconductivity induced magnetic screening volumes are quite large. As the pressure further increases to 8.1 GPa, we observe the third superconducting transition at about 8.2 K. The resistivity measurements under magnetic field allow us to determine the upper critical fields $\mu_0 H_{c2}$ of the superconducting phases. The upper critical field for the phase with $T_c = 3.92$ K is extremely low. Based on the Werthamer-Helfand-Hohenberg (WHH) theory, the estimated value of $\mu_0 H_{c2}$ for this phase is about 0.103 T, while the upper critical field for the phase with $T_c = 7$ K is very high with a value of about 4.56 T. Finally, we present a pressure dependent phase diagram of Bi single crystals. Our results reveal the interesting and rich physics in bismuth single crystals under high pressure.

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I. INTRODUCTION

Bismuth (Bi) is a very interesting element in terms of electronic properties. The hybridized p-orbitals of Bi exhibit tremendous and rich physics, and thus have received much attention. Firstly, the band structure calculation on Bi shows a feature of multiband and multi-Fermi pockets [1–3]. Due to the existence of many small electron and hole Fermi pockets, it shows the giant magnetoresistance effect [4]. In addition, as a very heavy element, Bi is supposed to have strong spin-orbital coupling effect [5]. Concerning superconductivity, early investigations gave segmental messages [6–10]. At room temperature, Bi shows sequential structure transitions by varying the applied pressure [11]: ambient phase Bi-I (As-type, $R3-mh$) to Bi-II (monoclinic, $c12/m1$) at about 2.55 GPa; Bi-II to Bi-III (host-guest structures, $I4/mcm$) at about 2.70 GPa and Bi-III to Bi-V (bcc, $Im-3m$) at about 7.7 GPa. The Bi-IV phase (orthorhombic, $Cmca$) occurs above the temperature of 450 K, therefore it is not relevant here concerning superconductivity. Except for the Bi-I and Bi-IV phases, all other phases mentioned above are reported to show superconductivity at low temperatures. In addition, amorphous Bi is also superconductive in the form of thin film with T_c of about 6 K [7]. Furthermore, granular Bi nanowires fabricated by deposition show two superconducting transitions at 7.2 K and 8.3 K [8]. Besides, in the study of some single crystals grown by Bi flux, interfacial superconductivity was also observed [12]. Although these pieces of knowledge have been already accumulated in the past on Bi, the detailed pressure dependent evolution of superconductivity and magnetic properties are hard to find in literature. Concerning the mysterious behavior of superconducting Bi under pressure, it is necessary to measure the basic superconducting properties of Bi. In addition, nowadays high pressure has become a very powerful tool for exploring new superconductors [13–15]. For the materials containing the Bi element, cautions must be taken when claiming superconductivity under pressure since a Bi impurity might exist in the sample. Our study will also serve as a useful reference for this purpose.

In this paper, we report the temperature dependent resistivity and magnetic susceptibility under pressures up to 10.5 GPa. The evolution of Bi-I to superconducting Bi-II and Bi-III phases induced by high pressure is shown by resistivity measurements. The measurements of magnetic susceptibility under high pressures reveal that the Bi-V phase becomes superconducting below 8 K at and above 8.1 GPa. Magnetization hysteresis loops and the superconducting phase diagram of bismuth under high pressures are also obtained.

II. EXPERIMENTAL METHOD

The Bi single crystals were taken from the commercial product of Bi granules (Alfa Aesar, 99.997% purity). The samples look shiny with the typical size of about 2 mm. Temperature dependent resistivity measurements were carried out with a physical property measurement system (PPMS-16T, Quantum Design). The resistive measurements at high pressures were accomplished by using the HPC-33 piston type pressure cell. The pressure was calibrated by measuring the T_c of lead. DC magnetization measurements were performed with a SQUID-VSM-7T (Quantum Design). The DC magnetic susceptibility measurements at high pressures were accomplished by using the diamond anvil cell (DAC) designed by the Honest Machinery Designer's office (HMD).

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A small piece of ruby was used as the pressure manometer. Daphne oil 7373 was used as the pressure transmitting medium in both resistive and magnetic susceptibility measurements to endeavor the hydrostatic condition. The maximum pressure of HPC-33 is about 3 GPa and the DAC can be up to 10 GPa at least. Due to the broadening of the ruby luminescence peak, the error of pressure given by the DAC technique at 9 GPa is about ±0.8 GPa. In addition, although the Daphne oil 7373 was also used in the DAC based DC magnetization measurements, it may not be possible to give a uniform static pressure. There is a slightly uniaxial-like pressure field inside the small pressurized space. Therefore the DAC based magnetic measurement may be called quasistatic, which will give the pressure inhomogeneity to a certain extent.

III. RESULTS AND DISCUSSION

Temperature dependent resistivity of a Bi single crystal under pressures up to 2.80 GPa is shown in Fig. 1. At ambient pressure, Bi adopts the hexagonal structure with semimetallic property, while, with increasing applied pressure, the resistivity enhances dramatically at low temperatures. An upturn of resistivity in the low temperature region appears at 2.2 GPa. This pressure-induced low-temperature upturn of resistivity was attributed to the semiconductor behavior [16,17]. We adopt this picture to interpret our data under low pressures. This semiconducting property becomes more clear at about 2.52 GPa. Considering the multiband feature of Bi, the semimetal to semiconductor transition may come from the Fermi level shift of Bi under pressure. Further increasing pressure to 2.63 GPa, superconductivity occurs at about 3.9 K. Then another superconducting phase with an onset temperature of about 7 K appears at about 2.80 GPa, as shown in the inset of Fig. 1(b). According to the structural phase diagram of Bi under high pressures [11], the Bi-I phase

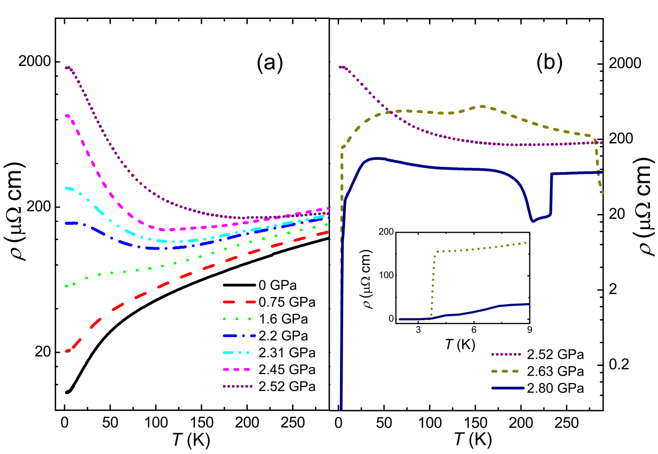

FIG. 1. Temperature dependent resistivity under pressures up to 2.80 GPa. Bi shows a semimetal to semiconductor (see text) transition at a pressure of about 1.6 GPa. Then it becomes superconducting at pressures above 2.63 GPa. There are two resistivity anomalies occurring in the temperature region from 200 K to 250 K under 2.80 GPa, which may be related to the phase transitions. The inset shows the one step superconducting transition under 2.63 GPa and the two step transitions under 2.8 GPa.

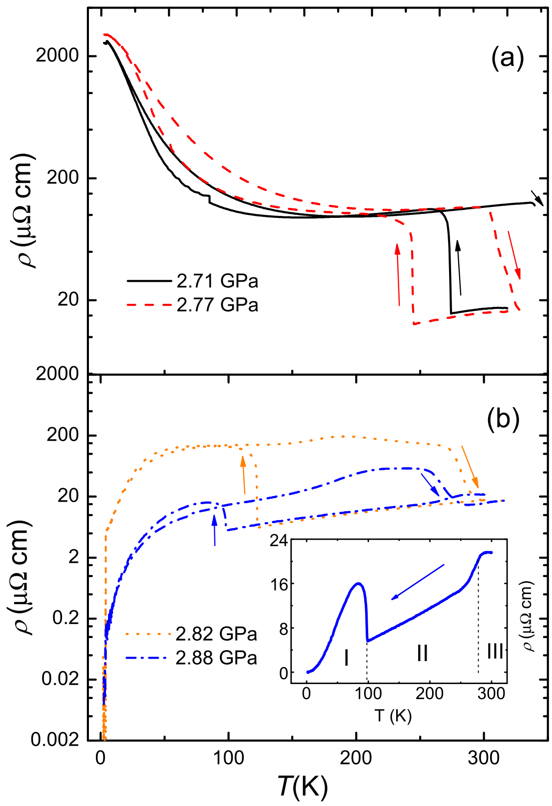

FIG. 2. (a) Temperature dependent resistivity of bismuth under 2.71 GPa (black solid line) and 2.77 GPa (red dashed line) on warming and cooling procedures. (b) Temperature dependent resistivity under 2.82 GPa (orange dot line) and 2.88 GPa (blue dot-dashed line) on warming and cooling procedures. The inset shows possible transitions from Bi-III to Bi-II and Bi-II to Bi-I.

transforms to Bi-II at about 2.55 GPa and Bi-II to Bi-III at about 2.70 GPa. Therefore we can probably regard Bi-II as the superconducting phase with $T_c = 3.92$ K, and Bi-III as the phase with $T_c = 7$ K, so the superconductivity induced by pressure is closely associated with structure transitions. As we can see, some other resistivity anomalies are also shown in the high temperature region under 2.63 GPa and 2.80 GPa. These anomalies may be related to the structural transitions of Bi, which is emphasized below.

In order to investigate the very sensitive pressure-induced structure transition among Bi-I, Bi-II, and Bi-III in the narrow pressure region (2.5–2.8 GPa), we have carried out detailed measurements of resistivity in the cooling down and warming up procedures under pressure, as shown in Fig. 2. The first transition marked here by a sudden rising of resistivity occurs at about 258 K under 2.71 GPa in the cooling down procedure, as shown in Fig. 2(a) by the black curve with an upward arrow. However in the warming up process, this transition shifts to about 320 K, which is barely seen in Fig. 2(a). When the pressure is increased to 2.77 GPa, the transition in the cooling down process moves to about 230.8 K, and it shifts to about 282.9 K in the warming up process, as shown by the red dashed lines. When pressure is further increased, the transition temperatures are generally suppressed to lower values. The data are shown, for examples, for the pressures at 2.82 GPa

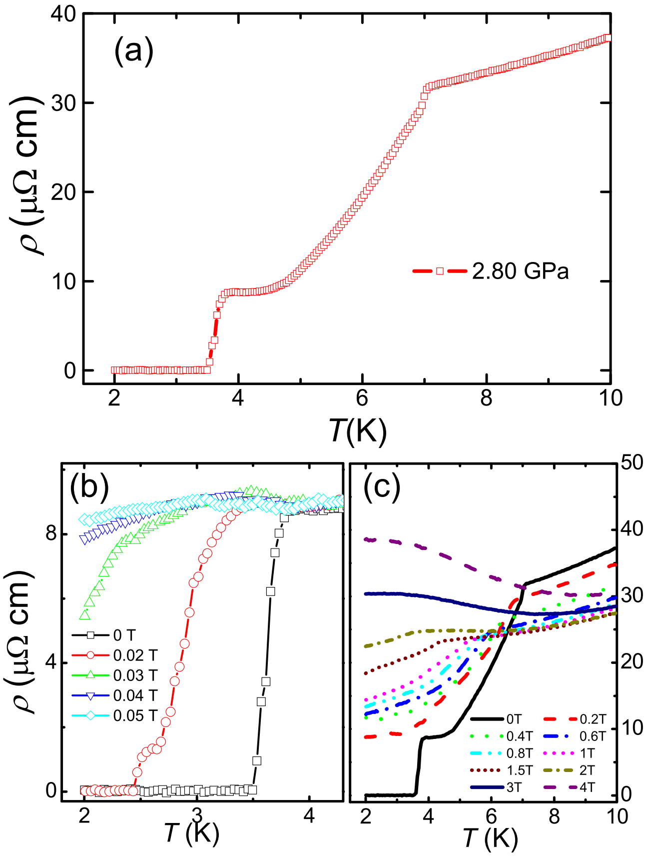

FIG. 3. (a) Enlarged view of the resistive transitions in the temperature range 2 K to 10 K under 2.8 GPa. Two superconducting transitions at 7 K and 3.9 K are clearly displayed. (b) and (c) The measured resistivity at various magnetic fields of phases Bi-II and Bi-III under 2.80 GPa.

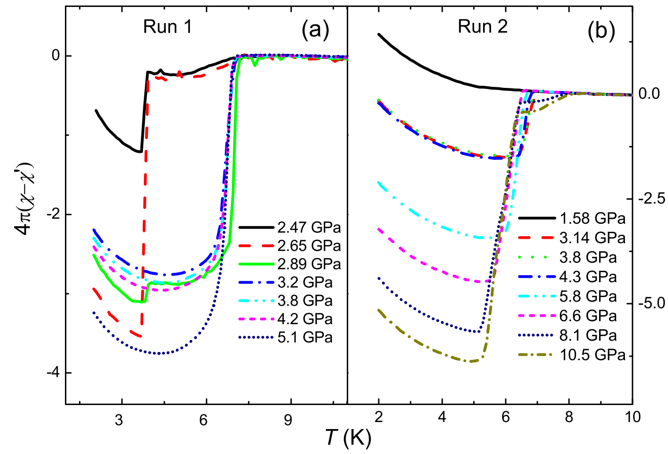

FIG. 4. Temperature dependence of zero-field-cooled (ZFC) magnetic susceptibility for Bi under pressures in two runs of measurements. (a) The measurements of run1 under pressures up to 5.1 GPa. Superconductivity first emerges at about 4 K under 2.47 GPa, then the sample totally transforms to the phase with $T_c = 7$ K under 3.2 GPa. (b) The measurements of run2 under pressures up to 10.5 GPa. A main superconducting transition occurs at about 7 K above 3.14 GPa, and another tiny diamagnetic fraction for the phase with $T_c = 8$ K shows up above 8.1 GPa. Due to the large magnetic background of DAC, we first subtract the background of the empty DAC, then we shift all curves to put the final value of magnetic susceptibility at 9 K to zero.

and 2.88 GPa in Fig. 2(b). The presence of large resistivity hysteresis versus temperature between cooling and warming procedures under a fixed pressure is clear and suggests this transition to be a first order transition. According to the structure phase diagram of bismuth [18], this transition may be the Bi-II to Bi-I phase transition when cooling the Bi-II phase to low temperature from room temperature. The transition temperatures of Bi-II to Bi-I is very sensitive to external pressures according to our measurements, and this is consistent with the steep slope of temperature versus pressure (T-P) phase boundary of Bi-II and Bi-I in Ref. [18]. When pressure is increased to 2.88 GPa, the Bi-II to Bi-I transition further moves to about 98 K on cooling, while another transition seems to occur at about 280 K as shown in the inset of Fig. 2(b). Due to the pressure limit of our experimental setup in the resistivity measurement, we cannot investigate this transition at higher pressures. But we suggest that this transition corresponds to Bi-III to Bi-II on cooling temperature. Similar resistivity behaviors were also reported in Ref. [19].

In Fig. 3(a), we plot the enlarged view of superconducting transitions at low temperatures at 2.80 GPa. Resistivity drops clearly at 7 K on the semimetallic background and then a sharp transition to zero resistivity occurs at 3.9 K. Both of these transitions are confirmed as superconducting transitions by magnetic measurements in the following sections. Then we measure the resistivity at different magnetic fields to obtain the upper critical fields of each phase. As shown in Fig. 3(b), the Bi-II phase has a quite low upper critical field. A field as low as 0.05 T can almost suppress the superconductivity completely above 2 K. In sharp contrast, the Bi-III phase has a much higher $\mu_0 H_{c2}$, as plotted in Fig. 3(c), although the T_c of Bi-III is only 1.79 times higher than that of Bi-II. With the suppression of superconductivity by external magnetic field, the resistivity shows an upturn behavior again in the low temperature region.

In Fig. 4(a), a sharp transition with a large diamagnetic signal can be clearly seen at 3.9 K under 2.47 GPa, which corresponds to the superconducting transition of phase Bi-II. Meanwhile, a transition with a tiny diamagnetic signal is also visible at about 7 K, which may reflect the superconducting transition corresponding to Bi-III. When we increase the pressure to 2.65 GPa, the diamagnetic volume of Bi-II becomes much larger than that of 2.47 GPa, while the diamagnetic volume of Bi-III phase almost keeps unchanged. Then, at 2.89 GPa, Bi-III becomes the dominant superconducting phase and the diamagnetic screening volume of Bi-II becomes smaller, comparing with that of Bi-III. For pressures from 3.2 GPa to 5.1 GPa, there only exists the Bi-III phase and the T_c slightly decreases with increasing pressure. In Fig. 4(b), we show another run of measurements with pressures up to 10.5 GPa. At 1.58 GPa, no superconducting transition can be seen, which is consistent with the resistivity measurements, while from 3.14 GPa to 6.6 GPa, the superconducting transition of Bi-III is shown and also the T_c slightly decreases with increasing pressure. When external pressure increases to 8.1 GPa, a superconducting phase with higher T_c (about 8 K) appears. Then its diamagnetic volume becomes larger

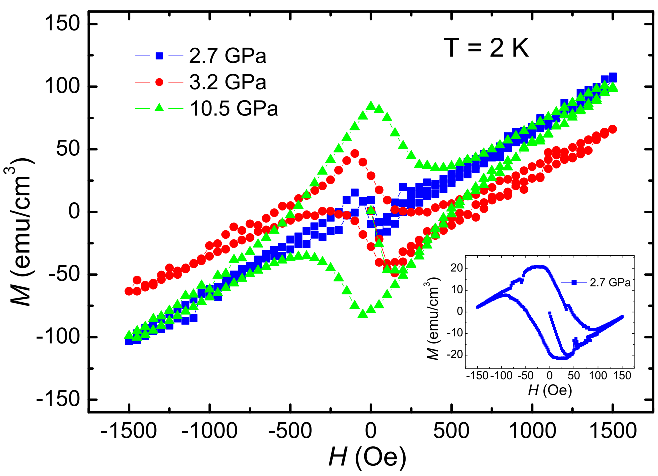

FIG. 5. Magnetization hysteresis loops (MHLs) at 2 K under pressures of 2.7 GPa (blue square), 3.2 GPa (red circle), and 10.5 GPa (green trigonal). The inset shows the MHL at 2.7 GPa measured in low magnetic field region considering the small value of upper critical field of phase Bi-II.

at 10.5 GPa and the T_c of this phase gets slightly enhanced. This phase may be recognized as the Bi-V phase. In order to show the superconductivity is bulk in nature, we present magnetization hysteresis loops (MHLs) in Fig. 5 under different pressures. Due to the quite low upper critical field of Bi-II, we further measured the MHLs in the low magnetic field region as shown in the inset of Fig. 5. MHLs clearly demonstrate the bulk superconductivity induced by pressure in bismuth. All of them show typical behaviors of type-II superconductors [20].

Next, we show the phase diagram of magnetic field versus temperature for Bi-II and Bi-III in Fig. 6. The H_{c2} curves are fitted with the simple formula for each phase [21] as follows

$$H_{c2}(T) = H_{c2}(0)\frac{[1-(T/T_c)^2]^\alpha}{[1+(T/T_c)^2]^\beta}. \quad (1)$$

We adopt this expression with two terms of $1-(T/T_c)^2$ and $1+(T/T_c)^2$ as components because they are the basic ingredients for the description of coherence length or upper

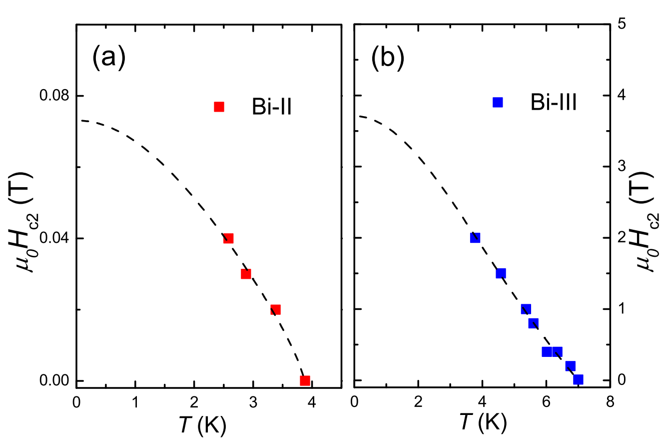

FIG. 6. $H(T)$ phase diagram for Bi-II (a) and Bi-III (b). The dashed black lines are fitting results by using Eq. (1).

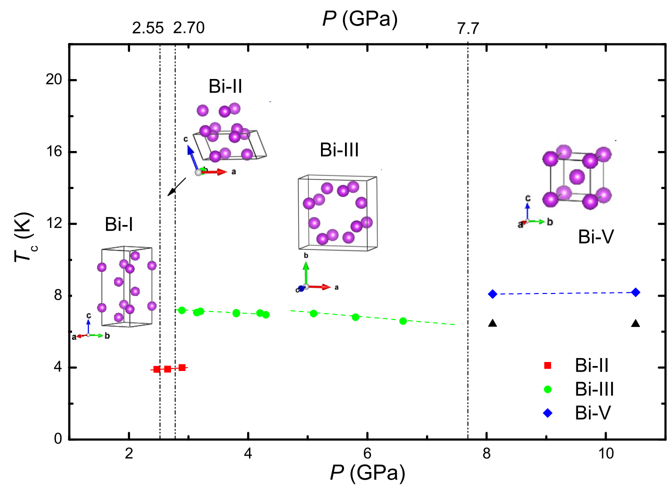

FIG. 7. Phase diagram of superconductivity in bismuth under pressures. Schematic pictures indicate the different crystal structures of Bi under pressures. The Bi-V phase with T_c of about 8 K emerges at about 8.1 GPa. The superconducting transitions above 8.1 GPa (black triangle) may come from the mixture of Bi-III and BI-V phases. The vertical dashed lines are roughly corresponding to the critical pressures of the three sequential structure transitions of Bi under pressures. The Bi-IV phase occurs above the temperature of 450 K, and therefore it is not shown in the phase diagram. The colored dashed lines are guidelines for the variation of T_c for each phase. Note the real area for Bi-II occupies only a small region from 2.55 to 2.7 GPa.

critical field. According to Ginzburg-Landau theory, $\alpha = \beta = 1$. We thus fit our data with this general formula. The obtained α and β values are 0.79 and 0.47 for Bi-II, 0.99 and 1.04 for Bi-III, respectively. The fitting curves are indicated by the black dashed lines in Fig. 6. As we can see, Bi-II has a very low upper critical field of about 0.073 T. This low upper critical field is similar to some other superconducting elements like tin (3.72 K, 0.0308 T), indium (3.40 K, 0.0286 T), and tantalum (4.48 K, 0.083 T) [22]. Comparing to the Bi-II phase, Bi-III has a much larger $\mu_0H_{c2}(0)$ of about 3.71 T as shown in Fig. 6(b). For type-II superconductors in the dirty limit, $H_{c2}(0)$ could also be given by $H_{c2}(0) = 0.691 \times \frac{dH_{c2}}{dT}|_{T_c} \times T_c$ [23,24]. According to this formula, the obtained $\mu_0H_{c2}(0)$ for Bi-II is about 0.103 T and 4.56 T for Bi-III, respectively. These calculated data are both larger than our previous fitting results. It remains to be understood why the Bi-II and Bi-III phases have such different upper critical fields.

The experimental results have been checked and the general behaviors are similar. In Fig. 7, we plot the phase diagram of superconductivity in bismuth under pressures. Bi starts to become superconductive with T_c of about 3.9 K by compressing it to about 2.5 GPa, accompanying with a structure transformation from Bi-I to Bi-II. Then, with increasing pressure slightly, Bi-II transforms to Bi-III under 2.8 GPa at room temperature. Bi-III also shows superconductivity at about 7 K, and T_c displays a small negative slope versus pressure. In the pressure range from 2.47 GPa to 2.89 GPa, Bi-II and Bi-III coexist, as shown by our magnetization measurements. Previous research on compressibility and resistometric measurements show that Bi has two further structure transitions, within the pressure range of Bi-III from 2.70 GPa to 7.7 GPa [25–27], while the recent high energy synchrotron radiation and x-ray absorption fine structure (XAFS) measurements have failed to observe these transitions [11,18,28,29]. Due to the precise structures determined by x-ray diffraction results, we adopt the phase diagram of structure versus pressure as described in Ref. [11]. By increasing pressure up to 8.1 GPa, the Bi-V phase emerges with superconducting transition temperature at about 8.1 K. We must mention that the two superconducting transitions on one curve with the pressure around 2.8 GPa and above 8.1 GPa may come from pressure inhomogeneity, which leads to the coexistence of two phases. This may be different from Bi nanowires which also show two superconducting transitions [8]. As shown in Fig. 7, the behavior of two superconducting transitions on one curve occurs near the critical pressure of two phase boundaries. Thus, the two superconducting transition phenomenon results from the possible mixture or coexistence of two phases with different structures at low temperatures. Overall, our work can explicitly show three superconducting phases with distinct transition temperatures. This will stimulate further studies on the interesting multiband system bismuth.

IV. SUMMARY

In summary, we have systematically investigated superconductivity in bismuth by applying high pressures. Resistivity under pressures up to 2.80 GPa reveals that the Bi-I phase has a semimetal to semiconductor transition under pressure and also confirms the superconductivity of Bi-II ($T_c = 3.9$ K) and Bi-III ($T_c = 7$ K). Resistivity under different magnetic fields were measured for Bi-II and Bi-III. By fitting the H_{c2} data with an empirical model, the $\mu_0 H_{c2}(0)$ for Bi-II and Bi-III are about 0.073 T and 3.71 T, respectively, which are slightly smaller than those determined by the WHH theory. Magnetic susceptibility measurements give consistent transition temperatures as the resistivity measurements for Bi-II and Bi-III. Beside the superconductivity from Bi-II and Bi-III under low pressures, the Bi-V phase also emerges with T_c of about 8 K at 8.1 GPa. Finally, we present the phase diagram of T_c versus pressure of Bi and relate it with the sequential structure transitions.

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