Type-I superconductivity in YbSb₂ single crystals

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We present evidence of type-I superconductivity in YbSb₂ single crystals from dc and ac magnetization, heat capacity, and resistivity measurements. The critical temperature and critical field are determined to be \( T_c \approx 1.3 \) K and \( H_c \approx 55 \) Oe. A small Ginzburg-Landau parameter \( \kappa = 0.05 \), together with typical magnetization isotherms of type-I superconductors, small critical field values, a strong differential paramagnetic effect signal, and a field-induced change from second- to first-order phase transition, confirms the type-I nature of the superconductivity in YbSb₂. A possible second superconducting state is observed in the radio-frequency susceptibility measurements, with \( T_{c(2)} \approx 0.41 \) K and \( H_{c(2)} \approx 430 \) Oe.

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I. INTRODUCTION

A long-held empirical belief has been that type-I superconductors are generally elementary metals and metalloids, while the majority of superconducting compounds exhibit type-II behavior. Among the vast array of known binary and ternary superconductors, the number of systems with type-I superconductivity is notably limited. 1-7

YbSb₂ was first claimed to be a type-I superconductor by Yamaguchi et al., 7 solely based on the shape of one \( M(H) \) isotherm at 0.4 K. Subsequently, a limited number of studies of the physical properties of YbSb₂ have been published. Among those, Sato et al. reported results of density functional theory (DFT) calculations, resistivity, and de Haas–van Alphen measurements, which revealed a quasi-two-dimensional Fermi surface. 8 Two other brief reports of resistivity under pressure and nuclear quadrupole resonance (NQR) measurements indicated that \( T_c \) is suppressed under pressure \( p = 0.4 \) GPa and that YbSb₂ is likely a weakly coupled \( s \)-wave superconductor. Given the scarcity of type-I superconducting compounds and the lack of a thorough characterization of the magnetic and thermodynamic properties of YbSb₂, a detailed analysis of the superconducting ground state in this compound is needed. In this paper, we report results of dc and ac magnetization, heat capacity, resistivity, and magnetic penetration depth, confirming the superconducting ground state with \( T_c \approx 1.3 \) K and \( H_c \approx 55 \) Oe. A discussion of the superconducting parameters, based on the BCS and Ginzburg-Landau (GL) theories, is also provided. The shape of the \( M(H) \) curves and a second- to first-order phase transition in specific heat below \( T_c \), together with a large differential paramagnetic effect (DPE), small critical field \( H_c \), and GL parameter \( \kappa \ll 1/\sqrt{2} \) provide strong evidence for the type-I superconductivity in YbSb₂. Moreover, the radio-frequency \((\text{rf})\) susceptibility data reveal a possible second superconducting transition with \( T_{c(2)} \approx 0.41 \) K and \( H_{c(2)} \approx 430 \) Oe.

II. EXPERIMENTAL METHODS

YbSb₂ single crystals were synthesized by a flux growth technique, using an excess amount of Sb. Elemental Yb (Ames Laboratory, 99.999%) and Sb (Alfa Aesar, 99.9999%) pieces in an atomic ratio of 1:9 were packed in an alumina crucible and sealed in a quartz ampoule under partial Ar pressure. The ampoule was heated up to 650 °C, kept at that temperature for 4 h, then slowly cooled down to 620 °C, after which the excess flux was removed in a centrifuge. The as-grown crystals were thin plates with a typical dimension of \( 5 \times 5 \times 0.2 \) mm². A 1:1:1 HCl-HNO₃-H₂O solution was used to remove the remnant flux from the surface of the crystals.

Room-temperature powder x-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max diffractometer with Cu Kα radiation and a graphite monochromator. Rietveld analysis was performed to determine the lattice parameters, using the RIETICA software package. 11

The dc magnetization measurements were performed in a commercial Quantum Design Magnetic Properties Measurement System (QD MPMS) with a 3He insert for temperatures between 0.5 and 2 K. For the platelike crystals, the shape was assumed to be ellipsoidal, and the demagnetization factor \( N_D \) was determined from tabulated values. 12 The ac magnetization was measured in a dilution refrigerator, using a standard ac susceptibility consisting of two oppositely wound pickup coils. An external modulation field of 0.1 Oe and 113.7 Hz was applied in the direction parallel to the crystal plate, and data were acquired by a lock-in amplifier. After background subtraction, the phase was shifted according to the excitation frequency. In order to obtain absolute values of the magnetization, the data were matched to the results from the QD MPMS measurements. The imaginary part \( \chi'' \) was set to zero at temperatures above \( T_c \), using an appropriate offset. The offset and the scaling to absolute values were the same for both the temperature and field sweeps.

The heat capacity of YbSb₂ was measured in a QD Physical Property Measurement System (PPMS) with a 3He option, using a thermal relaxation technique. To demonstrate the field dependence of the heat capacity, measurements were carried out in a magnetic field applied perpendicular to the crystal plate, with magnitudes ranging from 0 to 90 kOe. Temperature-dependent ac resistivity was also measured in the QD PPMS, utilizing a standard four-probe method. The sample was cut into a barlike shape, and four platinum wires were attached to the flat surface using Epo-Tek H20E silver epoxy. An ac current of \( i = 0.1 \) mA and \( f = 1000 \) Hz was applied along...
the in-plane direction, and resistivity data were taken during cooling.

The in-plane magnetic penetration depth $\Delta \lambda (T)$ was determined using a self-resonating tunnel-diode oscillator (TDR),\textsuperscript{13} operating at 16 MHz with an amplitude of $H_{ac} \approx 10$ mOe, with temperatures down to 50 mK, and in static magnetic fields up to $H_{dc} = 400$ Oe. The sample was mounted on a sapphire rod with the crystal plate perpendicular to both $H_{ac}$ and $H_{dc}$. Placing the sample into the inductor causes the shift of the resonant frequency $\Delta f(T) = -G(\chi(T))$, where $G$ is a calibration constant determined by physically pulling the sample out of the coil. With the characteristic sample size $R$, $\Delta \lambda$ can be obtained from $4\pi \chi = (\lambda / R) \tanh(R/\lambda) - 1$.\textsuperscript{14,15}

III. RESULTS AND DISCUSSION

The powder x-ray diffraction pattern of YbSb$_2$ is shown in Fig. 1. The pattern was refined using a ZrSi$_2$-type orthorhombic structure with space group $Cmcm$ and lattice parameters $a = 4.554$ Å, $b = 16.715$ Å, and $c = 4.267$ Å, in good agreement with the previously reported values.\textsuperscript{16} A small amount of remnant Sb flux ($\sim 5\%$) was found and is marked by a blue asterisk in Fig. 1.

Figure 2 shows the temperature-dependent dc magnetic susceptibility $\chi$ of YbSb$_2$, measured in a field $H$ parallel to the crystal plate. The ZFC and FC data are plotted as solid and dashed lines, respectively. Symbols) the demagnetization correction. It is clear that the corrected $M(H)$ curves show a steplike jump to zero near the critical field, characteristic of type-I superconductivity. The full magnetization loops [Fig. 3(b)] also have the shape typical of type-I superconductors.\textsuperscript{17–19}

The ac susceptibility $\chi'$ of YbSb$_2$ as a function of temperature is shown in Fig. 4. As the field increases from $H = 0$ to...
55 Oe, the onset temperature of the Meissner signal drops from 1.41 to 0.14 K. In a H = 60 Oe field, the superconductivity is further suppressed and cannot be detected down to 0.06 K. Similarly, a suppression of Hc with T from 56.3 Oe (T = 0.06 K) to 2.3 Oe (T = 1.28 K) is illustrated by the χ′(H) data in Fig. 5. The onset critical temperature Tc and critical field Hc values from ac susceptibility measurements are summarized in Table 1.

The field dependence of the superconducting transition of YbSb2 is further confirmed by heat capacity measurements in fields up to 60 Oe. The report7 as H increases, Tc monotonically decreases and drops below 0.4 K (the minimum available temperature for these measurements) at H = 60 Oe. The peak at the transition also becomes sharper and higher for H = 10 Oe, compared to that for H = 0, indicating a change from second- to first-order phase transition, commonly seen in type-I superconductors. As the field is further increased, a nonmonotonic change of the electronic and phonon specific heat coefficients γ and β is revealed by the Cp/T vs T2 plots (Fig. 6, left inset).

The phonon contribution can also be estimated using the Debye temperature θD(2K) ≈ 186 K. As expected for metals, the resistivity ρ increases monotonically with increasing temperature, as shown in Fig. 7. At high temperatures, a linear temperature dependence of ρ(T) is evident, as expected for metals. As seen in the top inset, the resistivity drops to zero at Tc = 1.25 K, with a residual resistivity ρ0(2K) = 0.53 μΩ cm just above Tc. The residual resistivity ratio, calculated as RRR = ρ(300 K)/ρ(2 K), is around 186, indicative of a good quality metal. At temperatures below 8 K and above Tc, the resistivity shows a quadratic dependence on temperature: ρ = ρ0 + AT2.

FIG. 5. (Color online) Field-dependent ac susceptibility of YbSb2, measured for various temperatures from 0.06 to 1.28 K.

FIG. 4. (Color online) Temperature-dependent ac susceptibility of YbSb2, measured in fields H up to 60 Oe.

FIG. 6. (Color online) Temperature-dependent heat capacity of YbSb2 for H = 0, 10, 20, 30, 40, 50, 60 Oe and 20, 60 kOe. The left inset shows Cp/T vs T2 for H = 0, 60 Oe, 20 kOe, and 60 kOe, showing a field-dependent Sommerfeld coefficient γ. The right inset shows the superconducting (squares) and normal (black line) electronic specific heat for H = 0, plotted as Cp/T vs T. An entropy conservation construct (red lines) is used to determine the jump in the electronic specific heat at Tc.
From a linear fit of $\Delta \rho = \rho - \rho_0$ vs $T^2$, the coefficient $A$ is determined to be 0.0013 $\mu\Omega$ cm K$^{-2}$. The Kadowaki-Woods (KW) ratio $A/\gamma^2 = 12.8 a_0$, where $a_0 = 10^{-3} \mu\Omega$ cm m$^2$ K$^2$ mJ is a nearly universal value observed in strongly correlated electron systems. This large KW ratio is consistent with the analogous value previously reported$^{21}$ and could be associated with electron-phonon scattering or enhanced electron correlations.

Based on the resistivity and heat capacity data, several superconducting parameters, such as the London penetration depth $\lambda_L$, coherence length $\xi$, Ginzburg-Landau parameter $\kappa$, and electron-phonon coupling constant $\lambda_{el-\text{ph}}$, can be estimated. With 4 formula units per unit cell volume ($V$), the electron density $n$ of YbSb$_2$ can be calculated as $n = 8/V = 2.483 \times 10^{-2}$ Å$^{-3}$, assuming the valence of Yb to be 2+. The Fermi wave vector $k_F$ can be roughly estimated if we assume a spherical Fermi surface, which gives $k_F = (3\pi^2 n)^{1/3} = 0.903$ Å$^{-1}$. The Fermi wave vector $k_F$, together with the Sommerfeld coefficient $\gamma = 3.18$ mJ mol$^{-1}$ K$^{-2} = 6.56 \times 10^{-5}$ J cm$^{-3}$ K$^{-2}$, yields the effective electron mass $m^* = h^2 k_F^2 / \pi^2 nk_B^2 = 1.39 m_0$, where $m_0$ is the free-electron mass. The London penetration depth $\lambda_L(0)$ and coherence length $\xi(0)$ can also be derived as $\lambda_L(0) = (m^*/\mu_0 n e^2)^{1/2} = 40$ nm and $\xi(0) = 0.18 h^2 k_F / k_B T_c m^* = 826$ nm. It results that the GL parameter $\kappa = \lambda_L(0)/\xi(0) = 0.05 \ll 1/\sqrt{2}$, confirming the type-I superconductivity in YbSb$_2$. According to the McMillan theory,$^{22}$ the electron-phonon coupling is given by

$$\lambda_{el-\text{ph}} = 1.04 + \mu^* \ln(\theta_D/1.45 T_c)$$

$$= (1 - 0.62 \mu^*) \ln(\theta_D/1.45 T_c) = 1.04,$$

where the Coulomb pseudopotential $\mu^*$ is usually between 0.1 and 0.15. Assuming $\mu^* = 0.13$, the electron-phonon coupling is estimated to be $\lambda_{el-\text{ph}} \approx 0.51$, suggesting that YbSb$_2$ is a weakly coupled BCS superconductor. Moreover, the $\lambda_{el-\text{ph}}$ value confirms the effective electron mass $m^*$ as calculated using $m^* = (1 + \lambda_{el-\text{ph}}) m_0$, which gives $m^* = 1.51 m_0$.

Figure 8 shows frequency $\Delta f(T) \sim \chi(T)$ measured for a 0.7 $\times$ 0.5 $\times$ 0.3 mm$^3$ sample. Data above $T_c$ represent a combination of magnetic and resistive responses in the normal state of YbSb$_2$. The skin depth at $T = 1.5$ K was estimated to be $\delta \approx 8.9$ $\mu$m, which is much smaller than any dimension of the sample. The skin depth $\delta$ was calculated with the residual resistivity $\rho_0 = 0.53 \mu\Omega$ cm and an operating frequency of 16 MHz. A slight upturn before the superconducting transition can be attributed to the response of some paramagnetic impurities. $T_c$ was determined as the temperature where $\Delta f(T)$ deviates from the normal-state behavior.

In the pure Meissner state (Fig. 8), for $H_{dc} = 0$, both ZFC and FC curves coincide. Additionally, apart from the superconducting transition, a small feature near 0.11 K was observed, as shown in the inset. This may be attributed to a phase associated with extrinsic magnetic impurities. In Fig. 9, the calculated superfluid density, $\rho = \lambda^2(0)/\lambda^2(T)$, is found to be consistent with a single-gap $s$-wave pairing in YbSb$_2$, except for the impurity contribution which modifies the curve at the lowest temperatures. In the presence of magnetic impurities with magnetic permeability $\mu(T)$, the actual measured penetration depth is renormalized as $\lambda_m = \sqrt{\mu(T)} \lambda$, so that the experimentally constructed superfluid density is

\[ \frac{\rho}{\rho_0} = \frac{\lambda^2(0)/\lambda^2(T)}{\lambda_m^2}. \]
the diamagnetism above the bulk Hc consistent with the results displayed in Fig. 8. The origin of the diamagnetism observed in the rf magnetization measurement is marked with a dashed line; the inset shows a zoomed-in view of the data points from thermodynamic measurements.

In nonzero magnetic field, ZFC-FC Δf curves (Fig. 8) show hysteresis up to H = 50 Oe. Interestingly, the FC data indicate strong repulsion below an intermediate temperature, marked with solid triangles, which systematically decreases with increasing H. This crossover no longer exists above 40 Oe, and ZFC data recover stronger repulsion. Above 70 Oe, which corresponds to first-order phase transition induced by magnetic field and isotherms (Fig. 2), a strong DPE signal in the ac magnetization is visible in specific heat data (Fig. 6). All these observations reveal unconventional behavior, as of yet not fully understood.

The superconducting and thermodynamic parameters of YbSb2 are summarized in Table I. Several traits of type-I superconductors have been observed in this compound, including a possible second superconducting state at lower temperatures observed in rf magnetization (Fig. 8), which reveals unconventional behavior, as of yet not fully understood. This calls for more experiments to elucidate the underlying physics in YbSb2.

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TABLE I. Measured and calculated superconducting and thermodynamic parameters of YbSb2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (K)</td>
<td>1.30 ± 0.2</td>
</tr>
<tr>
<td>Hc(0) (Oe)</td>
<td>55 ± 2</td>
</tr>
<tr>
<td>γ (mJ mol⁻¹ K⁻²)</td>
<td>3.18</td>
</tr>
<tr>
<td>β (mJ mol⁻¹ K⁻⁴)</td>
<td>0.90</td>
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<tr>
<td>θD (K)</td>
<td>186</td>
</tr>
<tr>
<td>ΔC/γTC</td>
<td>0.85</td>
</tr>
<tr>
<td>RRR</td>
<td>186</td>
</tr>
<tr>
<td>A(μΩ cm K⁻²)</td>
<td>0.0013</td>
</tr>
<tr>
<td>A/γ²(10⁻⁵ μΩ cm mol⁻² K² mJ⁻²)</td>
<td>12.8</td>
</tr>
<tr>
<td>kF (Å⁻¹)</td>
<td>0.903</td>
</tr>
<tr>
<td>m*(m0)</td>
<td>1.45 ± 0.06</td>
</tr>
<tr>
<td>λ∥(0) (nm)</td>
<td>40</td>
</tr>
<tr>
<td>ξ(0) (nm)</td>
<td>826</td>
</tr>
<tr>
<td>κ</td>
<td>0.05</td>
</tr>
<tr>
<td>λs−s</td>
<td>0.51</td>
</tr>
<tr>
<td>T(2) (K)</td>
<td>0.41</td>
</tr>
<tr>
<td>Hc(2)(0) (Oe)</td>
<td>430</td>
</tr>
</tbody>
</table>

and Δf (circles) below ~80 Oe can be fit to the expected BCS temperature dependence Hc(0) = Hc(0)[1 − (T/Tc)²] (solid line, Fig. 10 inset). This gives Hc(0) = 55 Oe and Tc = 1.30 K. The possible new superconducting state inferred from the rf magnetization (Fig. 8) can also be described with a similar equation, Hc(2)(0) = Hc(2)(0)[1 − (T/T(2))²] (dashed line, Fig. 10), which gives Hc(2)(0) = 430 Oe and T(2) = 0.41 K.

The superconducting and thermodynamic parameters of YbSb2 are summarized in Table I. Several traits of type-I superconductors have been observed in this compound, including a small GL parameter κ = 0.05, a typical shape of the dc M(H) isotherms (Fig. 2), a strong DPE signal in the ac magnetization (Fig. 5), small critical field values, and a change from second- to first-order phase transition induced by magnetic field and visible in specific heat data (Fig. 6). All these observations provide proof of the type-I superconductivity in YbSb2. In addition, a possible second superconducting state at lower temperatures is observed in rf magnetization (Fig. 8), which reveals unconventional behavior, as of yet not fully understood. This calls for more experiments to elucidate the underlying physics in YbSb2.