Charge-density-wave superconductor Bi$_2$Rh$_3$Se$_2$
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(Received 12 January 2007; published 16 February 2007)

We discovered a superconducting transition with the charge-density-wave state in a ternary compound Bi$_2$Rh$_3$Se$_2$. This compound crystallizes in the parkerite-type structure composed of sheets containing one-dimensional Rh-Rh chains. The electrical resistivity, magnetic susceptibility, thermoelectric power, sample length change, and x-ray diffraction measurements reveal that this compound is in the CDW state below 240 K. Furthermore, the specific heat and electrical resistivity measurements show a superconducting transition at ~0.7 K. The various superconducting parameters were determined, and the GL parameter κ(0) shows the considerably large value of 151 indicating an extreme type-II superconductor.

DOI: 10.1103/PhysRevB.75.060503 PACS number(s): 74.70.Dd, 72.15.Eb, 74.25.Fy

Collective states showing exotic electronic properties, such as superconductivity and charge-density-wave (CDW), have attracted a lot of interest. Peierls pointed out in his book that an electron-phonon interaction resulted in periodic and dielectric lattice distortions with a phase transition from metallic to insulating conductivity. At the same time, Fröhlich suggested a sliding of the collective state involving lattice displacements and electrons in the one-dimensional metal as a mechanism of superconductivity. His concept had been forgotten by an appearance of the Bardeen-Cooper-Schrieffer (BCS) theory but has revived in researches on the CDW state in one-dimensional conductors. The CDW state with such lattice distortions competes with a superconducting state because of the dielectric gapping of Fermi surface.

Recently, Gabovich and co-workers reviewed the properties of superconductors with CDW and discussed the competition between the CDW and superconducting states. Most of the CDW superconductivities were found in compounds with the well-known crystal structures; i.e., layered chalcogenides, NbSe$_3$, A15-, and C15-type intermetallic compounds, and so on. In these compounds, partial dielectric gapping causes a detrimental effect on superconductivity.

In this study, we have synthesized successfully a novel ternary compound Bi$_2$Rh$_3$Se$_2$ and have investigated its crystal structure and transport properties. This compound is found to crystallize in a parkerite-type structure composed of sheets containing one-dimensional Rh-Rh chains. In metal-rich chalcogenides, a superconducting transition with the CDW state was first discovered through the electrical resistivity, magnetic susceptibility, specific heat, thermoelectric power, sample length change, and x-ray diffraction measurements.

A polycrystalline Bi$_2$Rh$_3$Se$_2$ was prepared by mixing Bi, Rh, and Se in the stoichiometric ratio and heating in a silica tube at 1320 K for 6 h. It was cooled slowly (2 K/h) to 1020 K, and then quenched. Unfortunately, we could not obtain products for a single crystal structure analysis because of formation of twin or much more crystals. Thus, the crystal structure of the obtained product was identified by powder x-ray diffraction measurements (Rigaku RINT 2000 diffractometer) between 30 and 300 K. Magnetic susceptibilities were measured from 1.8 to 400 K in an applied field of 1 T using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5S). Electrical resistivity measurements were carried out in the temperature range of 0.35–400 K and in magnetic fields up to 1.5 T by a four-probe method in a Quantum Design PPMS equipped with a $^3$He refrigerator. Specific heat measurement was performed from 0.35 to 300 K by the thermal relaxation method with the PPMS. The thermoelectric power (TEP) was measured in the temperature range between 10 and 300 K by a differential method. The sample length change was measured by using strain gauges from 5 to 300 K. The copper expansivities were used to convert the experimental relative length changes to the absolute values.

The x-ray diffraction measurement at room temperature reveals that the obtained product crystallizes in a parkerite-type structure as a single phase. By the Rietveld analysis using RIETAN2000, the lattice parameters were determined to be $a=11.414(10)$ Å, $b=8.3709(9)$ Å, $c=11.989(1)$ Å, $\beta=89.153(3)^{\circ}$ (reliable factors; $R_p=12.9\%$, $R_f=4.2\%$).

The schematic crystal structure of Bi$_2$Rh$_3$Se$_2$ is illustrated in Fig. 1. In this structure, rhodium atoms are coordinated by selenium $[d$(Rh-Se)$]=2.39–2.41$ Å, bismuth $[d$(Rh-Bi)$]=2.70–2.93$ Å, and Rh $[d$(Rh-Rh)$]=2.86–2.99$ Å. The Rh-Rh bondings form one-dimensional chains along the a-axis having the short interatomic distances of $d$(Rh1-Rh4)$=2.86$ Å and $d$(Rh2-Rh3)$=2.86$ Å. These Rh chains are connected by Rh6 and Rh5 atoms with the longer Rh-Rh distances $d$(Rh1-Rh6)$=2.99$ Å and $d$(Rh2-Rh5) =2.87 Å, forming two-dimensional sheets perpendicular to the c axis. The shortest interatomic distance between two-dimensional sheets is 3.25 Å for the Bi-Se bonding, and this feature of the pseudo-two-dimensional crystal structure will cause low-dimensional peculiar behavior.

Figure 2(a) shows the temperature dependence of the electrical resistivity $\rho$. A superconducting transition is observed at 0.9 K, as will be discussed later. Above 260 K, the resistivity increases linearly with temperature, indicating a
typical metallic behavior. Below 250 K, the resistivity increases gradually with decreasing temperature and has a maximum around 190 K. Below 190 K, the resistivity shows a metallic behavior down to 1 K again. No hysteresis in the resistivity between the cooling and heating processes was observed around the anomaly temperature (~250 K), indicating that this phase transition is the second-order one.

Figure 2(b) shows the temperature dependence of the magnetic susceptibility $\chi$ after a diamagnetic correction ($\chi_{diam} = 2.66 \times 10^{-8}$ emu mol$^{-1}$). The positive values of $\chi$ indicate that Pauli paramagnetism dominates the magnetic susceptibilities in this compound. A Curie paramagnetic behavior at low temperatures is attributable to a small amount (<1.5%) of paramagnetic impurities which is undetectable in the x-ray diffraction profile. With decreasing temperature below 250 K, $\chi$ drops. The Pauli paramagnetic and Landau diamagnetic susceptibilities can be represented by $\chi_{Pauli} + \chi_{Landau} = N_A\mu_0\mu_0^2[1-m^2/3m^2]N(\varepsilon_F) = N(\varepsilon_F)$ using the density of states at the Fermi level $N(\varepsilon_F)$. The drop of $\chi$, which corresponds to the raise of $\rho$, indicates a loss of conduction electrons.

The temperature dependence of the thermoelectric power TEP for Bi$_2$Rh$_3$Se$_2$ is shown in Fig. 2(c). The TEP is negative over the whole temperature range. The value of TEP increases linearly with decreasing temperature and reaches a maximum at ~250 K. Below this temperature, TEP decreases rapidly, followed by a minimum at 95 K. Furthermore, with decreasing temperature, TEP increases toward zero and has a shoulder around 30 K ($\sim T_D/6$; $T_D$ is the Debye temperature) due to a phonon-drag, indicating a typical metallic behavior. The maximum at ~250 K is consistent with the onset of the anomaly as shown in the $\rho$-$T$ and $\chi$-$T$ curves. Since the TEP measurement is a sensitive probe of the density of states close to the Fermi surface, the rapid change around 250 K is attributable to the sudden change of the band structure.

Figure 2(d) shows the temperature dependence of the sample length change $\varepsilon = \delta L/L$. A shoulder is observed around 240 K in the $\varepsilon$-$T$ curve. To clarify this anomaly, the first derivative of $\varepsilon$ is also plotted in the same figure. A sharp peak is found at 242 K, indicating a lattice transformation in the Bi$_2$Rh$_3$Se$_2$. As observed in the $T$ dependence of $\rho$, $\chi$, TEP, and $\varepsilon$, it is considered that the second-order phase transition at ~250 K is caused by a deformation of the Fermi surface. Similar transitions are found in some CDW compounds.

In order to clarify the anomaly at ~250 K due to the CDW transition, we have carried out the x-ray diffraction measurements below 300 K. Figure 3(a) shows the x-ray diffraction profiles at 100 and 300 K in which the logarithm value of intensity is plotted as the longitudinal axis. In the $2\theta$ range between 10° and 40°, only one additional diffraction peak is found at ~35.5°. It is difficult to index this peak because of its broadness due to the overlap with some other reflections in this $2\theta$ region. This superlattice peak at several temperatures is normalized [see Fig. 3(b)] and the integrated peak intensity is plotted as a function of temperature in Fig. 3(c). The superlattice reflection for a CDW phase gives directly the CDW gap $\Delta_{CDW}$, i.e., the intensity is proportional to $\Delta_{CDW}^2$. According to the mean-field BCS theory, $\Delta_{CDW}$ can be represented by $\Delta_{CDW}(T)/\Delta_{CDW}(0) = tanh[(T_{CDW}/T) \times (\Delta_{CDW}(T)/\Delta_{CDW}(0))].$ The normalized $\Delta_{CDW}$ is also plotted as a solid line in Fig. 3(c) and is in good agreement with the obtained superlattice intensities. This behavior is consistent with that for the CDW compounds NbSe$_3$, (TaSe$_3$)$_3$I and K$_0$MoO$_3$. Unfortunately, we could not determine a wave vector of the CDW state from the powder x-ray diffraction. However, based on the results of the $\rho$, $\chi$, TEP, $\varepsilon$, and low-temperature x-ray measurements, we can conclude that the anomaly at ~250 K is the second-order phase transition from the normal metallic state to the CDW state with metallic conductivity.

Figures 4(a) and 4(b) shows the temperature and field dependences of resistivity of Bi$_2$Rh$_3$Se$_2$, respectively. As shown in Fig. 4(a), the resistivity in the zero field drops...
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The coherence length at zero temperature is found to be about 1130 mT. The Ginzburg-Landau coherence length at zero temperature is defined as the midpoint of the transition $T_c$ to the normal metallic state, the values of $T_c$ and 0.76 K, respectively. The critical temperature from specific heat data is defined as $T_c = 0.7$ K.

The value of $T_{c\text{mid}}$ decreases with increasing applied field [see Fig. 4(a)]. Assuming that Bi$_2$Rh$_3$Se$_2$ is a type-II superconductor, as will be justified below, the upper critical field at zero temperature can be estimated from

$$H_c(0) = \frac{\mu_0}{\pi} \frac{\xi(0)}{\xi_c(0)}$$

where $\xi(0)$ is the coherence length at zero temperature and $\xi_c(0)$ is the Ginzburg-Landau coherence length at zero temperature.

The specific heat curves of $C$ vs $T$ below 300 K and $C/T$ vs $T^2$ at low temperatures are given in Figs. 5(a) and 5(b), respectively. The $C/T$ curve shows the anomalies at the temperatures of the CDW ($T_{\text{CDW}} \approx 250$ K) and superconducting transitions ($T_c \approx 0.7$ K). A jump in the specific heat around 0.65 K is indicative of a bulk superconducting transition.

FIG. 3. (Color online) (a) Powder x-ray diffraction profiles at 100 and 300 K. (b) Powder x-ray diffraction profiles in the 2θ range between 35.5° and 36.5° at several temperatures. (c) Temperature dependence of the normalized superlattice integrated intensity.

FIG. 4. (Color online) (a) Temperature dependence of the electrical resistivity ($\rho$) under various magnetic fields. (b) Field dependence of the electrical resistivity ($\rho$) at several temperatures. (c) Temperature dependence of the upper critical fields [$\mu_0 H_c(T)$] determined from the electrical resistivity data.

The specific heat curves of $C$ vs $T$ below 300 K and $C/T$ vs $T^2$ at low temperatures are given in Figs. 5(a) and 5(b), respectively. The $C/T$ curve shows the anomalies at the temperatures of the CDW ($T_{\text{CDW}} \approx 250$ K) and superconducting transitions ($T_c \approx 0.7$ K). A jump in the specific heat around 0.65 K is indicative of a bulk superconducting transition.

The critical temperature from specific heat data is defined as the midpoint of the transition $T_c = 0.66$ K. The specific heat in the normal state is composed of the electron and phonon contributions $C = C_e + C_{\text{ph}}$. Above $T_c$ and much below the Debye temperature $\Theta_D$, $C/T = (C_e + C_{\text{ph}})/T = \gamma + 12R_0 T^2 / \Theta_D^2$. From the $C/T$ vs $T^2$ plot in the normal metallic state, the values of $\gamma$ and $\Theta_D$ were obtained to be 9.5 mJ/mol K$^2$ and 194 K, respectively. The electron-phonon coupling constant $\lambda_{e\text{ph}}$ is estimated from the McMillan equation for the superconducting transition temperature

$$T_c = \frac{\Theta_D}{\lambda_{e\text{ph}}^*} \exp\left(-\frac{1}{\lambda_{e\text{ph}}^*}ight),$$

where the Coulomb pseudopotential $\mu^*$ is assumed to be 0.13 empirically. The value of $\lambda_{e\text{ph}}$ is determined to be 0.45. This small $\lambda_{e\text{ph}}$ value suggests that Bi$_2$Rh$_3$Se$_2$ is classified into a weak-coupling superconductor.

The electronic specific heat $C_e$ was obtained by subtract-
shows an evident energy gap in the superconducting state. Below $T_c$, the $C-T$ data follows the exponential decay. On the other hand, the fitting of a $T^n$ function gives poor results. These fitting result shows that Bi$_2$Rh$_3$Se$_2$ is an $s$-wave superconductor. The normalized specific heat jump value $\Delta C/\gamma T^*_c$ is determined to be 1.35 and this value is slightly smaller than the limiting theoretical value ($\Delta C/\gamma T^{\text{mid}}_c=1.43$) of a weak-coupling superconductor. The result of the specific heat measurement reveals that Bi$_2$Rh$_3$Se$_2$ is a typical BCS weak-coupling superconductor.

The thermodynamic critical field $\mu_0H_c(T)$ can be obtained as a function of temperature using the specific heat data in both normal and the superconducting state. The difference in the entropy $\Delta S(T)$ between the normal and superconducting states was obtained from the thermodynamic relation $\Delta S(T) = S_n(T) - S_s(T) = \gamma T - \int_0^{T_s} C_{es}(T')/T' dT'$, where $S_n(T)$ and $S_s(T)$ are the entropies in the normal and superconducting states, respectively, and $C_{es}$ is the electronic specific heat in the superconducting state. The $C_{es}$ below 0.35 K is extrapolated by the exponential curve. The value of $\mu_0H_c(0)$ was obtained by the relation $G_c(T) - G_n(T) = \int_0^{T_s} [\Delta S(T')/T'] dT' = \mu_0 V m H_c(T)/2$, where $V_m$ is the molar volume. The value of $\mu_0H_c(0)$ is calculated to be 5.31 mT. On the other hand, the BCS theory predicts the magnitude of $\mu_0H_c(T)$ by the relation $\mu_0H_c(T) = [0.47 \mu_0 T^*_c V_m^{1/2}]^{1/2}$. The value of $\mu_0H_c(0)$ is obtained to be 5.34 mT, which is close to the value of $\mu_0H_c(T)=5.31$ mT obtained from the thermodynamic relation.

Moreover, the penetration depth $\lambda(0)$, GL parameter $\kappa(0)$ and lower critical field at zero temperature $\mu_0H_{c1}(0)$, are estimated from the following relations: $\mu_0H_{c1}(0) = \Phi_0/2\sqrt{2\pi \lambda(0)\xi_{GL}(0)}$, $\kappa(0) = \lambda(0)/\xi_{GL}(0)$, $\mu_0H_{c1} = \mu_0H_c \ln \kappa/\sqrt{2\kappa}$. By using the value of $\mu_0H_{c1}(0)=5.31$ mT, $\lambda(0)$, and $\kappa(0)$, and $\mu_0H_{c1}(0)$ are estimated to be 25700 Å and 151 and 0.12 mT, respectively. The considerably large value of $\kappa(0)$ indicates that Bi$_2$Rh$_3$Se$_2$ is an extreme type-II superconductor, like the high-$T_c$ cuprates, fullerenes and cobalt oxyhydrate.\(^{11}\)

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**Figure 5.** (Color online) (a) Temperature dependence of the specific heat ($C$) below 300 K. (b) Temperature dependence of the specific heat divided by temperature ($C/T$) at low temperatures. (c) Temperature dependence of the electronic specific heat ($C_e$) below 1 K. 

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