Pressure-induced superconductivity in $\text{Ag}_x\text{Bi}_{2-x}\text{Se}_3$  
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We investigated the pressure dependence of electric transport and crystal structure of $\text{Ag}$-doped $\text{Bi}_2\text{Se}_3$. In the sample prepared by $\text{Ag}$ doping of $\text{Bi}_2\text{Se}_3$, the Bi atom was partially replaced by $\text{Ag}$, i.e., $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$. X-ray diffraction patterns of $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$ measured at 0–30 GPa showed three different structural phases, with rhombohedral, monoclinic, and tetragonal structures forming in turn as pressure increased, and structural phase transitions at 8.8 and 24 GPa. $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$ showed no superconductivity down to 2.0 K at 0 GPa, but under pressure, superconductivity suddenly appeared at 11 GPa. The magnetic field ($H$) dependence of the superconducting transition temperature $T_c$ was measured at 11 and 20.5 GPa, in order to investigate whether the pressure-induced superconducting phase is explained by either $p$-wave polar model or $s$-wave model.  

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I. INTRODUCTION  
Topological insulators have been extensively studied in the past decade, because of their exciting electronic properties and possible application in electronics [1–15]. A topological insulator is a quantum matter, with a band gap in its bulk structure and gapless states at its surface. These electronic states are completely protected by time-reversal symmetry. Thus, a topological insulator is topologically different from a traditional insulator. The most studied topological insulator is $\text{Bi}_2\text{Se}_3$, which has a single Dirac cone [6]. The transport properties of $\text{Bi}_2\text{Se}_3$ suggest that its Fermi level does not cross the surface states but a conduction band [9–11], i.e., electrical transport shows metallic behavior in $\text{Bi}_2\text{Se}_3$. This is due to a deficiency of Se atoms, providing electrons to shift the Fermi level upward. The angle-resolved photoemission spectrum (ARPES) clearly shows the crossing of the Fermi level to the conduction band of $\text{Bi}_2\text{Se}_3$ [10,11]. To lower the Fermi level to match the Dirac point, $\text{Ca}$ doping of $\text{Bi}_2\text{Se}_3$ was performed, and the resistivity, scanning tunneling spectroscopy, and ARPES measurements showed the complete crossing of the Fermi level to the Dirac point [12,13]. $\text{Ca}$ atoms are substituted for Bi atoms to donate holes. Such a Fermi level tuning was also achieved by adjusting the value of $x$ in $\text{Bi}_{2-x}\text{Sr}_x\text{Te}_{2-y}\text{Se}_y$ [14,15].  
The first discovery of superconductivity in a topological insulator was achieved in Cu-doped $\text{Bi}_2\text{Se}_3$, providing a superconducting transition temperature $T_c$ as high as 3.8 K [16]. Here, it should be noted that the Cu atom is not substituted for Bi but is intercalated into the space between two $\text{Bi}_2\text{Se}_3$ layers with different orientations, which indicates electron donation to the $\text{Bi}_2\text{Se}_3$ layers. Subsequently, Sr doping of $\text{Bi}_2\text{Se}_3$, $\text{Sr}_{0.05}\text{Bi}_2\text{Se}_3$, led to superconductivity, with $T_c$ as high as 2.5 K [17]. Here it is reported that the Sr atom is intercalated into the space between layers, indicating electron doping of the $\text{Bi}_2\text{Se}_3$ layer. Furthermore, applying pressure to $\text{Sr}_{0.05}\text{Bi}_2\text{Se}_3$ provides superconductivity with a $T_c$ of 8.3 K at 14 GPa [18]. The application of pressure to $\text{Sr}_{0.05}\text{Bi}_2\text{Se}_3$ yielded three different superconducting phases: (1) The $T_c$ rapidly decreased with an increase in pressure up to 1 GPa. (2) A $T_c$ of 4 K emerged at 6 GPa, and slowly decreased up to 12 GPa. (3) A $T_c$ of 8.3 K was suddenly observed at 14 GPa, and it slowly decreased with increasing pressure up to 80 GPa, although the $T_c$ was still above 7 K at 80 GPa. The emergence of three superconducting phases in $\text{Sr}_{0.05}\text{Bi}_2\text{Se}_3$ may be closely related to that of three crystal phases. This superconductivity was assigned to a $p$-wave coupling. Pressure applied to nondoped $\text{Bi}_2\text{Se}_3$ also produced superconductivity, although no superconductivity was observed at ambient pressure [19]. The superconductivity emerged at 12 GPa, and the $T_c$ was 4.4 K. The $T_c$ rapidly increased with increasing pressure up to 17.2 GPa, reaching a maximum $T_c$ of 8.2 K. Further application of pressure up to 24 GPa resulted in a lowering of $T_c$, which remained constant at 24–32 GPa. This behavior is different from that of Sr-doped $\text{Bi}_2\text{Se}_3$. Furthermore, it was found that Nb doping of $\text{Bi}_2\text{Se}_3$ produced superconductivity with a $T_c$ as high as 3.2 K [20].
Here we report the preparation and characterization of Ag-doped Bi$_2$Se$_3$, and the pressure dependence of its crystal structure and transport properties. As described later, the Ag-doped Bi$_2$Se$_3$ is written as Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$, because the Ag was not intercalated into the Bi$_2$Se$_3$ lattice, but substituted for Bi atoms. Therefore, hole doping should be probably achieved for Bi$_2$Se$_3$, although not in Sr$_{0.05}$Bi$_2$Se$_3$ and Cu$_x$Bi$_2$Se$_3$, which correspond to electron-doped Bi$_2$Se$_3$ [16,17]. Based on this background, we strongly intended to induce superconductivity in hole-doped Bi$_2$Se$_3$ (or Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$) by applying pressure. If this could be achieved, it would be the first observation of superconductivity in hole-doped Bi$_2$Se$_3$ (i.e., the Fermi level of Bi$_2$Se$_3$ is downward tuned).

In this study, the pressure dependence of the crystal structure was determined from pressure-dependent powder x-ray diffraction (XRD) patterns at 0–30 GPa. Moreover, measurement of electric transport at 0–26 GPa showed the emergence of pressure-driven superconductivity at 11 GPa, and the maximum $T_c$ of 7 K was confirmed at 17 GPa. The pressure dependence of $T_c$ was significantly different from that of nondoped Bi$_2$Se$_3$ [19], and was similar to that of Sr$_{0.05}$Bi$_2$Se$_3$ [18]. The superconductivity was fully investigated from the magnetic field ($H$) dependence of $T_c$ at 11 and 20.5 GPa.

II. EXPERIMENTAL PROCEDURE AND CHARACTERIZATION

Crystals of Ag-doped Bi$_2$Se$_3$, Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$, were grown by a conventional melt-growth method using stoichiometric amounts of Ag, Bi, and Se powders. The detailed process was as follows: the powders were sealed in a quartz tube which was heated at 800°C for 12 h, then slowly cooled down to 650°C at the rate of 30°C/h, and then quenched with ice water. The obtained crystals showed a clear basal plane structure. An optical image of a crystal-like Ag$_{0.05}$Bi$_2$Se$_3$ lump is shown in Fig. 1(a).

The energy-dispersive x-ray spectroscopy (EDX) spectrum of the Ag$_{0.05}$Bi$_2$Se$_3$ lump (not shown) was recorded with an EDX spectrometer equipped with a scanning electron microscope (KEYENCE VE-9800-EDAX Genesis X2M). The EDX spectra were measured for five different positions of the Ag$_{0.05}$Bi$_2$Se$_3$ lump at room temperature. From the EDX spectra, the chemical composition of the Ag$_{0.05}$Bi$_2$Se$_3$ sample was determined to be Ag$_{0.069(7)}$Bi$_{2.944(8)}$Se$_{3.448}$, in which the quantity of Bi was adjusted to 2, showing the presence of Ag in this crystal. Since the deviation of stoichiometry for Se is a little large, this problem is discussed later.

The crystal structure was determined by single-crystal XRD measurement of the Ag$_{0.05}$Bi$_2$Se$_3$ crystal, which was obtained by cutting off a small piece (~100-μm scale) of the lump of Ag$_{0.05}$Bi$_2$Se$_3$, and using a Rigaku Saturn 724 diffractometer equipped with a Mo Kα source (wavelength $λ$ = 0.71073 Å); the measurement was performed at 100 K. The crystal structure was rhombohedral (space group: R$ar{3}$m) which is consistent with that of Bi$_2$Se$_3$ [21]. The lattice constants $a$ and $c$ were determined to be 4.146(6) and 28.66(4) Å, respectively, which are close to those of Bi$_2$Se$_3$ (4.18 and 28.7 Å) [21]. Admittedly, the $c$ values are not so expanded in Cu$_x$Bi$_2$Se$_3$ ($c$ = 28.736(1) Å [16]) and Sr$_x$Bi$_2$Se$_3$ ($c$ = 28.598 Å [17]) in which Cu and Sr are intercalated into the space between Bi$_2$Se$_3$ layers. The $c$ value [32.66(4) Å] of Ag-doped Bi$_2$Se$_3$ is an intermediate value between the $c$ values of Cu$_x$Bi$_2$Se$_3$ and Sr$_x$Bi$_2$Se$_3$. In any case, it is difficult to identify whether Ag is intercalated or substituted for Bi from the lattice constant $c$. A refined view of the crystal structure shows that no Ag atoms appear in any location other than the 6c and 3a sites, indicating that the Ag atom may not be intercalated, i.e., the chemical composition can be expressed as Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$. The structural information is fully described elsewhere [22].

Finally, a multiple-energy x-ray fluorescence hologram around a Ag atom in the Ag$_{0.05}$Bi$_2$Se$_3$ was measured at BL13XU of SPring-8. Ag Kα fluorescent x rays (22.16 keV) were collected using an avalanche photodiode detector via a cylindrical graphite crystal energy analyzer, at 11 different incident x-ray energies from 26.0 to 31.0 keV in steps of 0.5 keV. Experimental details are given elsewhere [23]. Figure 1(b) shows a real image of the local structure around a Ag atom, reconstructed from an x-ray fluorescence hologram of the Ag$_{0.05}$Bi$_2$Se$_3$ crystal using the Barton multiple-energy reconstruction algorithm [24]. This image suggests that the Ag atom is surrounded by six Bi atoms in a hexagonal arrangement, indicating that Ag is partially substituted for Bi. The chemical composition can be expressed as Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$. It would be written as Ag$_{0.059(7)}$Bi$_{1.941(4)}$Se$_{3.448(8)}$ if using the EDX's result. The stoichiometry of Se, 3.44(8), deviates from the nominal value of Se, 3.0. We further evaluated the stoichiometry from the EDX spectra measured for six Ag$_{0.05}$Bi$_2$Se$_3$ single crystals prepared in the same experimental conditions, including the above single crystal. The averaged stoichiometry was expressed as Ag$_{0.092}$Bi$_{1.91}$Se$_{3.16}$ (=Ag$_{0.092}$Bi$_2$Se$_{3.26}$). The averaged value of Se’s stoichiometry evaluated from single crystals is closer to 3.0 than the value evaluated for one selected single crystal described above. Actually, the estimated standard deviation is a little large, and it is unclear whether the Se is deficient or excessive in comparison with the nominal value 3.0. Thus, the stoichiometry of Se is a little scattered around 3.0 depending on the used crystals.

Therefore, we employ the EDX data only to confirm that Ag is contained in the crystal. Consequently, the sample’s chemical formula is written as Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$ throughout this paper by considering the substitution of Bi with Ag, and the scattering of stoichiometry of Se around 3.0 depending on crystals. The partial substitution of Bi with Ag indicates a possible hole doping in Ag$_{0.05}$Bi$_2$Se$_3$-Se$_3$, i.e., the Fermi level of Bi$_2$Se$_3$ is downward tuned. The drastic change of transport property in Ag$_{0.05}$Bi$_2$Se$_3$ with respect to that in Bi$_2$Se$_3$ also suggests a hole doping [22]. Namely, the transport property of Ag$_{0.05}$Bi$_2$Se$_3$ showed an insulating behavior at high temperature range, in contrast to a metallic one of Bi$_2$Se$_3$, which was reasonably explained by a downward shift of the Fermi level caused by hole doping.

Powder XRD patterns of the Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$ sample were measured under pressure at 297 K, using synchrotron radiation at BL12B2 of SPring-8; the wavelength $λ$ of the x-ray beam was 0.6889 Å. The powder sample obtained by grinding the Ag$_{0.05}$Bi$_1$$_{0.95}$Se$_3$ lump was used for the powder XRD measurement. A diamond-anvil cell (DAC) was used for the high-pressure XRD measurement, with the powder sample
FIG. 1. (a) Optical image of a crystal-like lump of $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$. (b) Real-space image of the local structure around a Ag atom in $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$ reconstructed from the x-ray fluorescence hologram. The Ag atom is at the origin of this image. (c) Crystal structure of $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$, determined from single-crystal x-ray diffraction analysis at 0 GPa.

III. RESULTS AND DISCUSSION

Figure 1(c) shows the crystal structure of $\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3$ as determined from single-crystal x-ray diffraction analysis at...
0 GPa. The crystal lattice consisted of two asymmetry units \((2 \times \text{Bi}_2\text{Se}_3)\), showing two-dimensional crystal structure. Figure 2(a) shows the XRD patterns at 0–30 GPa, which indicate clear structural phase transitions at 8.8 and 24 GPa. By analogy with the structural transitions of \(\text{Sr}_{0.065}\text{Bi}_2\text{Se}_3\) [18], the first structure below 8.8 GPa was assigned to a rhombohedral structure [space group: \(\text{R}3\text{~m} (\text{No.} \ 166)\)], while the second structure at \(8.8 \geq p \geq 21\) GPa and the third structure above 21 GPa were assigned, respectively, to monoclinic [space group: \(\text{C}2/m\) (No. 12)] and tetragonal structures [space group: \(\text{I}4/\text{mmm}\) (No. 139)]. The pressures driving structural transitions were almost the same as those, 8.1 and 25 GPa, for \(\text{Sr}_{0.065}\text{Bi}_2\text{Se}_3\). The first, second, and third structures are called phase I, phase II, and phase III, respectively. As seen from Fig. 2(a), small XRD peaks due to phase I are still found in addition to those of phase II at \(p = 8.8–11\) GPa, but the peaks due to phase I substantially disappear above 11 GPa. On the other hand, the peaks due to phase II are observed together with those due to phase III at \(p \geq 24\) GPa, although the intensity of the phase II peaks diminishes with pressure; the volume fractions of phase II and phase III were not determined in the pressure range, but the phase II drastically decreased when increasing pressure above 24 GPa. A similar pattern of behavior is also found in \(\text{Sr}_{0.065}\text{Bi}_2\text{Se}_3\) [18], i.e., the phase transition is not very sharp as pressure changes, but a bit broad.

Le Bail fitting was achieved for the XRD patterns of \(\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3\) by assuming the above crystal structures at each pressure. The lattice constants were determined by Le Bail fitting as follows. Lattice constants \(a\) and \(c\) at 0.18 GPa (\(\text{R}3\text{~m}\)) were 4.1420(1) and 28.612(3) Å, respectively. Constants \(a, b,\) and \(c,\) and \(\beta\) at 13 GPa (\(\text{C}2/m\)) were 13.637(1), 3.9252(6), and \(16.251(3)\) Å, and 148.874(4)°, respectively. Furthermore, \(a\) and \(c\) at 30 GPa (\(\text{I}4/\text{mmm}\)) were 3.4611(4) and 16.628(2) Å, respectively. Figures 2(b) and 2(c) show the pressure dependence of lattice constants and volume per one \(\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3\). As seen in Fig. 2(c), a discontinuous change of volume is observed at 8.8 and 24 GPa, indicating the first-order phase transition. To be exact, as seen from Fig. 2(c), the transition at 24 GPa may not be so sharp, i.e., the \(V\) of phase II approaches that of phase III at around 26 GPa. Thus, \(\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3\) shows pressure-induced multiple structural phase transitions as pressure varies from 0 to 30 GPa.

The \(M/H-T\) plot of \(\text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3\) at 0 GPa (not shown) did not show any superconducting transition down to 2.5 K,
implying that Ag$_{0.05}$Bi$_{1.95}$Se$_3$ is not a superconductor at 0 GPa. The $R$-$T$ plots of Ag$_{0.05}$Bi$_{1.95}$Se$_3$ at 0–6.4 GPa show no drop in $R$ even at low temperature [Fig. 3(a)], indicating no superconducting transition. On the other hand, a slight drop in $R$ was observed at 11 GPa [inset of Fig. 3(a)], indicating the emergence of a superconducting transition. The $T_c$ was 5.5 K at 11 GPa. To confirm that the drop was due to a superconducting transition, the $H$ dependence of the $R$-$T$ plot was investigated at 11 GPa from 0.0 to 2.5 T. It was seen that the $R$ drop was suppressed with $H$, and the $T_c$ decreased gradually [Fig. 3(b)]. With increasing pressure, the $R$ drop became clearer, as seen from Figs. 3(c)–3(e). The minimum $R$ below $T_c$ approached
FIG. 4. (a) Pressure dependence of $T_c$ in Ag$_{0.05}$Bi$_{1.95}$Se$_3$ ($T_c$–$p$ phase diagram). $h^*(t)$–$t$ plots of the superconducting phases in Ag$_{0.05}$Bi$_{1.95}$Se$_3$ at (b) 11 and (c) 20.5 GPa. The solid and dashed lines refer to the theoretical $h^*(t)$–$t$ curves ($s$-wave and $p$-wave model), respectively [see (b) and (c)].

zero. Furthermore, two step $R$ drops were observed in the pressure range of 17 to 24 GPa, and only a single drop was found above 24 GPa [see Fig. 3(e)]. The $H$ dependence of the $R$–$T$ plot was investigated at 20.5 GPa [Fig. 3(d)], and shows that the $R$ drop is suppressed with $H$, and the $T_c$ decreases gradually. Thus, it has been confirmed that the $R$ drop can be confidently assigned to a superconducting transition, a result that provides an observation of superconductivity in hole-doped Bi$_2$Se$_3$. The analyses of $R$–$T$ plots did not lead to consideration of the small drop of $R$ observed below 3.0 K, because of the possibility of a superconducting transition of rhenium showing the $T_c \leq 3.3$ K at 0–20 GPa, which was used inside of DAC, although no contact between electrodes and rhenium was confirmed at any pressure.

The absolute $R$ above $T_c$ (normal state) increased with increasing pressure up to 11 GPa, but it showed a complex change against pressure above 11 GPa as follows: (1) The $R$ value in the normal state suddenly decreased at 15 GPa, and gradually increased up to 20.5 GPa. (2) The $R$ value suddenly decreased at 21 GPa, and then it rapidly increased against pressure above 21 GPa. Aside from the behavior of the $R$ value at 21 GPa, the $R$ value in the normal state increases with increasing pressure above 11 GPa. At the present stage, such a complex change cannot be well explained, i.e., we cannot say clearly whether it is owing to an intrinsic behavior or a variation of experimental condition such as contact. Therefore, in this study we will comment on only a superconducting transition shown in $R$–$T$ plots (Fig. 3), because it can be unambiguously and exactly explored.

Figure 4(a) shows the pressure dependence of the $T_c$ of Ag$_{0.05}$Bi$_{1.95}$Se$_3$ which was determined from the $R$–$T$ plots shown in Figs. 3(a), 3(c), and 3(e). As seen in Fig. 4(a), superconductivity emerged in phase II, and no superconductivity is observed in phase I. Two superconducting phases (high-$T_c$ and low-$T_c$ phases) are observed at 17–24 GPa which is still in phase II categorized from XRD patterns. The high-$T_c$ phase
shows \( T_c \sim 7 \) K, while the low-\( T_c \) phase shows \( 3.6 \leq T_c \leq 5.5 \) K. The low-\( T_c \) phase completely disappeared in phase III. This behavior is similar to that of \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \), providing two superconducting phases in phase II [18]. However, two superconducting phases did not coexist in \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \), unlike in \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \).

Here, we suggest the scenario that a slow variation from phase II relating to low-\( T_c \) superconductivity to phase III relating to high-\( T_c \) superconductivity takes place before the structural transition of phase II to phase III is observed above 23 GPa. Namely, phase III may extend gradually from 17 GPa, suggesting that phase III is filamentary formed above 17 GPa before the formation of bulk phase III above 23 GPa. Although phase II is still observed above 23 GPa in the XRD pattern, a drastic decrease in phase II makes it difficult to detect the low-\( T_c \) phase above 23 GPa.

The behavior of \( T_c \) with pressure in \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) is significantly different from that in \( \text{Bi}_2\text{Se}_3 \) where only a single superconducting phase was observed above 10 GPa [19]. Precisely stated, the \( T_c \) of \( \text{Bi}_2\text{Se}_3 \) increases continuously up to 17.2 GPa, then decreases up to 20 GPa, and finally becomes constant above 24 GPa. Thus, the pressure dependence of \( T_c \) in \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) does not show similarity to \( \text{Bi}_2\text{Se}_3 \) but to \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \). Here, we must stress that the pressure-driven superconductivity in \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) relates closely to the structural phase transitions. Therefore, the electronic properties in phase II and phase III, where different superconducting phases emerge, must be clarified from the pressure-dependent Hall-effect and x-ray emission spectroscopy as well as theoretical calculation; we do not have any calculation supporting that the monoclinic and tetragonal phases of Ag-doped \( \text{Bi}_2\text{Se}_3 \) are topological materials. These works are now in progress.

Finally, we must consider whether this superconductivity should be categorized as "unconventional superconductivity" (or "topological superconductivity"). The previous study of the temperature dependence of the upper critical field, \( H_{c2} \), of \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \) showed that the superconductivity may originate in spin-triplet \( p \)-wave coupling [18]. In this study, the values of the reduced critical field, \( h^*(T) = \frac{H_{c2}(T)}{H_{c2}(0)} \), of \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) at 11 and 20.5 GPa were plotted as a function of \( t = T/T_c \) (Figs. 4(b) and 4(c)). The \( h^*(t)−t \) plot shown in Fig. 4(b) reflects the low-\( T_c \) phase observed at 11 GPa since the \( T_c \) and \( H_{c2} \) are obtained from the \( R \) drop, as shown in Fig. 3(b). As seen from Fig. 4(b), the observed \( h^*(t) \) value may not converge to 0.69 at \( t = 0 \), the value which is expected from the Werthamer-Helfand-Hohenberg theory, which refers to the \( s \)-wave dirty-limit superconductivity [25–27]. This behavior is the same as that of \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \) [18]. The \( h^*(0) \) value should become 0.80–0.85 for the \( p \)-wave polar model [18,26,28,29]. The observed \( h^*(t)−t \) plot [Fig. 4(b)] shows a linear relationship which may follow the \( p \)-wave model [see Fig. 4(b)]. However, the theoretical curve of \( s \)-wave clean limit may also follow the experimental \( h^*−t \) plot. As a consequence, the pressure-induced superconducting phase of \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) at 11 GPa may not definitely be identified to be an unconventional superconductor that follows the \( p \)-wave polar model, although the \( h^*−t \) plot of \( \text{Sr}_{0.065}\text{Bi}_2\text{Se}_3 \) at 19.5 GPa was followed by the above model [18]. Actually, the number of data points is insufficient for a complete identification of \( p \)-wave model for the pressure-induced superconducting phase of \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) at 11 GPa. In addition, the pressure-induced superconductivity of nondoped \( \text{Bi}_2\text{Se}_3 \) can also be classified as a topological superconductor from the \( h^*(t)−t \) plot [29]. Thus, we must obtain \( h^*(t) \) values in a wider \( t \) range to finally determine whether the pressure-induced superconductivity in Ag-doped \( \text{Bi}_2\text{Se}_3 \) is explained by the \( p \)-wave polar model, in the same manner as \( \text{Bi}_2\text{Se}_3 \) [29] and Sr doped \( \text{Bi}_2\text{Se}_3 \) [18].

The \( h^*(t)−t \) plot for the high-\( T_c \) phase of \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) found at 20.5 GPa is shown in Fig. 4(c); the \( T_c \) and \( H_{c2} \) are obtained from the \( R \) drop due to the high-\( T_c \) phase shown in Fig. 3(d). As seen from Fig. 4(c), it is unclear whether the observed \( h^*(t) \) values are followed by the \( p \)-wave model, because of insufficient \( h^* \) value against \( t \). Thus, the pressure-induced superconducting phase (high-\( T_c \) phase: \( T_c \sim 7 \) K) of \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) at 20.5 GPa should also be more carefully investigated, in the same manner as the superconducting phase at 11 GPa [Fig. 4(b)].

IV. CONCLUSIONS AND OUTLOOK

Two pressure-driven superconducting phases were found in \( \text{Ag}_{0.05}\text{Bi}_{1.95}\text{Se}_3 \) at \( p \geq 11 \) GPa where two crystal phases (phase II and phase III) appeared. The low-\( T_c \) superconducting phase (\( T_c = 5.5 \) K) appeared at 11 GPa, and its \( T_c \) value decreased gradually with increasing pressure up to 15 GPa; the \( T_c \) value in the low-\( T_c \) phase became 3.6 K at 15 GPa and it did not vary up to 24 GPa. The high-\( T_c \) superconducting phase (\( T_c = 7 \) K) emerged suddenly at 17 GPa, and it did not change up to 26 GPa. The low-\( T_c \) and high-\( T_c \) phases coexisted up to 24 GPa. Above 24 GPa, only a high-\( T_c \) phase was observed. To sum up, the superconductivity in Ag-doped \( \text{Bi}_2\text{Se}_3 \) is superconductivity realized in hole-doped \( \text{Bi}_2\text{Se}_3 \), in which the Fermi level should be moved downward from the conduction band; the Fermi level of nondoped \( \text{Bi}_2\text{Se}_3 \) crosses the conduction band [9–11].

We could not definitely conclude whether the superconducting phases observed at 11 and 20.5 GPa can be categorized as unconventional topological superconductor which follows \( p \)-wave polar model, because of insufficient \( h^*−t \) plot. Nevertheless, this study may provide this research field with a useful starting point for studying topological superconductivity, as well as pressure-driven superconductivity. The mechanism of pressure-induced superconductivity in \( \text{Ag}_x\text{Bi}_{2−x}\text{Se}_3 \) must be further pursued.

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