Type-I superconductivity in KBi$_2$ single crystals

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Abstract

We report on the detailed transport, magnetic, thermodynamic properties and theoretical calculation of KBi$_2$ single crystals in superconducting and normal states. KBi$_2$ exhibits metallic behavior at a normal state and enters the superconducting state below $T_c = 3.573$ K. Moreover, KBi$_2$ exhibits low critical fields in all measurements, field-induced crossover from second- to first-order phase transition in specific heat measurements, the typical magnetization isotherms of type-I superconductors, and a small Ginzburg–Landau parameter $\kappa_{GL} = 0.611$. These results clearly indicate that KBi$_2$ is a type-I superconductor with a thermodynamic critical field $H_{c2} = 234.3$(3) Oe.

Keywords: type-I superconductivity, bismuth compounds, superconductor critical magnetic field

(Some figures may appear in colour only in the online journal)

1. Introduction

Superconductivity is one of the most attractive topics in the area of condensed matter physics, not only because of the great application potential of superconductors (SCs), with high transition temperatures and critical fields, but also due to the importance of understanding the Cooper pairing mechanism—especially for unconventional superconductivity beyond the Bardeen–Cooper–Schrieffer (BCS) mechanism. According to the Ginzburg–Landau (GL) theory, the value of the GL parameter $\kappa_{GL}$, which is the ratio of penetration depth to coherence length, classifies SCs into two categories: type-I SCs when $\kappa_{GL} < 1/\sqrt{2}$ and type-II SCs when $\kappa_{GL} > 1/\sqrt{2}$ [1]. Most superconducting compounds belong to type-II SCs and have been studied extensively. In contrast, type-I SCs are thought empirically to occur mainly in elementary metals and metalloids, and type-I superconducting compounds are very rare [2]. Recently, however, several binary and ternary compounds were found to be type-I SCs, for instance, YbSb$_2$ [3, 4], TaS$_2$ [5], LaPd$_2$Ge$_2$ [6], LaRh$_5$Si$_2$ [7], (Lu, Y, La)Pd$_2$Si$_2$ [7], LaRhSi$_3$ [8], Ag$_2$Pb$_2$O$_9$ [9], ScGa$_3$ and LuGa$_3$ [10]. These studies break the empirical relationship between type-I superconductivity and elemental metals and enlarge the family of type-I SCs to binary and ternary compounds.

Some of the binary bismuth compounds show superconductivity, such as KBi$_2$ (3.6 K) [11], SrBi$_3$ (5.62 K) [12], BaBi$_3$ (5.69 K) [12], Rh$_3$Bi$_{14}$ (2.94 K) [13], and In$_3$Bi (5.9 K) [14]. For KBi$_2$, except regarding the superconducting transition temperature $T_c$, studies on its physical properties are scarce and classification of its superconductivity has not yet been identified [11, 15]. In this work, we performed a detailed characterization and analysis of the physical properties for KBi$_2$ single crystals in superconducting and normal states. The experimental and theoretical calculation results undoubtedly indicate that KBi$_2$ is a type-I SC in the dirty limit. As far as we know, this is the first type-I SC in bismuth compounds.

2. Experimental

Single crystals of KBi$_2$ were grown by the flux method with a K:Bi = 1:9 molar ratio. K pieces (99.9%) and Bi shot (99.9%) were mixed and put into an alumina crucible, covered with quartz wool and then sealed into a quartz tube with a partial pressure of Argon. The quartz tube was heated to 580 °C.
for 12 h and then slowly cooled to 280 °C, at which point the crystals were decanted with a centrifuge. Single crystals with a typical size of $1.8 \times 1.8 \times 1 \text{ mm}^3$ were obtained, exhibiting a metallic luster. The x-ray diffraction (XRD) of the powdered small crystals and a single crystal was performed using a Bruker D8 x-ray machine with Cu $K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at room temperature. Rietveld refinement of the XRD patterns was performed using the code TOPAS4 [16]. Electrical transport, magnetization and specific heat measurements were performed in a Quantum Design PPMS-14. First-principles electronic structure calculations were carried out with the projector augmented wave method [17] as implemented in the VASP package [18]. The generalized gradient approximation of Perdew–Burke–Ernzerh [19] was adopted for the exchange-correlation potential. The kinetic energy cutoff of the plane-wave basis was set to be 350 eV. A supercell containing 2 K atoms and 4 Bi atoms and a $6 \times 6 \times 6$ k-point mesh for Brillouin zone sampling was employed. Gaussian smearing with a width of 0.05 eV was used around the Fermi surface. In structure optimization, both cell parameters and internal atomic positions were allowed to relax until the forces were smaller than 0.01 eV Å. The spin–orbital coupling (SOC) effect was included for the density of states (DOS) calculations.

3. Results and discussion

As shown in figure 1(a), KBi$_2$ is isostructural to MgCu$_2$ (Laves phase) [15, 20, 21]. Each unit cell of KBi$_2$ has 8 K atoms and 16 Bi atoms. Every four Bi atoms form a tetrahedron and

![Figure 1](image1)

**Figure 1.** (a) Crystal structure of KBi$_2$. The large red and small blue balls represent K and Bi atoms, respectively. The green rectangle marks the (1 1 1) plane. (b) The Kagomé net of Bi atoms in the (1 1 1) plane. (c) Powder XRD pattern of KBi$_2$. (d) XRD pattern of a KBi$_2$ single crystal. The extra peaks in the XRD patterns (labeled with the #$ symbol) originate from a residual Bi flux. Inset: photo of a typical KBi$_2$ single crystal. The length of one grid in the photo is 1 mm.

![Figure 2](image2)

**Figure 2.** (a) The temperature dependence of electrical resistivity $\rho(T)$ of KBi$_2$ single crystals at zero field. Inset: an expanded view of the low-temperature data showing the superconducting transition. The $T_{c,\text{onset}}$ at zero field is marked by an arrow. (b) The low-temperature dependence of $\rho(T)$ of a KBi$_2$ single crystal at various magnetic fields from 0 to 200 Oe.
these tetrahedra connect to each other by vertex-sharing to form a three-dimensional network. The K atoms arrange in a diamond lattice which is intertwined with the network of Bi tetrahedra. On the other hand, it can be seen that there are two-dimensional (2D) Kagomé nets of Bi atoms in the (1 1 1) plane, figure 1(b), which connect together along the [1 1 1] direction by other Bi layers. It can also be seen that the K atoms locate right above and below the center of the hexagons of Bi atoms in the 2D Kagomé nets. The powder XRD pattern of KBi$_2$ can be well indexed using the Fdm$_3$ bar space group (MgCu$_2$-type structure) figure 1(c). The refined lattice parameters are $a = 0.9523(2)$ nm with $R_p = 5.88$, $R_{wp} = 8.69$ and $\chi^2 = 1.28$, which are close to the values reported in the literature ($a = 0.95223(2)$ nm) [15]. There are some extra peaks that can be ascribed to the diffraction of the residual Bi flux. The XRD pattern of a KBi$_2$ single crystal indicates that the surface of the crystal is parallel to the (1 1 1) plane figure 1(d). The KBi$_2$ crystals prefer to form triangular surfaces, as shown in the inset of figure 1(d). This characteristic is consistent with the single crystal XRD pattern, as well as its crystallographic symmetry.

Figure 2(a) shows the temperature dependence of electrical resistivity $\rho(T)$ for a KBi$_2$ single crystal at zero field. It can be seen that KBi$_2$ exhibits metallic behavior and the curve $\rho(T)$ is convex above 25 K, with a tendency to saturate at a high temperature. This is the typical shape of resistivity for a sample in which the dominant scattering mechanism is electron-phonon scattering. The residual resistivity ratio (RRR), defined as $\rho(300\,\text{K})/\rho(4\,\text{K})$, is about 72.5, indicating the high quality of the single crystal. On the other hand, at zero field, there is a sharp superconducting transition in the $\rho(T)$ curve with $T_{c,\text{onset}} = 3.549\,\text{K}$ and a transition width $\Delta T_c \sim 0.1\,\text{K}$ (inset of figure 2(a)). The transition temperature is consistent with previous magnetic susceptibility measurements ($T_c = 3.5\,\text{K}$) [15]. Moreover, with an increasing magnetic field, the superconducting transition shifts to lower temperatures gradually and the transition width also becomes wider for $H \perp (1 1 1)$ figure 2(b). Surprisingly, at a very low field ($H = 200\,\text{Oe}$), the $T_c$ is suppressed below 2 K.

Figure 3(c) shows the dc magnetization isotherms $4\pi M(H)$ of a KBi$_2$ single crystal at various temperatures (from 2 K to...
Figure 4. (a) The low-temperature specific heat $C_p/T$ versus $T^2$ of a KBi$_2$ single crystal in a series of magnetic fields from 0 to 307 Oe. (b) The temperature dependence of specific heat from 2.2 K to 300 K at a zero field. The solid line shows the classic value of specific heat at a high temperature limit. Inset: the temperature dependence of electronic specific heat plotted as $C_p/T$ versus $T$ at a zero field.

3.6 K for $H$ $(1 1 1)$ at the low-field range. It can be seen that the magnetic fields corresponding to the maximum absolute values of magnetic moment are very close to those where $4\pi M(H)$ becomes zero. Based on this, two different assumptions can be made: either (i) KBi$_2$ is a type-II SC in which the upper critical field $H_{c2}$ is very small and close to the lower critical field $H_{c1}$, or (ii) KBi$_2$ is a type-I SC and the departure from the ideal step-like transition at the critical field may be attributed to a strong pinning of the domain walls in the intermediate state or to unclear demagnetization [23]. For the latter case, the critical field $H_c$ is defined as the field where the sample enters a normal state ($M(H) = 0$). On the other hand, when the temperature decreases, the critical field shifts to a higher field. Even at the lowest measuring temperature (2 K), however, the critical field is still remarkably small ($\sim 160$ Oe). The full magnetization loop of KBi$_2$ measured at 2 K for $H$ $(1 1 1)$ is shown in figure 3(d). It can be seen that the hysteresis is very small. The small critical field accompanying the weak magnetization hysteresis and the shape of the $M(H)$ loop similar to other type-I superconducting compounds, such as YbSb$_2$ [3, 4] and LaRhSi$_3$ [8], suggest that KBi$_2$ is more like a type-I than a type-II SC.

The specific heats of KBi$_2$ single crystals at various fields are shown in figure 4(a). At zero field, there is a jump at 3.573 K, indicating the bulk superconductivity of KBi$_2$. The transition temperature is also consistent with the $T_c$ obtained from resistivity and magnetization measurements. More importantly, the specific-heat jump at the superconducting transition at $H = 7$ Oe is much sharper and higher than that at zero field, which is a unique feature of type-I SCs and indicates that there is a crossover from second- to first-order phase transition when a field is applied. This behavior has been observed in other type-I intermetallic SCs, such as YbSb$_2$ [3, 4], LaRhSi$_3$ [8], ScGa$_3$, and LuGa$_3$ [10]. Therefore, specific heat measurements further support the idea that KBi$_2$ is a type-I SC. On the other hand, the superconducting transition shifts to a lower temperature with increasing field and superconductivity is suppressed below 2.2 K when $H > 157$ Oe. In the normal state ($H = 307$ Oe), the electronic specific heat coefficient $\gamma$ and phonon specific heat coefficient $\beta$ are obtained using the linear fit $C_p/T = \gamma + \beta T^2$. The fitted $\gamma$ and $\beta$ are 1.3(4) mJ mol$^{-1}$ K$^{-2}$ and 3.10(4) mJ mol$^{-1}$ K$^{-4}$, respectively. The latter gives the Debye temperature $\Theta_D = 123.4(5)$ K using the formula $\Theta_D = (12\pi^4 N R / 5 \beta)^{1/3}$. The electron–phonon coupling $\lambda_{e-\phi}$ can be estimated with the values of $\Theta_D$ and $T_c$ using McMillan’s theory [24],

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

where $\mu^*$ is the repulsive screened Coulomb potential and is usually between 0.1 and 0.15. Setting $\mu^* = 0.13$, the calculated $\lambda_{e-\phi}$ is 0.774, implying that KBi$_2$ is an intermediately or strongly coupled BCS SC. Figure 4(b) shows the specific heat of KBi$_2$ measured from 2.2 K to 300 K at zero field. The specific heat at a high temperature approaches the value of $3NR$ at 300 K, where $N$ is the atomic number in the chemical formula ($N = 3$) and $R$ is the gas constant ($R = 8.314$ J mol$^{-1}$ K$^{-1}$), consistent with the Dulong–Petit law. The electronic specific heat $C_{es}$ at zero field (inset of figure 4(b)) is obtained by subtracting the lattice contribution from the total specific heat. The extracted electronic specific heat jump at $T_c$ ($\Delta C_{es}/\Delta T_c = 6.06$) is much larger than the weakly coupled BCS value 1.43, indicating strongly coupled superconductivity in KBi$_2$ [24].

The thermodynamic critical field $H_c(T)$ can be obtained by integrating the differences of specific heats and the specific heat. The relationships between $H_c(T)$ and $T$ are shown in figure 4(b). At zero field, there is a jump at 3.573 K, indicating the bulk superconductivity of KBi$_2$. The transition temperature is also consistent with the $T_c$ obtained from resistivity and magnetization measurements. More importantly, the specific-heat jump at the superconducting transition at $H = 7$ Oe is much sharper and higher than that at zero field, which is a unique feature of type-I SCs and indicates that there is a crossover from second- to first-order phase transition when a field is applied. This behavior has been observed in other type-I intermetallic SCs, such as YbSb$_2$ [3, 4], LaRhSi$_3$ [8], ScGa$_3$, and LuGa$_3$ [10]. Therefore, specific heat measurements further support the idea that KBi$_2$ is a type-I SC. On the other hand, the superconducting transition shifts to a lower temperature with increasing field and superconductivity is suppressed below 2.2 K when $H > 157$ Oe. In the normal state ($H = 307$ Oe), the electronic specific heat coefficient $\gamma$ and phonon specific heat coefficient $\beta$ are obtained using the linear fit $C_p/T = \gamma + \beta T^2$. The fitted $\gamma$ and $\beta$ are 1.3(4) mJ mol$^{-1}$ K$^{-2}$ and 3.10(4) mJ mol$^{-1}$ K$^{-4}$, respectively. The latter gives the Debye temperature $\Theta_D = 123.4(5)$ K using the formula $\Theta_D = (12\pi^4 N R / 5 \beta)^{1/3}$. The electron–phonon coupling $\lambda_{e-\phi}$ can be estimated with the values of $\Theta_D$ and $T_c$ using McMillan’s theory [24],

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The thermodynamic critical field $H_c(T)$ can be obtained by integrating the differences of specific heats and the specific heats divided by temperature between the zero field superconducting (s) and normal (n) states ($H = 207$ Oe) (free energy analysis) [8, 25],

$$-H_c(T)^2/8\pi = \Delta F(T) = \Delta U(T) - T \Delta S(T)$$

$$\Delta U(T) = \int_T^{\infty} [C_c(T') - C_n(T')]dT'$$

$$\Delta S(T) = \int_T^{\infty} C_n(T')dT'$$

where $\Delta F(T)$, $\Delta U(T)$, and $\Delta S(T)$ are the differences of free energy, internal energy, and entropy between zero field superconducting and normal states. The relationship between the $T_c$ and critical fields determined from magnetization, resistivity, specific heat measurements and free energy analysis.
The calculated density of states (DOS) of KBi$_2$. The black, red and blue lines correspond to the total DOS, partial DOS of the Bi-$p$ state and the partial DOS of the K-$s, p$ state, respectively. The dotted line represents the Fermi energy level, $E_F$.

is summarized in the $H - T$ phase diagram, figure 5. It can be seen that all of the data is almost on one line, confirming the consistency of critical fields from different measuring methods and undoubtedly indicating that all of these critical fields are thermodynamic $H_c(T)$. The dotted line gives the free energy fitting that uses the BCS temperature dependence $H_c(T) = H_c(0)[1 - (T/T_c)^2]$. This gives the zero-temperature $H_c(0) = 234.3(3)$ Oe and $T_c = 3.561(1)$ K, close to those values obtained from different experimental methods.

Figure 6 shows the calculated density of state (DOS) of KBi$_2$. The shape of the DOS is somewhat different from the previous result [15], because the SOC which is significant for bismuth is considered in the present calculation. The finite DOS at a Fermi energy level ($E_F$) indicates the metallic ground state, consistent with the experimental results. The DOS near $E_F$ is mainly contributed by the Bi-$p$ state and the contribution of K is negligible, indicating that K atoms transfer almost all of the valence electrons to the Bi atoms—i.e. the valence state of K is +1 and the three-dimensional network of Bi can be thought of as polyanion [15].

The calculated total DOS at $E_F$ is 1.77 states/eV f.u. giving the carrier density $n = 6.33 \times 10^{22} \text{cm}^{-3}$ using the free-electron model. The calculated Fermi wave vector $k_F$ equals 12.33 nm$^{-1}$ using the formula $k_F = (3\pi^2 n)^{1/3}$. Then, the effective electron mass can be determined as $m^* = 3\hbar^2/2(k_F^2k_BT_e) = 0.312 m_e$, where $k_B$ is the Boltzmann constant and $m_e$ is the free-electron mass. With a derived $m^*$ and $n$, the London penetration depth is calculated as $\lambda_L(0) = (m^*/\mu_B\rho_e)^{1/2} = 11.8$ nm [26]. Meanwhile, the coherence length is determined by using the BCS relation $\xi(0) = 0.18\hbar^2k_F/(k_B\mu_B^*m^*)$ [26], which gives $\xi(0) = 1.76$ $\mu$m. Assuming a simple model of a spherical Fermi surface ($S/S_F = 1$), the mean free path $l_m$ is estimated as $l_m = 1.27 \times 10^2(\rho_e)^{2/3}/S/S_F^{-1} = 13.9$ nm, where $\rho_e$ is the low-temperature normal state resistivity (5.76 $\mu$ $\Omega$ cm at 4 K) [26]. This clearly indicates that the electronic mean free path is considerably smaller than the BCS coherence length ($l_m/\xi(0) = 0.008$), suggesting that KBi$_2$ can be classified as an SC in the dirty limit. In the dirty limit, the GL parameter $\kappa_{GL} = 0.72\lambda_L(0)/l_m = 0.611$ [26], which is smaller than 1/$\sqrt{2}$, further confirming that KBi$_2$ is a type-I SC. Moreover, the zero-temperature Ginzburg–Landau (GL) coherence length in the dirty limit $\xi_{GL}(0)$ can be obtained from the relations $\xi_{GL}(0) = 8.57 \times 10^{-3}(10\gamma\rho_eT_e/V)^{1/2}$ [26] giving $\xi_{GL}(0) = 133.7$ nm. According to the definition of $\kappa_{GL} = \lambda_L(0)/\xi_{GL}(0)$, the derived zero-temperature GL penetration depth $\lambda_{GL}(0)$ is 81.7 nm. The superconducting and thermodynamic parameters of KBi$_2$ are summarized in table 1.

### Table 1. Physical parameters of KBi$_2$ in superconducting and normal states.

| Parameter | Value       |
|----------|-------------|
| $T_c$ (K) | 3.573       |
| $H_c$ (Oe) | 234.3(3)   |
| RRR      | 72.5        |
| $\gamma$ (mJ mol$^{-1}$ K$^2$) | 1.3(4) |
| $\phi_0$ (K) | 123.4(5) |
| $\lambda_{ep}$ (nm) | 0.774 |
| $\Delta C_{eq}/T_e$ | 6.06 |
| $m^*$ ($m_e$) | 0.312 |
| $\lambda_L(0)$ (nm) | 11.8 |
| $l_m$ (nm) | 13.9 |
| $\xi_{GL}(0)$ (nm) | 133.7 |
| $\lambda_{GL}(0)$ (nm) | 81.7 |
| $\kappa_{GL}$ | 0.611 |

4. Conclusion

In summary, a single crystal of KBi$_2$ has been successfully grown from a Bi flux. Resistivity, magnetization and specific heat measurements indicate that KBi$_2$ demonstrates bulk superconductivity with $T_c = 3.573$ K. Further analysis of the experimental results indicates that KBi$_2$ is a type-I BCS
SC in the dirty limit with an intermediate or strong coupling strength. The thermodynamic critical field is 234.3(3) Oe and the calculated GL parameter $\kappa_{GL} = 0.611$. This study not only deepens our understanding of type-I superconductivity, but will also stimulate further work on discovering other type-I SCs in binary or ternary compounds.

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