Evidence for *s*-wave superconductivity in noncentrosymmetric Re_3W from magnetic penetration depth measurements

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We report measurements of the temperature dependence of the magnetic penetration depth $\lambda(T)$ in noncentrosymmetric superconductor Re_3W. We employed two experimental techniques: extraction of $\lambda(T)$ from magnetic dc susceptibility, measured on a powder sample, and the rf tunnel diode resonator technique, where a bulk polycrystalline sample was used. The results of both techniques agree: the temperature dependence of the penetration depth can be well described by weak-coupling, dirty-limit, *s*-wave BCS theory where we obtain $\Delta(0)/k_BT_C=1.76\pm0.05$. No evidence for unconventional pairing resulting from the absence of the inversion symmetry is found.

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I. INTRODUCTION

Superconductors possessing a crystal structure without an inversion center are a focus of current research.[1–13] The lack of inversion symmetry means that parity P is not a good quantum number, i.e., electronic states cannot be labeled as either even or odd under inversion $\mathbf{r}\rightarrow-\mathbf{r}$. As a consequence, a Cooper pair's internal angular momentum $\mathbf{S}$ is not necessarily even ($S=2n$) or odd ($S=2n+1$) under such transformation (n=integer). The physical interaction that breaks inversion symmetry is the antisymmetric spin-orbit interaction. Its presence may lead to a pairing state with a mixed singlet-triplet character. This, in turn, may form nodes in the gap function, easily detectable by measurements of the magnetic penetration depth $\lambda(T)$.[14]

A fully gapped, isotropic pairing state produces a thermally activated behavior of the superfluid density, $\rho_s \propto \lambda^{-2}(T) \propto 1-[2\pi\Delta(0)/T]^{1/2}e^{-\Delta(0)/k_BT}$ at low temperatures, meaning that $\lambda^{-2}(T)$ hardly changes at $T<0.3T_C$ (for a review, see Ref. 14). On the other hand, it is known that line nodes in the gap cause the superfluid density to display a power law behavior, $\lambda^{-2}(T)\propto 1-aT^n$, where n may equal 1 (such is the case in clean *d*-wave cuprates[15,16]), 2 (dirty cuprates[17]), 3 [T^3 behavior was reported in electron-doped $Pr_{1.86}Ce_{0.14}CuO_4$ (Ref. 18) and in certain organic superconductors[19]].

As for the compounds without inversion symmetry, a nonexponential temperature dependence of $\lambda^{-2}(T)$ that implies a superconducting gap with nodes has, indeed, been found in $CePt_3Si$ (Ref. 2) and Li_2Pt_3B.[3]

The model of Hayashi *et al.*[4] allows the calculation of the temperature-dependent $\lambda(T)$ for a given magnitude of singlet and triplet (or *s*-wave and *p*-wave) components. It produces a good agreement with experiment in the case of noncentrosymmetric Li_2Pt_3B and Li_2Pd_3B.[3]

Superconductivity in the intermetallic compound Re_3W was first studied in the 1960s.[20,21] It was found to have a superconducting transition temperature $T_C\sim 9$ K and a crystal structure without an inversion center. This makes it a good system for the present study, because we can access the low-temperature region, $T<0.3T_C$, needed to relate the change of the penetration depth to the gap structure. Another reason why this material is a good candidate is that atomic numbers Z of both constituents are large, 75 for Re and 74 for W. Large Z promotes spin-orbit interaction, which breaks the inversion symmetry. Re_3W crystallizes in a so-called α-Mn or A12 structure. As far as we know, there has been no detailed calculation of electronic spectra for this particular structure or subsequent experimental work on this material since the original work.[21] In fact, we are aware of only two investigations on the Re-W system: a purely metallurgical study by Tournier *et al.*[22] and a calculation of stability of various Re-W phases by Persson *et al.*[23]

II. EXPERIMENT

Re_3W samples used in the present study were prepared from elemental starting materials (Alfa AESAR) containing less than 0.001% total impurities. Powdered Re was mixed with powdered W in the molar ratio 3:1, and the mixture was pressed into pellets using a hydraulic press. Subsequently, pellets were individually arc-melted in high-purity Ar atmosphere and then annealed for 14 days at 1773 K in either an atmosphere of flowing high-purity argon or high vacuum, and then allowed to cool. Synchrotron x-ray powder diffraction patterns were collected at the X7A beamline at the Brookhaven National Laboratory. Time-of-flight neutron diffraction data were collected at the HIPD diffractometer at the Los Alamos Neutron Scattering Centre.

The diffraction pattern of Re_3W can be almost completely indexed assuming I-centered cubic (α-Mn) lattice (trace amount of Re metal could be detected with an estimated weight fraction of 1%). The Rietveld refinement has shown that the studied material belongs to the symmetry group $I\bar{4}3m$, with cubic unit cell size $a=9.596\,56(5)$ Å. The sym-

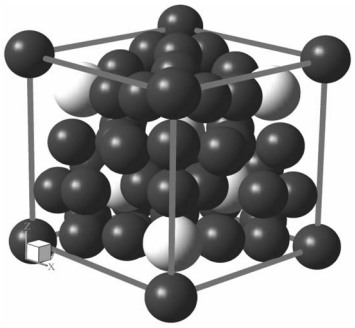

FIG. 1. Crystal structure of noncentrosymmetric Re_3W, obtained by Rietveld refinement of x-ray and neutron powder diffraction data. From neutrons, the position 8c (white) is occupied predominantly by W. Atoms shown in black can be either Re or W.

metry group $I\bar{4}3m$ includes an inversion axis of fourth order and, therefore, lacks an inversion center. The crystal structure is shown in Fig. 1.

Neutron diffraction data indicate considerable Re/W redistribution, i.e., a deviation from the stoichiometric 3:1 ratio at each crystallographic site. The exact distribution pattern over the four available sites cannot be established unambiguously from the present data. However, it is likely that the (8c) position (located at about a third of the way along the unit cell diagonal, shown in white in Fig. 1) is occupied exclusively by W. The arrangement of these crystallographically equivalent sites in the unit cell demonstrates the absence of inversion.

Pair distribution function analysis of neutron diffraction data revealed only minor deviations from the average (crystallographic) structure. Consequently, the disorder effects, e.g., a reduction of the electronic mean free path, are associated predominantly with the compositional disorder (the three remaining sites occupied jointly by Re and W).

We have measured the magnetic penetration depth $\lambda(T)$ by two well-established and independent methods: through measurement of the dc susceptibility $\chi(T)$ of a collection of small particles dispersed in epoxy, and from the change in resonance frequency of a tunnel-diode driven oscillator operating at 10 MHz.

In the first technique, a bulk sample of annealed Re_3W (T_C=7.4 K) was ball-milled into a powder with resulting particle size of the order of 10 μm. The particle size distribution and an average aspect ratio of 0.6 were determined by direct optical microscopy analysis. Eight milligrams of powder (±0.1 mg) were mixed with epoxy in a gelatin capsule and cured for an hour at room temperature in an applied magnetic field of 6 T. Curing in field induces alignment of the paramagnetic particles with their long dimension parallel to the field, thereby reducing their demagnetizing ratio. Measurement of the dc susceptibility of this sample was performed in a Quantum Design MPMS superconducting quantum interference device magnetometer in the applied field of 3 Oe at temperatures down to 1.85 K ($0.25T_C$).

The epoxy and other addenda showed an insignificant amount of diamagnetism, about 0.5% that of the actual sample in the above temperature range. Care was taken to ensure the linearity of response, i.e., independence of the

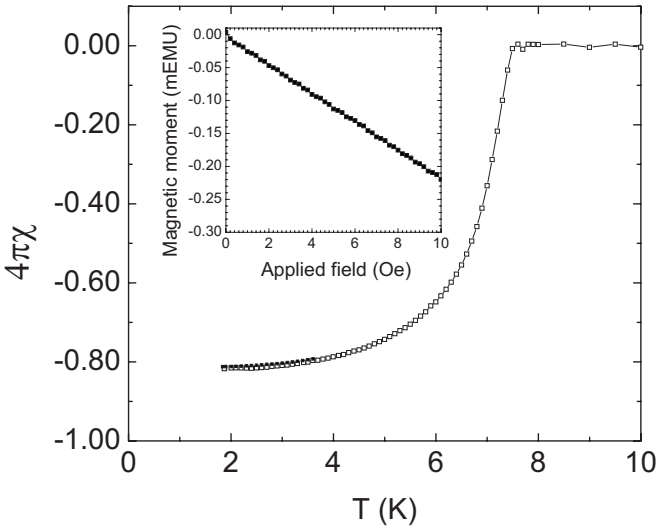

FIG. 2. dc susceptibility vs T for powder Re_3W. Applied field is 3 Oe. Higher resolution data were taken at lower temperature, $T<3.6$ K (solid squares). Inset: The magnetic moment is linear in field up to at least 10 Oe (T=5 K).

measured χ on the applied field strength. The inset of Fig. 2 shows that at T=5 K, the measured magnetic moment is linear in field up to at least 10 Oe. It should be mentioned that samples cured in zero field and likely having randomly oriented particles did not have an appreciable linear region.

It is unclear to us at present why the T_C of our material is lower than originally reported in Ref. 20. Our samples were annealed for an extended time at high temperature, then quenched, while the original work dealt with unannealed material. Unannealed material made in our laboratory has T_C close to the original finding, albeit with high degree of inhomogeneity. The phase diagram of the Re-W system shows multiple phases near 3:1 composition. It is possible that more than one of them is superconducting.

For the analysis of the experimental data, we assume that the powder particles have an elongated ellipsoidal shape with short semiaxis R and use the expression (see, e.g., Ref. 24)

$$4\pi\chi = -\frac{1}{1-D}\left(1 - \frac{3\lambda}{R}\coth\frac{R}{\lambda} + \frac{3\lambda^2}{R^2}\right) \quad (1)$$

to relate the measured susceptibility to λ. With D=1/3, the equation above is appropriate for a sphere, but we use it here with an average particle's demagnetizing factor D=0.22, based on the measured aspect ratio. Next we average over the measured particle size distribution and invert Eq. (1) numerically to obtain λ. Since it is λ/R that enters Eq. (1), it turns out that accurate knowledge of particle sizes is important only for the determination of the absolute value of λ, but not for the normalized quantity $\lambda(T)/\lambda(0)$. In our case, the particles are still large compared with the penetration depth, therefore we do not obtain the correct absolute value of λ. The temperature dependence $\lambda(T)/\lambda(0)$, on the other hand, is insensitive to R. The absolute value of the penetration depth for our samples was estimated from measurements of the

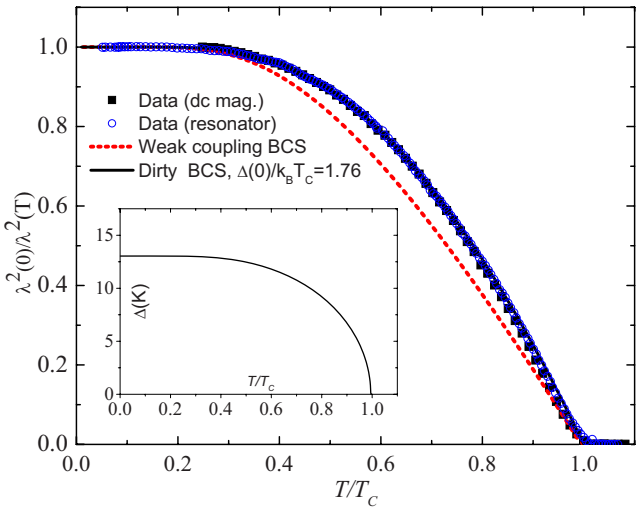

FIG. 3. (Color online) Temperature dependence of normalized superfluid density $\lambda^2(0)/\lambda^2(T)$. Squares, data from dc magnetization measurement; circles, tunnel-diode resonator method; dotted line, clean limit, weak-coupling BCS curve $\lambda_L^{-2}(T)$; and solid line, dirty-limit BCS calculation with $\Delta(0)/k_BT_C=1.76$, weak-coupling value. Inset: Energy gap $\Delta(T)$.

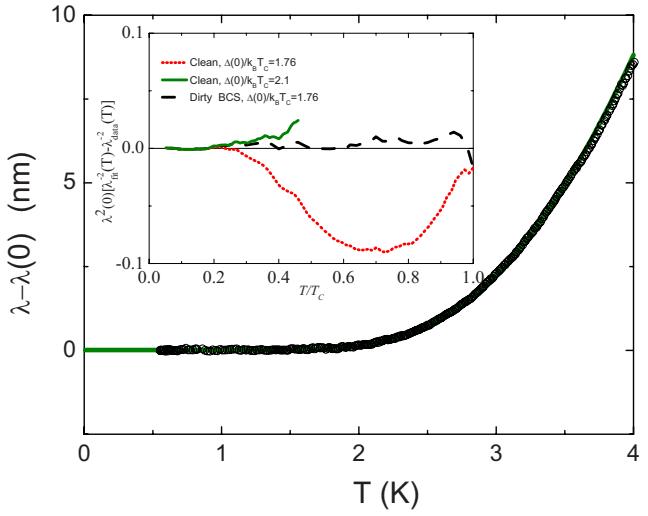

FIG. 4. (Color online) Low-temperature change in $\lambda(T)$ relative to zero-temperature value $\lambda(0)$. The solid line is a clean-limit BCS fit, producing $[\Delta(0)/k_BT_C]_{\text{clean}}=2.1$. Inset: Quality of fit for dirty limit [Eq. (2)] (black dash) and clean limit with $[\Delta(0)/k_BT_C]_{\text{clean}}=1.76$ (red dots) and 2.1 (green solid line).

lower and upper critical fields and the Ginzburg-Landau parameter κ, yielding $\lambda(T=0)=300\pm10$ nm.

The second technique is the tunnel-diode resonator where a self-resonating LC tank circuit is powered by a tunnel diode.[14,25] A bulk polycrystalline sample was used. The sample is inserted into a coil, whose inductance then changes and causes the shift of the resonant frequency, Δf. This shift is proportional to the magnetic susceptibility χ of the sample and, thus to the London penetration depth λ (in the Meissner state), $\Delta f=-4\pi\Delta f_0\chi$, where Δf_0 is a sample shape and volume dependent calibration constant. At low temperatures, $\chi=-(4\pi)^{-1}[1-\lambda/R\tanh(R/\lambda)]$, where R is the effective sample dimension.[25] High stability (0.1 ppb) where ppb denotes parts per 10^9 and small excitation field amplitude ($\sim$20 mOe) result in sub-Angstrom precision of the measurements.

III. RESULTS

We will discuss both the powder sample and bulk sample measurements together. The dc susceptibility $\chi(T)$ is shown in Fig. 2. Higher resolution data were taken between 1.85 and 3.6 K (solid squares) by averaging the magnetic moment over several measurements at each temperature.

The extracted normalized superfluid density $\lambda^2(0)/\lambda^2(T)$ is shown in Fig. 3 by solid squares (dc susceptibility) and open circles (resonator experiment).

Measurements in polycrystals are somewhat difficult to quantify, so we attempt to describe the data from several angles. Figure 3 (main frame) shows the extracted superfluid density [in the case of the resonator, $\lambda(0)=300$ nm was used in the data analysis]. The agreement between the two measurements is excellent. Data are shown by symbols, and lines through the data are s-wave weak-coupling BCS theory in the dirty limit, for which the superfluid density is (theory in Ref. 26)

$$\left[\frac{\lambda^2(0)}{\lambda^2(T)}\right]_{\text{dirty}}=\frac{\Delta(T)}{\Delta(0)}\tanh\left(\frac{\Delta(T)}{2k_BT}\right). \tag{2}$$

The temperature dependent gap, $\Delta(T)$, was obtained as a solution of the self-consistent gap equation in the full temperature range (Fig. 3, inset). Both data sets can be fitted well by the above equation, where we obtain $[\Delta(0)/k_BT_C]_{\text{dirty}}=1.76\pm0.05$, the standard BCS value. It is possible to get a good fit assuming weaker electronic scattering, but this would require slightly increased coupling strength. In order to estimate the maximum deviation from weak coupling, we calculate the London penetration depth in the clean limit according to[26]

$$\left[\frac{\lambda^2(0)}{\lambda^2(T)}\right]_{\text{clean}}=1+\int_{\Delta(T)}^{\infty}\frac{\partial f}{\partial E}\frac{E}{\sqrt{E^2-\Delta^2(T)}}dE, \tag{3}$$

where $E=[(\varepsilon-\mu)^2+\Delta(T)^2]^{1/2}$ is the elementary excitation energy and $f=[e^{E/k_BT}+1]^{-1}$ is the Fermi function. This expression assumes isotropic s-wave pairing state and spherical Fermi surface. The dashed line in Fig. 3 is the clean-limit BCS result with $\Delta(0)=1.76k_BT_C=1.1$ meV, shown for comparison. Loosening the constraint on $\Delta(0)$ and treating it as an adjustable parameter, we performed fitting of the low-temperature portion of the $\lambda(T)$, as shown by the solid line in Fig. 4. The advantage of this procedure is that it does not require assumptions regarding $\lambda(0)$. The best fit was achieved at $[\Delta(0)/k_BT_C]_{\text{clean}}=2.1\pm0.1$. This serves only as an upper bound on the gap magnitude. As discussed below, we believe this material to be in the dirty limit, where Eq. (2) applies. The dirty BCS fit to the data is essentially perfect in the entire temperature range, as shown in the inset of Fig. 4.

IV. DISCUSSION

The main conclusions that we draw from the data are that the superfluid density in these Re_3W samples is adequately described within a BCS framework and no appreciable influence of spin-triplet pairing is detected. This makes Re_3W different from a $CePt_3Si$ but similar to Li_2Pd_3B.[3] In the latter case, the spin-triplet component of the order parameter was noticed, but it was smaller than spin singlet, thus making for a nodeless (but anisotropic) gap. In our case, however, no contribution from spin triplet is detected at all. This is somewhat surprising, given the large atomic numbers of both Re and W, which must promote strong spin-orbit interactions in this material.

A possible reason for the absence of a spin-triplet component may be significant disorder. From resistivity measurements, we estimated an electronic mean free path of 1.5 nm, while the BCS coherence length is much longer, $\xi_0 = \hbar v_F / \pi \Delta_0 \approx 200$ nm with a reasonable assumption about the Fermi velocity, $v_F \simeq 10^6$ m/s. Thus, the material appears to be quite dirty because of Re/W disorder, as mentioned before. If the order parameter has nodes, even nonmagnetic impurities suppress T_C very effectively (this happens, for example, in high-T_C cuprates). It is possible that the triplet component has been effectively suppressed by scattering. In Refs. 10 and 11, the effect of impurities on mixed-pairing superconductivity was considered. The end result was that the unconventional pairing channel was suppressed by nonmagnetic impurities, similar to the Abrikosov-Gorkov T_C suppression in conventional superconductors by impurities with permanent magnetic moments. In contrast, disorder reduces T_C in the conventional channel, but does not suppress it to zero.

Finally, in *d*-wave cuprates, scattering fills in electronic states at the gap nodes, thereby suppressing the superfluid density at low temperatures and changing T-linear to T^2 behavior.[17] It is possible that a similar mechanism is at play here, masking a power law behavior of $\lambda^{-2}(T)$.

In closing, we suggest that Re_3W material with less disorder should be explored to clarify the existence of mixed-parity pairing in this compound.

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