Superconducting and normal-state properties of the noncentrosymmetric superconductor Re₆Zr

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We systematically investigate the normal and superconducting properties of noncentrosymmetric Re₆Zr using magnetization, heat capacity, and electrical resistivity measurements. Resistivity measurements indicate Re₆Zr has poor metallic behavior and is dominated by disorder. Re₆Zr undergoes a superconducting transition at \( T_c = (6.75 \pm 0.05) \) K. Magnetization measurements give a lower critical field, \( \mu_0 H_{c1} = (10.3 \pm 0.1) \) mT. The Werthamer-Helfand-Hohenberg model is used to approximate the upper critical field \( \mu_0 H_{c2} = (11.2 \pm 0.2) \) T, which is close to the Pauli limiting field of 12.35 T and which could indicate singlet-triplet mixing. However, low-temperature specific-heat data suggest that Re₆Zr is an isotropic, fully gapped s-wave superconductor with enhanced electron-phonon coupling. Unusual flux pinning resulting in a peak effect is observed in the magnetization data, indicating an unconventional vortex state.

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1. INTRODUCTION

In superconductors, the inversion symmetry of the crystallographic structure plays a central role in the formation of the Cooper pairs. In conventional superconductors, each Cooper pair is formed from two electrons which belong to the same Fermi surface with a symmetric orbital state and an antisymmetric spin state. The discovery of superconductivity in CePt₃Si, a material which lacks inversion symmetry, has generated considerable experimental and theoretical interest in the physics of noncentrosymmetric (NCS) superconductors \([1–3]\). The absence of inversion symmetry in NCS materials introduces an antisymmetric spin-orbit coupling \([4,5]\) which can result in a splitting of the spin-up and spin-down conduction electron energy bands. This splitting of the Fermi surface, lifting the degeneracy of the conduction electrons, may result in a superconducting pair wave function that is an admixture of spin-singlet and spin-triplet states. Several examples of NCS superconductors where it has been established that the order parameter is not unconventional, for example, BiPd \([6]\) and PbTaSe₂ \([7]\). Singlet-triplet mixing can result from conventional superconducting systems, for example, the triplet pairing seen in Li₂(Pd, Pt)₃Si \([8–11]\), and upper critical fields close to or exceeding the Pauli limiting field \( H_{c2} \). A theoretical analysis of the possible pairing states demonstrated that a mixing of spin-singlet and spin-triplet pairing is possible in this noncentrosymmetric superconducting compound \([33,34]\). Here, we present a comprehensive characterization of the normal and superconducting states of this intermetallic compound through studies by magnetization, electronic transport, and heat capacity. We estimate several normal-state parameters of Re₆Zr such as the electronic specific-heat contribution \( \gamma_n \), residual resistivity \( \rho_0 \), and the hyperfine contribution to the specific heat. Using the electronic-transport and heat-capacity measurements, we estimate the Debye temperature by using the parallel-resistor model, the Debye lattice contribution to the specific heat at low temperature, and the Debye-Einstein model. Several superconducting parameters, including the lower and upper critical fields \( H_{c1} \) and \( H_{c2} \), the coherence length \( \xi_{cd} \), and the penetration depth \( \lambda_{cd} \), are estimated. The specific-heat jump \( \Delta C/\rho_0 T_c \), the superconducting gap \( \Delta_0/k_B T_c \), and the temperature dependence of the specific heat at low-temperature suggest that Re₆Zr is an isotropic, fully gapped s-wave superconductor with enhanced electron-phonon coupling. We also present evidence of unusual flux pinning not normally seen in low-\( T_c \) systems.
II. EXPERIMENTAL DETAILS

Polycrystalline samples of Re₆Zr were prepared by arc melting stoichiometric quantities of high-purity (4N) Zr and Re in an arc furnace under an argon (5N) atmosphere on a water-cooled copper hearth. The sample buttons were melted and flipped several times to ensure phase homogeneity. The observed weight loss during the melting was negligible. Powder x-ray diffraction data confirmed the α-Mn crystal structure and the phase purity of the samples. A low (\(\chi_{dc} = 5.8 \times 10^{-4}\)) nearly temperature independent normal-state dc susceptibility indicates there are no magnetic impurities from the Zr.

The normal and superconducting states of Re₆Zr were characterized by magnetization \(M\), ac susceptibility \(\chi_{ac}\), ac resistivity \(\rho\), and heat capacity \(C\) measurements. The dc magnetization measurements were performed as a function of temperature \(T\) at fixed field or as a function of applied magnetic field \(\mu_0 H\) at a fixed temperature in a Quantum Design Magnetic Property Measurement System (MPMS) magnetometer in temperatures ranging from 1.8 to 300 K and under magnetic fields up to 5 T. The ac susceptibility measurements were also performed in a Quantum Design MPMS with an ac applied field of 0.3 mT and a frequency of 30 Hz in dc magnetic fields up to 5 T. For field-dependent magnetization studies an Oxford Instruments vibrating sample magnetometer (VSM) was used with magnetic fields up to 10 T. Heat capacity was measured using a two-tau relaxation method in a Quantum Design Physical Property Measurement System (PPMS) at temperatures ranging from 1.9 to 300 K in magnetic fields up to 8 T. Lower-temperature measurements down to 0.5 K were carried out with a \(^3\)He insert. The samples were attached to the measuring stage using Apiezon N grease to ensure good thermal contact. Electrical resistivity measurements were made using a conventional four-probe ac technique with a measuring frequency of 113 Hz and a current of 5.1 mA in a Quantum Design PPMS. The measurements were performed at temperatures ranging from 1.9 to 300 K in magnetic fields up to 9 T. The shape of the sample used for the majority of the measurements was a rectangular prism to allow the demagnetization factor to be evaluated [35] and minimized along one direction.

III. RESULTS AND DISCUSSION

A. Electrical resistivity

Figure 1(a) shows the resistivity as a function of temperature \(\rho(T)\) of a polycrystalline Re₆Zr sample from 2 to 300 K in zero field. The small value of the residual resistivity ratio, RRR = \(\rho(300 \text{ K})/\rho(10 \text{ K})\) ≈ 1.09, and the high normal-state resistivity at 10 K indicate poor metallic behavior. This is comparable to other Re compounds such as Re₆Hf with a RRR quoted from 1.08 to 1.4 [36,37], Re₂₄Ti₅ with RRR ~ 1.3 [38], and Nb₀.₁₉Re₀.₈₂ with RRR ~ 1.3 [16]. A sharp, zero-field superconducting transition (\(\Delta T_c = 0.20 \text{ K}\)) can be seen clearly in Fig. 1(b) at \(T_c = (6.76 \pm 0.05) \text{ K}\). \(T_c\) is gradually suppressed with increasing applied magnetic field [see Fig. 1(b)], and the transition is broadened so that \(\Delta T_c = 0.28 \text{ K}\) at 9 T.

At temperatures greater than \(\sim 50 \text{ K}\) the \(\rho(T)\) of Re₆Zr is seen to flatten. This characteristic is similar to that seen in many superconductors containing d-block elements including BiPd [39]. It has been proposed that in certain compounds at high temperatures the resistivity saturates at a value that corresponds to the mean free path on the order of the inter-atomic spacing [40]. This idea was further developed by Wiesmann et al. [41] who found empirically that \(\rho(T)\) could be described by the parallel-resistor model:

\[
\rho(T) = \frac{1}{\rho_{sat}} + \frac{1}{\rho_{ideal}(T)}^{-1},
\]

where \(\rho_{sat}\) is the saturated resistivity at high temperatures and is independent of \(T\), and \(\rho_{ideal}(T)\) is the “ideal” contribution which according to Matthiessen’s rule is:

\[
\rho_{ideal}(T) = \rho_{ideal,0} + \rho_{ideal,t}(T).
\]
Here $\rho_{\text{ideal},0}$ is the ideal temperature-independent residual resistivity and $\rho_{\text{ideal},L}(T)$ is the temperature-dependent contribution which can be expressed by the generalized Bloch-Greweisen model [42]

$$\rho_{\text{ideal},L}(T) = C \left( \frac{T}{\Theta_R} \right)^n \int_0^{\Theta_R/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx,$$

(1c)

where $\Theta_R$ is the Debye temperature obtained from resistivity measurements, $C$ is a material-dependent pre-factor and $n = 3$–5 depending on the nature of the carrier scattering. Fig. 1(c) shows the normal-state resistivity data from 10 to 290 K fit using Eq. (1a). It was found that a value of $n = 3$, which takes into account umklapp scattering between bands, achieved the best fit giving $\rho_{\text{sat}} = (167 \pm 2) \mu \Omega \text{cm}$, $C = (315 \pm 6) \mu \Omega \text{cm}$ and $\Theta_R = (237 \pm 2) \text{K}$. The measured residual resistivity, $\rho_0 = (142 \pm 2) \mu \Omega \text{cm}$, which is related to $\rho_{\text{ideal},0}$ and $\rho_{\text{sat}}$ by

$$\rho_0 = \frac{\rho_{\text{ideal},0} \rho_{\text{sat}}}{\rho_{\text{ideal},0} + \rho_{\text{sat}}},$$

(2)

is consistent with the values of the fit. This electrical resistivity data is in close agreement with that previously reported in Ref. [43].

**B. Heat capacity**

The temperature dependence of the heat capacity divided by temperature, $C/T$, versus $T^2$ from 2 to 10 K is shown in Fig. 2(a), where a sharp jump at $(6.75 \pm 0.05) \text{K}$ indicates a bulk superconducting transition. The sharpness of this peak gives an indication of the high quality of the sample. We analyzed the normal-state data $C/T$ versus $T^2$ between 4.4 and 10 K at $\mu_0 H = 0 \text{T}$ using

$$C/T = \gamma_0 + \beta_3 T^2 + \beta_5 T^4,$$

(3)

where $\gamma_0$ is the normal-state Sommerfeld electronic-heat-capacity contribution, $\beta_3$ is the Debye lattice-heat-capacity contribution, and $\beta_5$ is from higher-order lattice contributions. A fit using Eq. (3) can be seen in Fig. 2(b) which gives $\gamma_0 = (26.9 \pm 0.1) \text{mJ mol}^{-1} \text{K}^{-2}$, $\beta_3 = (0.35 \pm 0.02) \text{mJ mol}^{-1} \text{K}^{-4}$ and $\beta_5 = (1.2 \pm 0.3) \mu \text{J mol}^{-1} \text{K}^{-6}$. The Debye temperature, $\Theta_D$, can then be calculated using

$$\Theta_D = \left( \frac{12 \pi^4 R N}{5 \beta_3} \right)^{1/3},$$

(4)

where $R$ is the molar gas constant and $N$ is the number of atoms per unit cell. Equation (4) gives $\Theta_D = (338 \pm 9) \text{K}$ which is slightly higher than the previously reported value [34].

Figure 2(c) shows the temperature dependence of the heat capacity up to 300 K. There is no sign of any structural phase transition, and the value of $C$ at 300 K is $169.5 \text{J mol}^{-1} \text{K}^{-1}$, which is close to classical Dulong-Petit value for Re$_2$Zr of $174.6 \text{J mol}^{-1} \text{K}^{-1}$ and is consistent with $\Theta_D > 300 \text{K}$. We fit the normal-state data using a Debye-Einstein function. It was found that by including the additional Einstein term to the Debye model for lattice heat capacity the fit could be significantly improved. Figure 2(c) shows heat-capacity data from 10 to 300 K, which was fit with [44]

$$C(T) = \gamma_0 T + n \delta C_{\text{Debye}} \left( \frac{T}{\Theta_D} \right) + n(1 - \delta) C_{\text{Einstein}} \left( \frac{T}{T_E} \right),$$

(5a)
where δ is the fractional contribution of $C_{\text{Debye}}$, $n$ is the number of atoms in a formula unit (f.u.), $C_{\text{Debye}}$ is given by

$$C_{\text{Debye}} \left( \frac{T}{\Theta_D} \right) = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$

(5b)

and $C_{\text{Einstein}}$ is given by

$$C_{\text{Einstein}} \left( \frac{T}{\Theta_E} \right) = 3R \frac{z^2 e^z}{(e^z - 1)^2},$$

(5c)

where $z = T_E/T$ and $T_E$ is the Einstein temperature. The fit was performed using a fixed value $\gamma_0 = 26.9$ mJ mol$^{-1}$ K$^{-2}$ to help reduce the number of free parameters. We obtained $\delta = 0.912 \pm 0.002$, $\Theta_D = (258 \pm 1)$ K, and $T_E = (652 \pm 12)$ K. The difference between $\Theta_D$ and $\Theta_E$ is also expected due to the limitations of the generalized parallel-resistor model.

In Fig. 2, at very low temperatures, an upturn in $C/T$ appears in magnetic fields above 6 T. This anomalous contribution to the specific heat is proportional to $T^{-3}$, which suggests that it is due to the high-temperature tail of a nuclear Schottky anomaly. The specific heat of the measured Re$_6$Zr can be expressed as

$$C(T, B) = C_{el}(T, B) + C_{ph}(T) + C_{hf}(T, B),$$

(6)

where $C_{el}$ is the electronic contribution, $C_{ph}$ is the Schottky contribution, and $C_{hf}$ is the phonon contribution. The high-temperature approximation of the nuclear hyperfine contribution to the specific heat was modeled by $C_{hf} = A_0 T^{-2}$, where $A_0$ is a field-dependent parameter. $A_0$ is estimated to be $\sim 1.4$ mK mol$^{-1}$ at 8 T, which is consistent with the value previously obtained for pure rhenium [45,46]. The results of this analysis raise a note of caution.

A hyperfine contribution to the specific heat has also been seen in other Re-based α-Mn compounds, Nb$_{0.14}$Re$_{0.86}$ [47] and Re$_6$Hf [37], as well as in pure Re [45,46], indicating that a Schottky anomaly may always be present in Re-based superconductors at low temperatures. Mazidian et al. demonstrated that in order to establish the presence of point or line nodes in the superconducting gap, the heat capacity needs to be fit below $T_c/10$ [48]. Modifications by a magnetic field below $T_c$ to both $C_{el}(T, B)$ and $C_{hf}(T, B)$ mean that a precise evaluation of the temperature dependence of the electronic specific heat and hence the gap structure in all Re-based NCS superconductors, including those with an α-Mn structure, may be challenging, as this will require an accurate evaluation of the hyperfine contribution to the specific heat.

C. Magnetization and lower critical field

Figure 3(a) shows the dc susceptibility data $\chi_{dc}(T)$ taken in zero-field-cooled warming (ZFCW) and field-cooled cooling (FCC) modes in an applied field of 1 mT. These data confirm that Re$_6$Zr is a superconductor with $T_c = (6.70 \pm 0.05)$ K. The sample exhibits a full Meissner fraction for the ZFCW. There is almost no flux expulsion on reentering the superconducting state during FCC. The strong pinning is consistent with a disordered system. Magnetization versus field sweeps in low fields (0 to 16 mT) at several temperatures are shown in Fig. 3(b). The lower critical field, $H_{c1}(T)$, is determined from the first deviation from linearity of the initial slope as the field is increased. In Fig. 3(c) the resulting $H_{c1}(T)$ values are plotted against temperature. Ginzburg-Landau (GL) theory gives

$$H_{c1}(T) = H_{c1}(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right].$$

(7)

Fitting the data using Eq. (7), $H_{c1}(0)$ was estimated to be $(10.3 \pm 0.1)$ mT.

The ac susceptibility versus temperature measurements $\chi_{ac}(T)$ shown in Fig. 4 confirm the superconducting transition of $T_c = (6.70 \pm 0.05)$ K. In dc bias fields less than $H_{c1}(0)$ the sample exhibits a full Meissner fraction. The out-of-phase component of the ac susceptibility $\chi''(T)$ contains a sharp maximum close to $T_c$ and falls to zero for lower temperatures. This is consistent with the strong flux pinning seen in the low-field FCC $M(T)$ data. For applied fields much greater than $H_{c1}(0)$, $T_c$ is suppressed, and a full Meissner fraction is not seen due to partial flux penetration. An anomalous dip can be seen close to $T_c$, suggesting flux is being reexpelled from the sample due to unusual flux dynamics. At lower temperature, $\chi''(T)$ exhibits a broad maximum, indicating losses due to flux motion in dc applied fields $\mu_0 H \geq 2$ T.
Further evidence of unusual flux pinning in Re₆Zr can be seen in the $M(H)$ loops taken in the both the superconducting quantum interference device (SQUID) magnetometer and the VSM (see Fig. 5), suggesting that the observed features cannot simply be attributed to the significant movement of the sample in a magnetic field or the magnetic field sweep rate. As is evident from Fig. 5(a), above $H_{c1}(0)$, Re₆Zr exhibits the conventional behavior for a type-II superconductor, with a hysteresis in the magnetization $\Delta M$ decreasing with increasing temperature and magnetic field. For applied fields close to $H_{c2}(T)$ this hysteresis $\Delta M$ disappears, and the magnetization becomes reversible as vortices appear to become unpinned. The inset in Fig. 5(a) shows how this irreversibility field $H_{irr}$ varies with temperature. These data were collected using a plate-shaped sample with the field applied in the plane of the plate, i.e., with the demagnetization factor of the sample minimized. By changing the sample orientation with respect to the applied field a change in vortex pinning is observed, as can be seen in Figs. 5(b) and 5(c), where the demagnetization factor was maximized. In Figs. 5(b) and 5(c) a clear secondary maximum (fishtail) is observed. As the sample is cooled, there is a slight shift to higher magnetic field in the onset and the peak of the fishtail. This behavior is not normally observed in low-$T_c$ superconductors but is quite common in the high-$T_c$ oxides and in some two-dimensional superconducting materials, indicating unconventional vortex states. The symmetry of the

FIG. 5. (a) Magnetization vs magnetic field at several temperatures for Re₆Zr. The data were collected in a VSM on a plate-shaped sample with the demagnetization factor of the sample minimized. The inset shows how the irreversibility field $H_{irr}$ varies with temperature. (b) Magnetization vs magnetic field at several temperatures collected in a vibrating sample magnetometer with the demagnetization factor of the Re₆Zr sample maximized. A secondary maximum (fishtail) can clearly be seen in the magnetization at around 1.25 T. The left inset shows the 5 and 6 K curves between 0 and 3.5 T. $H_{irr}$ and $H_{c2}$ are indicated in the right inset showing the 3.5 K curve between 2 and 10 T. (c) Magnetization vs magnetic field at several temperatures collected in the SQUID magnetometer. The fishtail can also be clearly seen in a magnetic field of $\sim$1.25 T.
vortex states in high-quality single crystals of Re₆Zr is needed to explore the vortex physics further. Instead, the Werthamer-Helfand-Hohenberg (WHH) model given by the Ginzburg-Landau formula is not appropriate. The jump in specific heat in zero field indicates the onset of bulk superconductivity. The transition temperature is defined to be the midpoint of the transition, giving $T_c = (6.75 \pm 0.05) \text{ K}$. The data in Fig. 6(a) were fit using the BCS model of the specific heat given in Ref. [49]. The entropy $S$ was calculated from

$$S = -\frac{6}{\pi^2} \int_0^\infty \frac{\Delta_0}{k_B T_c} [f \ln f + (1-f) \ln(1-f)] dy,$$

where $f$ is the Fermi-Dirac function given by $f = [1 + \exp(E/k_B T)]^{-1}$ and $E = \Delta_0 \sqrt{y^2 + \delta(T)^2}$, where $y$ is the energy of the normal-state electrons and $\delta(T)$ is the temperature dependence of the superconducting gap calculated from the BCS theory. The specific heat of the superconducting state is then calculated by

$$\frac{C}{\gamma_{nT_c}} = T \frac{d(S/\gamma_{nT_c})}{dT}.$$ 

The superconducting gap $\Delta_0/k_B T_c$ was estimated to be $1.86 \pm 0.05$, which is in agreement with Ref. [34]. For conventional BCS superconductors a value of 1.76 is expected, and the larger value for Re₆Zr indicates that the electron-phonon coupling is slightly enhanced. $\Delta C/\gamma_{nT_c} = 1.60 \pm 0.02$ is also larger than the 1.43 expected for conventional BCS superconductors and agrees with the values reported in Refs. [34,43]. A fit was also attempted using a two-gap model, but it was found that $\Delta_0/k_B T_c$ for the two gaps iterated to the same value, indicating that the material has a single gap.

To determine whether the superconducting gap is isotropic (exponential) or anisotropic (power law) it is necessary to determine the temperature dependence of the electronic component of the heat capacity down to low temperature, as shown in Fig. 6(b). Due to the difficulties in approximating the zero-field hyperfine contribution in the specific heat this contribution has also been included in Fig. 6(b). Figure 6(b) shows fits to several power laws of the form $b \times T^{N}$, where $b$ is a constant. Setting $N = 2$ or 3 the fits are poor, while $N = 5.8$ gives a good fit to the data, although this provides no physical insight. The $(C_{el} + C_{hf})$ data are best described by an exponential temperature dependence, suggesting an isotropic fully gapped $s$-wave BCS superconductor. To obtain the true nature of the superconducting gap heat-capacity data well below $T_c/10$ need to be analyzed [48]. From Fig. 6(a) it can be seen that the specific heat is rather low. A more complete understanding of the hyperfine term is required to make any further progress with this analysis. Nuclear quadrupole measurements have also been performed on Re₆Zr and provide further evidence of a conventional BCS gap symmetry [50].

### D. Superconducting gap

The jump in specific heat in zero field indicates the onset of bulk superconductivity. The transition temperature is defined as the midpoint of the transition, giving $T_c = (6.75 \pm 0.05) \text{ K}$. The data in Fig. 6(a) were fit using the BCS model of the specific heat given in Ref. [49]. The entropy $S$ was calculated from

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### E. Upper critical field

In order to measure the upper critical field as a function of temperature $H_{c2}(T)$, the shift in $T_c$ in magnetic fields of up to 9 T was determined from heat-capacity and resistivity data. Figure 7 shows how $H_{c2}$ varies with $T$. At temperatures just below $T_c$ it is clear that $H_{c2}$ increases linearly with decreasing $T$, and this indicates that the temperature dependence of $H_{c2}$ given by the Ginzburg-Landau formula is not appropriate. Instead, the Werthamer-Helfand-Hohenberg (WHH) model was used. This allows $H_{c2}(0)$ to be calculated in terms of the spin-orbit scattering and Pauli spin paramagnetism [51], as it is expected that spin-orbit coupling may be strong due to the presence of the rhenium.
where $t = T/T_c$, $\lambda_{so}$ is the spin-orbit scattering parameter, $\alpha_M$ is the Maki parameter, $\psi$ is the digamma function, $\tilde{h}$ is the dimensionless form of the upper critical field given by

$$\tilde{h} = \frac{4H_{c2}(t)}{\pi^2} \left( \frac{dH_{c2}}{dT} \right)_t^{-1},$$

(11)

and $\gamma = \sqrt{(ah)^2 - (\frac{3}{4})^2}$. It is estimated that $\mu_0H_{c2}(0) = (11.2 \pm 0.2)T$, close to the value reported by Ref. [34] but below the Pauli paramagnetic limiting field $\mu_0H_{Pauli}$ of $(12.35 \pm 0.09)T$.

The WHH expression has three variables: the Maki parameter $\alpha_M$, the spin-orbit scattering parameter $\lambda_{so}$, and the gradient at $T_c$. In their original work [51], WHH state that $\alpha_M$ is not an adjustable parameter and needs to be obtained from experimental data; thus, $\alpha_M$ was not varied during the fitting.

The Maki parameter can be estimated experimentally by using the WHH expression

$$\alpha_M = \sqrt{\frac{2}{\lambda_{c2}^{orb}(0)}} \frac{\mu_0H_{c2}(0)}{H_{co}(0)},$$

(12)

where $H_{c2}^{orb}$ is the orbital limiting field given by

$$H_{c2}^{orb}(0) = -\alpha T_c \left. \frac{-dH_{c2}(T)}{dT} \right|_{T = T_c},$$

(13)

where $\alpha$ is the purity factor, which for superconductors in the dirty limit is 0.693. The initial slope $-dH_{c2}(T)/dT|_{T = T_c}$ was found to be 2.44 T/K, giving $\mu_0H_{c2}^{orb}(0) = (11.41 \pm 0.05)T$. From Eq. (12) we obtain $\alpha_M = 1.31$, and the relative size of the Maki parameter indicates that the Pauli limiting field is non-negligible. Fixing $\alpha_M = 1.31$ produced $\lambda_{so} = 18 \pm 5$. It was found that this model is highly dependent on the starting values as an equally good fit, as judged by the reduced $\chi^2$, could be obtained by allowing the Maki parameter to vary. $\alpha_M$ was found to drift towards zero in nearly all cases along with $\lambda_{so}$, which would also tend to zero when allowed to vary. Unsurprisingly, the initial gradient $-dH_{c2}(T)/dT|_{T = T_c}$ was found to remain constant within error.

In the first case with $\alpha_M$ fixed, the value for the spin-orbit term seems unusually large. There are several reasons why the WHH model may misrepresent what is happening in the system:

1. **Two-gap superconductor.** While the analysis of the superconducting gap was assumed to be a single gap, it is possible that Re$_6$Zr is a two-gap superconductor where the gaps are of a similar magnitude, and this would give rise to some enhancement of $H_{c2}$ [52].

2. **Granularity.** The polycrystalline sample of Re$_6$Zr will contain grain boundaries. The upper critical field will be increased above the bulk value once the grain size becomes smaller than the coherence length [53] (the grain size is unknown, so contributions from this source are unclear).

3. **Spin-orbit coupling.** Strong spin-orbit coupling effects can yield large enhancements of $H_{c2}$ such that the temperature dependence of $H_{c2}$ can become linear, although in the dirty limit this enhancement should be weaker [54]. In order to obtain a more accurate value for $\mu_0H_{c2}(0)$ high-field, low-temperature measurements of $H_{c2}$ are needed in order to determine the form of the $\mu_0H_{c2}(T)$ curve much closer to $T = 0$ K.

### F. Properties of the superconducting state

The results of resistivity, heat-capacity, and magnetization measurements can now be combined in order to estimate some of the important superconducting properties of Re$_6$Zr. The Ginzburg-Landau coherence length $\xi_{GL}(0)$ can be estimated using $\mu_0H_{c2}(0)$ from [55]

$$H_{c2}(0) = \frac{\Phi_0}{2\pi \xi^2_{GL}(0)},$$

(14)

where $\Phi_0 = 2.07 \times 10^{-15}$ Wb is the magnetic flux quantum. We calculate $\xi_{GL}(0) = (5.37 \pm 0.09)$ nm, $\mu_0H_{c1}(0)$, and $\xi_{GL}(0)$ can be used to calculate the Ginzburg-Landau penetration depth $\lambda_{GL}(0)$ from the relation

$$H_{c1}(0) = \left( \frac{\Phi_0}{4\pi \lambda^2_{GL}(0)} \right) \ln \left( \frac{\lambda_{GL}(0)}{\xi_{GL}(0)} \right).$$

(15)

Using $\mu_0H_{c1} = 10.3$ mT and $\xi_{GL}(0) = 5.37$ nm, we calculated $\lambda_{GL}(0) = (247 \pm 4)$ nm. The Ginzburg-Landau parameter can now be calculated by the relation

$$\kappa_{GL} = \frac{\lambda_{GL}(0)}{\xi_{GL}(0)}.$$ 

(16)

This yields a value of $\kappa_{GL} = 46.2 \pm 0.8$. For a superconductor to be classed as a type-II superconductor $\kappa_{GL} \geq \frac{1}{\sqrt{2}}$. It is clear that Re$_6$Zr is a strong type-II superconductor.

The thermodynamic critical field $H_c$ can be calculated using $\xi_{GL}(0)$ and $\lambda_{GL}(0)$ using the relation

$$H_{c2}^{cal}(0) = \frac{\Phi_0}{2\sqrt{2\pi \xi^2_{GL}(0)\lambda_{GL}(0)}},$$

(17)

from this $H_{c2}^{cal}(0)$ is estimated to be $(175 \pm 3)$ mT. The thermodynamic critical field can be experimentally estimated from the difference between the free energies per unit volume.
of the superconducting and normal states $\Delta F$ by [55]

$$\frac{H_0^2(T)}{8\pi} = \Delta F = \int_{T_c}^{T} \int_{T_c}^{T} \frac{C_s - C_n}{T^q} dT' dT',$$  \hspace{1cm} (18)

where $C_s$ and $C_n$ are the heat capacities per unit volume. From Eq. (18) we obtain $H_0^2(0) = (130 \pm 2) \text{ mT}$.

In order to calculate the electronic mean free path and London penetration depth in Re$_6$Zr the Sommerfeld coefficient can be written as [56]

$$\gamma_e = \left(\frac{\pi}{3}\right)^{2/3} \frac{k_B^2 m^* V_{\text{fkm}} n^{1/3}}{\hbar^2 N_A},$$  \hspace{1cm} (19)

where $k_B$ is the Boltzmann constant, $N_A$ is the Avogadro constant, $V_{\text{fkm}}$ is the volume of a formula unit, $m^*$ is the effective mass of quasiparticles, and $n$ is the quasiparticle number density per unit volume. The electronic mean free path $\ell_e$ can be estimated from the residual resistivity $\rho_0$ by the equation

$$\ell_e = \frac{3\pi^2 n^2}{e^2 \rho_0 m^* \gamma_e^2},$$  \hspace{1cm} (20)

where the Fermi velocity $v_F$ is related to the effective mass and the carrier density by

$$n = \frac{1}{3\pi^2} \left(\frac{m^* v_F}{\hbar}\right)^3.$$  \hspace{1cm} (21)

In the dirty limit the penetration depth is given by

$$\lambda_{\text{GL}}(0) = \lambda_L \left(1 + \frac{\xi_0}{\ell_e}\right)^{-1/2},$$  \hspace{1cm} (22)

where $\xi_0$ is the BCS coherence length and $\lambda_L$ is the London penetration depth, which is given by

$$\lambda_L = \left(\frac{m^*}{\mu_0 \hbar^2}\right)^{1/2}.$$  \hspace{1cm} (23)

The Ginzburg-Landau coherence length is also affected in the dirty limit. The relationship between the BCS coherence length $\xi_0$ and the Ginzburg-Landau coherence $\xi_{\text{GL}}$ at $T = 0$ is

$$\xi_{\text{GL}}(0) = \frac{\pi}{2\sqrt{3}} \left(1 + \frac{\xi_0}{\ell_e}\right)^{-1/2},$$  \hspace{1cm} (24)

Equations (19)–(24) form a system of four equations. To estimate the parameters $m^*$, $n$, $\ell_e$, and $\xi_0$ this system of equations can be solved simultaneously using the values $\gamma_e = 26.9 \text{ mJ mol}^{-1} \text{ K}^{-2}$, $\xi_{\text{GL}} = 5.37 \text{ nm}$, and $\rho_0 = 142 \text{ $\mu$G cm}$. For comparison, two values of $\lambda_{\text{GL}}$ have been used: 247 nm is taken from Eq. (15), and 356 nm is taken from the $\mu$SR study in Ref. [34]. The results are shown in Table I. From the mean free path $\ell_e$ calculated in Eq. (20) and $\xi_0$ calculated in Eq. (24), it is clear that $\xi_0 > \ell_e$, indicating that Re$_6$Zr is in the dirty limit. We find that these values are in close agreement with those previously reported for Re$_6$Zr [43].

The bare-band effective mass $m_{\text{band}}^*$ can be related to $m^*$, which contains enhancements from the many-body electron-phonon interactions [57]

$$m^* = m_{\text{band}}^*(1 + \lambda_{\text{el-ph}}),$$  \hspace{1cm} (25)

where $\lambda_{\text{el-ph}}$ is the electron-phonon coupling constant. The electron-phonon coupling constant gives the strength of the interaction between electron and phonons in superconductors. This can be estimated from McMillan's theory [58] from $\Theta_D$ and $T_c$,

$$\lambda_{\text{el-ph}} = \frac{1.04 + \mu^*/(\Theta_D/1.45T_c)}{\left(1 - 0.62\mu^*/(\Theta_D/1.45T_c)\right) - 1.04},$$  \hspace{1cm} (26)

where $\mu^*$ is the repulsive screened Coulomb parameter, which can have a value between 0.1 and 0.15, but for intermetallic superconductors a value of 0.13 is typically used. Using $T_c$ and $\Theta_D$ taken from Fig. 2(b), a value of $\lambda_{\text{el-ph}} = 0.67 \pm 0.02$ is obtained, suggesting this a moderately coupled superconductor. Using this value of $\lambda_{\text{el-ph}}$ and Eq. (25), a value for $m_{\text{band}}^*$ can be found, as seen in Table I. Recently, these parameters have also been determined for the related compound Re$_6$Hf [36,37]. By substituting Zr by Hf the spin-orbit coupling should be enhanced, and it was hoped that this would provide an increase in the contribution of the spin-triplet component in the superconducting ground state. From the measurements performed in Refs. [36,37] it is clear that Re$_6$Zr and Re$_6$Zr are very similar and that the spin-orbit-coupling strength seems to have little effect on the properties of polycrystalline samples at least. Uemura et al. have described a method for classifying superconductors based on the ratio of the critical temperature $T_c$ to the effective Fermi temperature $T_F$ [59]. The values of $m^*$ and $n$ taken from Table I can used to calculate an effective Fermi temperature for Re$_6$Zr using

$$k_B T_F = \frac{\hbar^2}{2m^*} \left(\frac{3\pi^2 n}{\gamma_e^2}\right)^{2/3},$$  \hspace{1cm} (27)

and the result is presented in Table I. It has been observed that the high-$\Theta_D$, organic, heavy-fermion, and other unconventional superconductors lie in the range $0.01 \leq T_c/T_F \leq 0.1$ [59–61]. However, Re$_6$Zr lies outside of the range for unconventional superconductivity, supporting the view that the superconducting mechanism is primarily conventional.

### IV. SUMMARY

In summary, single-phase polycrystalline samples of Re$_6$Zr were prepared by the arc-melting technique. Powder x-ray diffraction data confirmed the cubic, noncentrosymmetric $\alpha$-Mn crystal structure and the phase purity of the samples. The normal-state and superconducting properties of...
Re₆Zr were studied using magnetization, heat-capacity, and resistivity measurements. We have established that Re₆Zr is a moderately coupled superconductor with a transition at $T_c = (6.75 \pm 0.05)K$. In the normal state, resistivity measurements show that Re₆Zr has poor metallic behavior that fit these data with a parallel-resistor model. Specific-heat experiments show that Re₆Zr has poor metallic behavior that any structural phase transitions down to low temperature.

The superconducting order parameter is well described by an isotropic s-wave pairing symmetry and enhanced electron-phonon coupling, despite the observation of spontaneous magnetization associated with TRS breaking being observed at temperatures below the superconducting transition in previous work [34]. This suggests Re₆Zr has a superconducting ground state that features a dominant s-wave component, while the exact nature of the triplet component is undetermined. In order to determine if the superconductivity is nonunitary, further experimental work on high-quality single crystals, as well as further analysis of “clean” and “dirty” samples to examine the role grain boundaries and impurities play in determining the superconducting behavior of Re₆Zr, is vital.

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**TABLE II.** Normal-state and superconducting properties of Re₆Zr.

| Re₆Zr property | Units | Value |
|----------------|-------|-------|
| $T_c$          | K     | 6.75 ± 0.05 |
| $\rho_0$       | $\mu\Omega\ \text{cm}$ | 142 ± 2 |
| $\rho_{sat}$   | $\mu\Omega\ \text{cm}$ | 167 ± 2 |
| $\Theta_R$ (from resistivity) | K | 237 ± 2 |
| $\Theta_0$ (from Sommerfeld coefficient) | K | 338 ± 9 |
| $\Theta_0$ (from Debye-Einstein fit) | K | 258 ± 1 |
| $T_E$         | K     | 652 ± 12 |
| $\gamma_0$    | mJ mol⁻¹ K⁻² | 26.9 ± 0.1 |
| $\beta_3$     | mJ mol⁻¹ K⁻⁴ | 0.35 ± 0.02 |
| $\beta_5$     | $\mu J$ mol⁻¹ K⁻⁶ | 1.6 ± 0.1 |
| $\lambda_{el-ph}$ |       | 0.67 ± 0.02 |
| $\Delta C/\gamma_0 T_c$ |       | 1.60 ± 0.02 |
| $\Delta_0/\kappa_0 T_c$ |       | 1.86 ± 0.05 |
| $\mu_0 H_1(0)$ | mT | 10.3 ± 0.1 |
| $\mu_0 H_2(0)$ | T | 11.2 ± 0.2 |
| $\mu_0 H^{cal}(0)$ | mT | 175 ± 3 |
| $\mu_0 H^{exp}(0)$ | mT | 130 ± 2 |
| $\mu_0 H_{orbital}(0)$ | T | 11.41 ± 0.05 |
| $\mu_0 H_{Pauli}(0)$ | T | 12.35 ± 0.09 |
| $\xi_{GL}(0)$ | nm | 5.37 ± 0.09 |
| $\lambda_{GL}(0)$ | nm | 247 ± 4 |
| $\kappa_{GL}(0)$ |       | 46.2 ± 0.8 |

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