Letter

Niobium in the clean limit: An intrinsic type-I superconductor

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Niobium is one of the most researched superconductors, both theoretically and experimentally. It is enormously significant in all branches of superconducting applications, from powerful magnets to quantum computing. It is therefore imperative to understand its fundamental properties in great detail. Here, we use the results of recent microscopic calculations of anisotropic electronic, phonon, and superconducting properties, and apply a thermodynamic criterion for the type of superconductivity, more accurate and straightforward than a conventional Ginzburg-Landau parameter κ-based delineation, to show that pure niobium is a type-I superconductor in the clean limit. However, disorder (impurities, defects, strain, stress) pushes it to become a type-II superconductor.

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I. INTRODUCTION

Niobium metal is one of the most important materials for superconducting technologies, from superconducting radio-frequency (SRF) cavities [1], to superconducting circuits for sensitive sensing [2] and quantum informatics [3]. Numerous experimental works report measurements on different samples, from almost perfect single crystals to disordered films [3–12]. Likewise, numerous theories explore its properties from microscopic calculations to phenomenological theories [1,13–19]. It is impossible to acknowledge a multitude of relevant references, so we will limit ourselves to the specific topic of this Letter.

Despite various attempts, first-principles calculations of the absolute values of the critical fields, in particular the upper critical field H_{c2}, remain in poor agreement with experiment. As a result, either the temperature dependence of the normalized field, usually as introduced by Helfand and Werthamer, $h^* \equiv H_{c2}(T)/T_c H'_{c2}(T = T_c)$ [20], is calculated [21], or calculations use experimental parameters, such as Fermi velocities v, to fit the data [15]. Considering that $H_{c2} \sim v^{-2}$, this makes a significant difference. As we show in this Letter, this is no fault of the theorists, but rather a quite ambiguous experimental determination of the critical fields. This, in turn, is no fault of the experimentalists, because it is clear that Nb is extraordinarily susceptible to the disorder with its experimental residual resistance ratio RRR $\equiv R(300\text{ K})/R(T_c)$, ranging between 3 and 90 000 [4,9].

Previously, the problem of the identification of the type of superconductivity was analyzed in detail at arbitrary temperatures [22,23]. It was argued that instead of a conventional criterion based on the Ginzburg-Landau parameter, $\kappa = \lambda/\xi$, one has to use the ratio of the upper and thermodynamic critical fields, $h_{c2,c} \equiv H_{c2}/H_c$. Alternatively, it could be the ratio of $h_{c,c1} \equiv H_c/H_{c1}$, but superheating [24,25] and various surface barriers [26,27] make the experimental determination of the lower critical field H_{c1} difficult. Only when $h_{c2,c} > 1$ do vortices form and the material can be identified as a type-II superconductor. As it is shown in Refs. [22,23], the κ-based criterion coincides with the thermodynamic criterion only at T_c, and not even within a small temperature interval below T_c. In other words, the slopes of the temperature-dependent $h_{c2,c}(T)$ and $\kappa(T)$ are different at T_c. In anisotropic superconductors, the same sample can be type I in one orientation of the magnetic field, and type II in another [22].

Of course, in the case of significantly different λ and ξ, the difference between the two criteria is not that important and this is why the type of most superconductors was correctly identified using the Ginzburg-Landau parameter κ. Moreover, it is well known that there are practically no proven nonelemental type-I superconductors, except for a few suggested compounds, such as $Ag_5Pb_2O_6$ [28], $YbSb_2$ [29], OsB_2 [30], and $PdTe_2$ [31]. However, until the intermediate state is directly observed instead of a mixed state of Abrikosov vortices by magnetosensitive imaging techniques, the type-I status of these materials will remain "pending."

Niobium seems to be a difficult case, because, by all accounts, it is situated close to the crossover boundary and can be easily moved deeper into the type-II side by nonmagnetic disorder, which increases the London penetration depth λ and decreases the coherence length ξ. Magnetic disorder, on the other hand, pushes a superconductor into the opposite direction Recently high-quality magneto-optical imaging of Nb single crystals with RRR = 500 has revealed directly and unambiguously a clear structure of the intermediate state [12].

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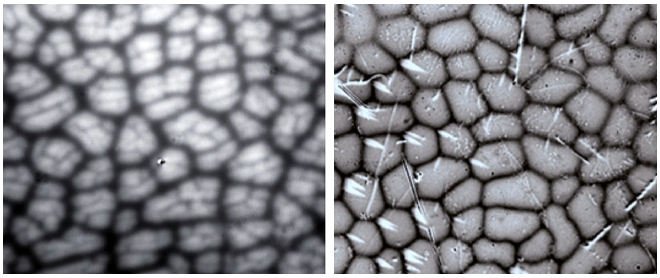

FIG. 1. Left: The intermediate state in a single-crystal Nb [Ref. [12], Fig. 3(a)]. Right: The intermediate state in a single-crystal Pb, [Ref. [33], Fig. 2(g)]. [Left frame reprinted with permission from S. Ooi, M. Tachiki, T. Konomi, T. Kubo, A. Kikuchi, S. Arisawa, H. Ito, and K. Umemori, Observation of intermediate mixed state in high-purity cavity-grade Nb by magneto-optical imaging, Phys. Rev. B **104**, 6 (2021). Copyright (2021) by the American Physical Society.]

These images are strikingly similar to images by one of us (R.P.) for the commonly accepted type-I superconductor, pure lead [32–34]. They are so similar that the authors of Ref. [12] write in their paper, "The observed patterns of the IMS [intermediate mixed state] are rather similar to that of the Meissner and normal domains in the intermediate state of the type-I superconductor, Pb reported by Prozorov *et al.* [32,33]." This is, indeed, the case.

The tendency to type-I behavior of elemental metals is not unique to niobium. A clear crossover from a type-I (confirmed by magneto-optical imaging [35]) to a type-II regime upon introduction of nonmagnetic scattering was convincingly demonstrated in tantalum [35,36]. In known type-II vanadium, the Ginzburg-Landau parameter κ approaches the borderline value of $1/\sqrt{2}$ toward type-I behavior with an increase of the residual resistivity ratio [37].

Figure 1 compares the intermediate state structure in niobium and lead single crystals. The visual similarity is remarkable. Of course, depending on the material, its properties, and the proximity to the crossover boundary, the fine details vary. For example, here the field-cooled (FC) image is shown for Nb, and zero-field-cooled (ZFC) image is shown for Pb. Upon field cooling, the intermediate state in Pb breaks into a corrugated laminar structure, whereas in Nb it apparently further breaks into large flux tubes, only reinforcing our earlier conclusion that the equilibrium topology of the intermediate state in type-I superconductors is tubular, rather than laminar [32]. Since the textbooks tell us that the true intermediate state structure is described as laminar, stripy, or labyrinthlike, the observation of the tubular features was often interpreted as some kind of crossover "intermediate mixed state" when vortices gather into "domains" as illustrated in Fig. 4(e) of Ref. [12]. However, no evidence of individual vortices was found in such structures. For a variety of magneto-optical images of superconductors, the reader is referred to Ref. [38]. In our interpretation, the authors of Ref. [12] have observed a genuine intermediate state in a clean-limit Nb crystal, proving experimentally that Nb is a type-I superconductor. We now check whether the microscopic theory agrees.

II. PROPERTIES OF NIOBIUM FROM THE MICROSCOPIC THEORY

Recently, based on the density functional theory (DFT) calculations of the electron and phonon band structures, microscopic superconducting properties of elemental niobium were determined using Eliashberg formalism [19]. It was found that pure Nb is a two-active-band, two-gap superconductor. The bands are moderately anisotropic with temperature-dependent anisotropies. The more anisotropic band 2 dominates the electronic properties. For analytical estimates, we use isotropic BCS formulas, but then we use two-band averaged rms values from Ref. [19]. Specifically, $v = \sqrt{\langle v^2 \rangle}$, the rms value of the Fermi velocity is given by $v = \sqrt{n_1 v_1^2 + n_2 v_2^2}$, where partial densities of states (DOS), $n_{1,2} = N_{1,2}(0)/(N_1 + N_2)$, and a similar equation was used for the rms superconducting gap. We compare analytical results with the full numeric evaluation of anisotropic equations. This Letter uses cgs units throughout. We calculate critical fields analytically at $T = 0$ and $T = T_c$ and their ratios and compare them with the Ginzburg-Landau criterion for the type of superconductor.

Here, we summarize the parameters used from Ref. [19]. The densities of states at the Fermi level are $N_1(0) = 6.33 \times 10^{33} \mathrm{ergs}^{-1}\,\mathrm{cm}^{-3}$, $N_2(0) = 3.98 \times 10^{34}\ \mathrm{ergs}^{-1}\,\mathrm{cm}^{-3}$, $N_{\mathrm{tot}}(0) = 4.61 \times 10^{34}\ \mathrm{ergs}^{-1}\mathrm{cm}^{-3}$. The averaged rms velocities are $v_1 = 4.37 \times 10^7$ cm/s, $v_2 = 7.62 \times 10^7$ cm/s, and the two-band average, $v = 7.26 \times 10^7$ cm/s. The rms averaged superconducting gaps are $\Delta_1(0) = 3.14 \times 10^{-15}$ ergs, $\Delta_2(0) = 2.53 \times 10^{-15}$ ergs, and $\Delta(0) = 2.62 \times 10^{-15}$ ergs. For comparison, the weak-coupling BCS gap is $\Delta_{\mathrm{BCS}}(0) = 1.7638 T_c = 2.27 \times 10^{-15}$ ergs with $T_c = 9.33$ K. The Fermi energy of Nb is $E_F = 5.32$ eV $= 8.52 \times 10^{-12}$ ergs [39]. The total carrier density is $n = 5.56 \times 10^{22}$ cm^{-3} and the effective electron mass is $m^* = 2.14 m_e$ [13]. Note that two-band averaged values are very close to band 2 values, reflecting its dominant character.

Let us now estimate various quantities using analytic limiting cases from the BCS theory. The upper critical field at $T = 0$ is given by [20]

$$H_{c2}(0) = \frac{\phi_0}{2\pi\xi^2} = \frac{\phi_0 \pi k_B^2 T_c^2}{2\hbar^2 v^2} \exp(2 - C),$$

where $C = 0.577\,216$ is the Euler constant. Technically, two bands will have two different characteristic coherence lengths [40]. Of course, there is only one upper critical field, but a formal substitution of the bands' Fermi velocities gives $H_{c2}(0) = 1053$ and 346 Oe for bands 1 and 2, respectively. These values are far from the reported values of 3–5 kOe [4,15,21]. For the two-band average, $H_{c2}(0) = 381$ Oe. The coherence lengths formally corresponding to these fields are $\xi(0) = 56$ and 97 nm for bands 1 and 2, respectively, and $\xi(0) = 93$ nm for the two-band average. For comparison, the BCS coherence length is

$$\xi_0 = \frac{\hbar v}{\pi \Delta(0)},$$

which gives $\xi_0 = 47$ and 101 nm for bands 1 and 2, respectively, and $\xi_0 = 98$ nm for the two-band average.

The thermodynamic critical field is given by

$$H_c(0) = 2\sqrt{\pi N(0)}\sqrt{\langle \Delta^2(0)\rangle},$$

and we obtain $H_c(0) = 1993$ Oe. Note a substantial difference between this value and the much lower "upper" critical fields above. On the other hand, this field scale is quite close to what was determined as experimental critical fields in clean samples [4,14], considering that it is very difficult to distinguish hysteresis loops of relatively pure niobium and, for example, lead with some pinning [32].

III. TYPE-I SUPERCONDUCTIVITY IN CLEAN-LIMIT NIOBIUM METAL

According to Ref. [22], the natural way to predict the type of a superconductor is to examine the ratio of $h_{c2,c} \equiv H_{c2}/H_c$. While Ref. [22] provides a recipe for calculating this ratio at all temperatures, here we only need to consider $T = 0$ and $T = T_c$ for which analytic expressions are available. If the gap anisotropy is described by the order parameter, $\Delta(T, k) = \Psi(T)\Omega(k)$, where the angular part is normalized over the Fermi-surface average, $\langle\Omega^2\rangle = 1$, then for the magnetic field along the c axis [22],

$$h_{c2,c}(0) = \frac{\phi_0 k_B T_c}{\hbar^2 v_0^2\sqrt{\pi N(0)}} \exp\left\langle \Omega^2 \ln\frac{|\Omega|}{\mu_z}\right\rangle, \tag{1}$$

where $\mu_z = (v_x^2 + v_y^2)/v_0^2$, and v_0 is the characteristic velocity scale (equal to Fermi velocity in the isotropic case),

$$v_0 = \left(\frac{2E_F^2}{\pi^2\hbar^3 N(0)}\right)^{1/3}.$$

For band 2, we have $v_{0,2} = 6.81 \times 10^7$ cm/s and using total DOS, $v_{0,\text{tot}} = 6.48 \times 10^7$ cm/s. In particular, for the isotropic case, $\langle\mu_c\rangle = 2/3$, and $\langle\ln\mu_c\rangle = 2(\ln 2 - 1)$, which then reproduces the Helfand-Werthamer result [20],

$$h_{c2,c}(0) = \frac{\phi_0 k_B T_c}{\hbar^2 v_0^2\sqrt{\pi N(0)}} \exp[-2(\ln 2 - 1)].$$

Using the two-band average, we obtain $h_{c2,c}^{\text{2bands}}(0) = 0.221$, while using only band 2 we obtain $h_{c2,c}^{\text{band2}}(0) = 0.216$.

For $T \to T_c$ we have in general

$$h_{c2,c}(T_c) = \frac{3\sqrt{2}\phi_0 k_B T_c}{\hbar^2 v_0^2\sqrt{7\zeta(3)\pi N(0)}} \frac{\sqrt{\langle\Omega^4\rangle}}{\langle\Omega^2\mu_z\rangle}, \tag{2}$$

where $\zeta(3) = 1.2021$ is Riemann's zeta function. In the isotropic case this reduces to

$$h_{c2,c}(T_c) = \frac{3\sqrt{2}\phi_0 k_B T_c}{\hbar^2 v_0^2\sqrt{7\zeta(3)\pi N(0)}}.$$

For the two-band average we obtain $h_{c2,c}^{\text{2bands}}(T_c) = 0.175$, and for band 2, $h_{c2,c}^{\text{band2}}(T_c) = 0.171$. Looking at the previous two equations it is easy to see that their ratio is a pure number, $h_{c2,c}(0)/h_{c2,c}(T_c) = 1.263$, independent of material properties. However, the ratio does depend on the anisotropy of the Fermi surface and of the order parameter via Fermi-surface averages of the terms containing functions of $\Omega(k)$. Indeed, the result for the Fermi-surface average appearing in Eq. (1) based on the band structure and Eliashberg results for the Fermi velocity and anisotropic gap function at $T/T_c = 0.32$ yield

$$\left\langle \Omega^2 \ln\left(\frac{|\Omega|}{\mu_z}\right)\right\rangle = 0.98, \tag{3}$$

which gives $h_{c2,c}(0) \approx 0.319$. Thus, pure, single-crystalline Nb is in the type-I limit based first-principles calculations of the gap and Fermi-surface anisotropy [19].

An additional method to verify the consistency of the above analysis is to use the fact that at $T = T_c$ [22],

$$h_{c2,c}(T_c) = \sqrt{2}\kappa_{\text{GL}},$$

where Ginzburg-Landau κ_{GL} is given by

$$\kappa_{\text{GL}} = \frac{3\phi_0 k_B T_c}{\hbar^2 v^2\sqrt{7\zeta(3)\pi N(0)}}.$$

Evaluating for the two-band average, we obtain at T_c, $\kappa_{\text{GL}} = 0.123$, and then indeed $\sqrt{2}\kappa_{\text{GL}} = 0.175 = h_{c2,c}(T_c)$. In another limit, $T = 0$, we can evaluate $\kappa(0) = \lambda(0)/\xi(0)$. In the isotropic approximation, the London penetration depth becomes

$$\lambda(0) = \frac{c}{e}\sqrt{\frac{m^*}{4\pi n}} \approx 33 \text{ nm}.$$

Thus,

$$\kappa(0) = \frac{33 \text{ nm}}{93 \text{ nm}} = 0.355 < \frac{1}{\sqrt{2}} = 0.71.$$

Therefore, even this simple estimate based on isotropic London theory gives the value of κ corresponding to type-I superconductivity. A more straightforward thermodynamic criterion based on the ratio of the critical fields gives the values of $h_{c2,c}$ clearly lower than one, which places niobium in the domain of type-I superconductivity. The situation, however, quickly changes with the addition of nonmagnetic scattering. The upper critical field grows linearly with the scattering rate [40–42] and quickly exceeds H_c. Magnetic impurities, on the other hand, would bring H_{c2} down, but they will also suppress T_c [23,41].

For applications of SRF cavities for particle accelerator technology it is desirable to stabilize Nb closer to a type-I phase where one can increase the superheating field by engineering the disorder profile very close to the superconducting-vacuum interface, leaving much of the London penetration region in the clean limit [43,44]. In quantum informatics where thin films are used, perhaps switching to the epitaxial growth instead of ablation-type sputtering would improve the RRR, and hence improved device performance.

IV. CONCLUSIONS

It is shown that using the parameters of recent microscopic calculations of superconducting and electronic properties of pure Nb, the estimated ratio of the upper and thermodynamic critical fields, H_{c2}/H_c, changes from 0.22 at $T = 0$, to 0.18 at T_c. These values place clean-limit niobium squarely into the domain of type-I superconductivity. This conclusion is firmly supported by the direct magneto-optical observation of the intermediate state in Nb single crystals with RRR = 500 [12]. It is suggested that ever-present disorder and impurities drive the real material to a type-II side in most samples studied by experimentalists so far.

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