Superconducting state in the metastable binary bismuthide Rh$_3$Bi$_{14}$ single crystals

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We report detailed magnetic, transport and thermodynamic properties of metastable Rh$_3$Bi$_{14}$ single crystals in superconducting and normal state. We show that Rh$_3$Bi$_{14}$ is nearly isotropic, weak to (intermediately) coupled BCS superconductor, whereas the electronic resistivity above superconducting $T_c = 2.94$ K is dominated by the phonon scattering in the large unit cell with pores filled by Bi atoms. Superconductivity is strongly influenced by the nature of atoms that fill the voids in the crystal structure.

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I. INTRODUCTION

Complex crystal structures with atomic subunits often show significant electronic and magnetic tunability through incorporation of various elements in the (sub)structure. Examples include covalently bonded IV group thermoelectric clathrates that are under influence by the lattice parameters, even in intermetallic systems where delocalized metallic bonds are present. Cluster units may substantially define physical properties whereas their size may considerably deviate from the length scales defined by the lattice parameters, even in intermetallic systems where covalently bonded polycation framework and anions (Bi$_2$ or Br$_2$ in the channels), which leads to the higher compressibility along a axis when compared to those along b and c axes mainly controlled by the covalently bonded polycation.

Magnetization measurement indicates that Rh$_3$Bi$_{14}$ is a superconductor with $T_c = 2.82(5)$ K. Although the crystal structure and chemical bonding have been studied, the studies on physical properties, especially in connection with superconductivity are still lacking. In this work, we report detailed analysis of Rh$_3$Bi$_{14}$ physical properties in the superconducting and normal states. We show that electronic scattering in the normal state is dominated by phonons, whereas in its superconducting state Rh$_3$Bi$_{14}$ is an isotropic, weakly to (intermediately) coupled BCS superconductor.

II. EXPERIMENTAL

Single crystals of Rh$_3$Bi$_{14}$ were grown by the flux-growth method with Rh:Bi = 5:95 molar ratio. Rh pieces (99.9 %) and Bi shot (99.9 %) were weighed, combined into alumina crucible, covered with quartz wool and sealed into the quartz tube with partial pressure of argon. The quartz tube was heated to 1000 °C held constant for 2 h and then cooled at a rate of -3.5 °C/h to 300 °C where crystals were decanted. Single crystals with typical size $0.5\times0.2\times0.2$ mm$^3$ were obtained. Crystal structure and phase purity were examined by powder and single crystal X-ray diffraction pattern (XRD) with Cu K$_{\alpha}$ radiation ($\lambda = 0.15418$ nm) using a Rigaku MiniFLEX X-ray machine. The structure parameters are extracted by fitting the XRD spectra using the Rietica software. Crystal was oriented using Bruker SMART APEX II single crystal X-ray diffractometer. The composition of Rh$_3$Bi$_{14}$ single crystal was determined by examination of multi-
III. RESULTS AND DISCUSSION

All powder X-ray reflections (Fig. 1(c)) can be indexed in the $Fdd2$ space group. The refined lattice parameters are $a = 0.6891(1)$ nm, $b = 1.7388(1)$ nm, $c = 3.1718(2)$ nm with $R_p = 5.220$, $R_{wp} = 6.720$ and $\chi^2 = 0.919$, consistent with the values reported in literature. On the other hand, we also refined the lattice parameters using single crystal XRD. The lattice parameters are $a = 0.707(3)$ nm, $b = 1.755(5)$ nm and $c = 3.154(8)$ nm, which are also close to the result obtained from powder XRD and previous results. EDX spectrum of a single crystal (Fig. 1(d)) confirms the presence of only Rh and Bi with the average atomic ratios Rh:Bi = 3.0(4):13.8(4).

The temperature dependent electrical resistivity $\rho(T)$ of Rh$_3$Bi$_{14}$ is shown in Fig. 2(a). The sharp resistivity drop with $T_{c,\text{onset}}$ = 3.04 K is caused by superconducting transition (inset of Fig. 2(a)). The residual resistivity ratio(RRR), defined as $\rho(295K)/\rho(3.04K)$, is about 9.3. The curve $\rho(T)$ is convex above 50 K, with a tendency to saturate at high temperature. The saturation of $\rho(T)$ could be related to the Ioffe-Regel limit when the charge carrier mean free path is comparable to the interatomic spacing and/or to the two-band conductivity.

According to the phenomenological model,

$$\frac{1}{\rho(T)} = \frac{1}{\rho_{\text{ideal}}} + \frac{1}{\rho_{\text{sat}}} \quad \text{with } \rho_{\text{sat}} \approx \frac{e_F}{\pi \Omega_p^2 \alpha} \quad (1)$$

where $e_F$ is the Fermi velocity, $\Omega_p$ is the plasma frequency, $\alpha$ is interatomic spacing and $\rho_{\text{ideal}} = \rho_r + \rho_i(T)$. The $\rho_i(T)$ is the inelastic resistivity due to the phonon contribution whereas $\rho_{\text{sat}}$ is the saturation resistivity. Phonon contribution can be explained by the Bloch-Grüneisen formula:

$$\rho_i(T) = \left(\frac{c}{\Theta_D}\right)^5 \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \quad (2)$$

where $\Theta_D$ is the Debye temperature, $c$ is a constant which depends on the electronic structure of the metal through the Fermi velocity $v_F$ and the density of states at the Fermi energy. The fitting result over the full temperature range of $\rho_F$ is shown in Fig. 2(a) as a solid line, revealing an excellent agreement between the model and data for $\rho_r = 60.0(4) \, \mu\Omega \cdot$cm, $\rho_{\text{sat}} = 640(2) \, \mu\Omega \cdot$cm, $\Theta_D = 95.0(8) \, K$, $c = 27.7(6) \times 10^4 \, \mu\Omega \cdot$cm.

To confirm the presence of bulk superconductivity in Rh$_3$Bi$_{14}$ single crystals, the magnetization is measured...
The value of \( H^c_1 \) at which the field starts to penetrate into the sample can be determined by examining the point of deviation from the Meissner line on the initial slope of the magnetization curve. The first penetration field \( H^c_1 \) is not the same as the real lower critical field \( H_c1 \), due to the geometric effect. The \( H_c1 \) can be deduced from the \( H^c_1 \), assuming that the magnetization \( M = -H_c1 \) when the first vortex enters into the sample. Thus \( H_c1 \) has been rescaled to \( H = H_a - NM \) and \( H_c1 = H^c_1(1 - N) \) where \( N \) is the demagnetization factor and \( H_a \) is the external field. We estimate demagnetization factors 0.47, 0.23 and 0.59 for \( H \parallel a \), \( H \parallel b \) and \( H \parallel c \) by using \( H_c1 = H^c_1 / \tanh(\sqrt{0.36b/\alpha}) \), where \( a \) and \( b \) are width and thickness of a plate-like superconductor. 

The corrected data are plotted in Fig. 3(b), (c) and (d). Considering the demagnetization factors, the obtained slopes of the linear fitting at the lowest temperature of our measurements \( T = 1.8 \) K are -0.972(2), -0.988(2) and -0.987(2), very close to -1 \((4\pi M = -H)\) for all field directions. Thus the full Meissner shielding effect in our measurement provides a reliable way to determine the value of \( H_c1 \).

With increasing magnetic fields (Fig. 4(a) and (b)) the superconducting transition width broadens and the onsets of transition shift to lower temperatures gradually for both \( H \parallel b \) and \( H \parallel c \). When \( H = 6 \) kOe, the superconducting transition cannot be observed above 1.9 K for both field directions. It is interesting to observe kinks in the \( R(T) \) curves below \( T_c \) under fields for both field directions. The kinks are becoming more pronounced with the increasing field. The origin of these kinks implies rich vortex physics, similar to NbSe\(_2\). The upper critical field \( H_{c2} \) is determined by the criterion of 90% of the normal state resistivity at various fields for both field directions (Fig. 4(c)). The slopes \( dH_{c2}/dT \) for \( H \parallel b \) and \( H \parallel c \) are equal to -6.47(5) kOe/K and -6.01(11) kOe/K, respectively. For dirty limit superconductors, \( H_{c2}(0) \) can be obtained from the Werthammer-Helfand-Hohenberg
The thermodynamic critical field $H_{c2}$ can be obtained from $H_{c2}(0) = \Phi_0 / \pi \xi(0)$, according to the anisotropic Ginzburg-Landau (GL) theory, we assume $\xi_a \sim \xi_c$ and coherence length $\xi(0)$ can be estimated from the $H_{c2}(0)$ with: $H_{c2}(0) = \Phi_0 / [2\pi \xi_a(0) \xi_c(0)]$ and $H_{c2}(0) = \Phi_0 / [2\pi \xi_a(0) \xi_b(0)]$, where $\Phi_0 = 2.07 \times 10^{-15}$ Wb. Based on the values of $H_{c2}(0)$ and $H_{c3}(0)$, GL parameters $\kappa_i(0)$ is obtained from the equation $H_{c2}^i(0)/H_{c3}^i(0) = 2\kappa_i^2(0)/\ln \kappa_i(0)$, where $i$ denotes the field applied along $i$ direction. The thermodynamic critical field $H_{c1}(0)$ can be obtained from $H_{c1}(0) = H_{c2}^i(0) / [\sqrt{2} \kappa_i(0)]$. The GL penetration lengths are evaluated by the equations $\kappa_b(0) = \lambda_b(0)/\xi_c(0)$ and $\kappa_a(0) \approx \kappa_c(0) = \lambda_a(0)/\xi_c(0) = [\lambda_b(0)\lambda_c(0)/\xi_c(0)\xi_b(0)]^{1/2}$. The anisotropy is $\gamma_{anis} = H_{c2}^b(0)/H_{c2}^a(0) = \xi_b(0)/\xi_c(0)$. All of the obtained parameters are listed in Table 1.

$$\lambda_e-ph = \frac{\mu^* \ln(1.45 T_c / \Theta_D) - 1.04}{1.04 + \ln(1.45 T_c / \Theta_D)(1 - 0.62 \mu^*)}$$

and assuming the common value for the Coulomb pseudopotential $\mu^* \approx 0.13$. The value of $\lambda_e-ph$ is determined to be 0.74(1) by using $T_c = 2.94$ K and $\Theta_D = 113.9(7)$ K. The value of $\lambda_e-ph$ implies intermediate or weakly coupled BCS superconductivity. The electronic specific heat $C_e$ in the superconducting state (Fig. 5(b)) is obtained by subtracting the lattice contribution estimated from the total specific heat. The extracted specific heat jump at $T_c$ ($\Delta C / \gamma T_c = 1.8(2)$) is somewhat larger than the weak coupling value 1.43, and also points to intermediate coupling strength $\lambda_e-ph$.

Rh$\text{Bi}_{12}$Br$_2$ has similar structure to Rh$\text{Bi}_{14}$, but the two Bi4 atoms are replaced by the Br atoms. Rh$\text{Bi}_{12}$Br$_2$ is a metal above 2 K without superconducting transition. From theoretical calculation, the density of state (DOS) at Fermi energy is similar for both compounds, however the contributions of atoms (s and p states of Bi) at Bi4 position to DOS are nearly removed when voids in the crystal structure are filled with...
TABLE I. Superconducting parameters of Rh$_3$Bi$_{14}$.

|       | $T_c$ (K) | $H_{c2}^K$ (Oe) | $H_{c2}^0$ (Oe) | $\kappa_i(0)$ | $\xi_i(0)$ (nm) | $\lambda_i(0)$ (nm) | $\gamma_{anis}$ | $\gamma_n$ | $\beta$ | $\lambda_{c-\rho n}$ | $\Theta_D$ | $\Delta C/\gamma_n T_c$ |
|-------|----------|----------------|----------------|--------------|----------------|-------------------|----------------|----------|-------|-----------------|----------|----------------|
| $i=a$ | 2.94     | 90(1)         |                | 273(4)       | 1.08(3)       | 8(1)              | 22.39(4)       | 0.74(1)  | 113.9(7) | 1.8(2)          |         |                  |
| $i=b$ | 63(1)    | 13.4(1)       | 5.4(1)         | 17.4(2)      | 16.9(2)       | 166(8)            |               |           |        |                 |         |                  |
| $i=c$ | 93(1)    | 12.4(2)       | 6.7(1)         | 13.1(2)      | 15.71(6)      |                   |               |           |        |                 |         |                  |

Br atoms. Therefore, the superconductivity in Rh$_3$Bi$_{14}$ might be related to the s and p states of Bi atom in the interstitial Bi4 position of Rh$_3$Bi$_{14}$.

IV. CONCLUSION

In summary, we present a comprehensive study of the normal and superconducting state properties of metastable intermetallic superconductor, Rh$_3$Bi$_{14}$. The temperature dependence of resistivity $\rho(T)$ above the superconducting transition can be explained by the phonon scattering. Rh$_3$Bi$_{14}$ is an isotropic, weakly to intermediate-coupled BCS superconductor. Presence (absence) of superconductivity in Rh$_3$Bi$_{14}$ (Rh$_3$Bi$_{12}$Br$_2$) suggests that the nature of atoms that fill the pores in the structure is rather important.

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