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Comments on deviations of the penetration depth of niobium from BCS calculations

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The temperature and frequency dependences of the magnetic field penetration depth $\lambda(T,\omega)$ of superconducting Nb show deviations from the BCS theory. These deviations are discussed. It is indicated that inhomogeneities in Nb can adequately account for them.

Up till now, all measurements on the change of the magnetic field penetration depth in Nb [1–7] with temperature $\Delta\lambda(T)$ could not be described by the BCS theory[8] for homogeneous Nb with a smooth surface. Attempts to parameterize the deviations in behavior from homogeneous Nb include two energy gaps[1] and shorter mean free paths (mfp) near the surface.[4–7] Proposed explanation for the deviations are surface roughness[2,3] and inhomogeneities in superconducting Nb.[4,5] In the following we will explain that surface roughness is not able to consistently describe the experiments—in contrast to inhomogeneities. In the experiments such inhomogeneities in the polycrystalline Nb develop most likely while cooling Nb from elevated temperatures in uhv and handling in air at room temperatures, where strong oxidation[9] together with O and H [10] dissolution occurs.

Before we discuss the present model, the $\Delta\lambda(T)$ measurements proposed in Ref. 8 have to be summarized: At low frequencies ($<10^8$ Hz) $\Delta\lambda(T)$ is measured with a cylindrical Nb sample, which is part of a LC circuit.[1–3,7] In the GHz region $\Delta\lambda(T)$ is measured by the eigenfrequency of a Nb cavity surrounded by vacuum. A typical plot of the low-frequency behavior is shown in Fig. 1.[7] There the prominent deviations from the BCS theory are as follows: The *step* at about 7 K $\{y=[1-(T/T_c)^4]^{-1/2}\approx 1.15\}$; see also Refs. 1–3. The *steep slope* $d\lambda/dT$ between 8 and 9 K. This slope is steeper by a factor of 2 compared to the slope given by the bulk mfp of about 1200 Å. Accompanied with the above two deviations is a change[2] of $d\lambda/dT$ near T_c, because

$$\int_0^{T_c} dT\,\frac{d\lambda}{dT} = \lambda_{NL} = \text{normal conduction penetration depth}$$

does not change.

The step at 7 K occurs for various surface treatments, viz., ultrahigh vacuum (uhv) treatment, electropolish and chemical polish or anodization. The step is quite large and corresponds, e.g., at 30 kHz in Fig. 1, to a 600-Å-superconductor pushing out the field. The enhanced slope $d\lambda/dT$ between 8 and 9 K varies with treatment being the smallest after anodizing of heat-treated samples. Up until now no quantitative relation between surface treatment and the mentioned deviations from the BCS theory have been found. This is due to the fact that the surface treatments are only understood qualitatively. For example, it is usually assumed that electropolishing or anodizing gives smoother surfaces than a uhv treatment. But even for a given treatment, like the uhv firing,[3] one cannot compare different experiments, because the vacuum is not measured at the hot Nb sample; it is measured near the cold pump. In addition, all the experimental samples have been handled in air, where strong oxidation[9] and hydrogen pickup[10] are known to occur. Hence, the Auger measurements cited in Refs. 2 and 3 are not representative of sample surfaces used in the measurement of $\Delta\lambda(T)$.

The above-mentioned deviations (see, for example, Fig. 1) cannot be explained consistently by *roughness* of the surface alone: As calculated in Ref. 11, one needs grooves of a depth and separation of $4\lambda(T)$ to obtain an enhancement of the geometry factor G of about 80%; and the surfaces[2–4,6,7] are smoother as shown by scanning electron microscopy. Beside this quantitative argument, roughness cannot explain the step at 7 K and its disappearance with frequency.

In contrast to roughness, *inhomogeneous superconducting* Nb can explain the $\Delta\lambda(T,\omega)$ results. Such inhomogeneities are, for example, indicated most clearly by H_{c2} close to the surface being by more than a factor of 2 larger than H_{c2} of the bulk.[12] Among the inhomogeneities, grain boundaries and some habit planes are most effective, especially because O [13] and H [14] segregate to such internal surfaces. Below 400 °C H and O dissolve, diffuse,[14,15] and precipitate in a surface layer, especially along habit planes, so that these regions become superconducting below 7 K.[16] Above 7 K these nor-

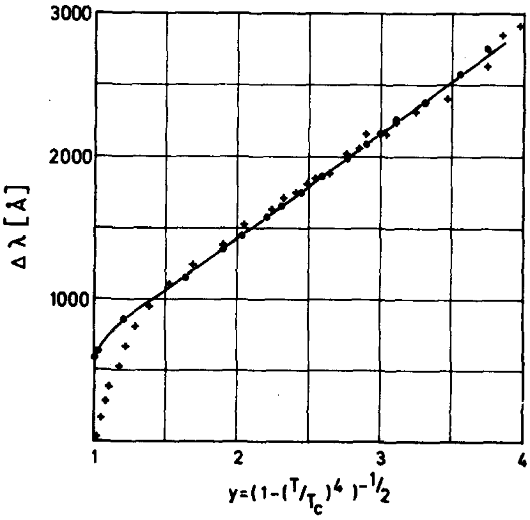

FIG. 1. Penetration depth change $\Delta\lambda(T, 3\times10^4$ Hz) with temperature (+) of a machined and chemically polished (2 μ) Nb sample (Ref. 7). The BCS theory (●) between 8 and 9 K fits the data (+) with a surface mean free path $l_s\simeq 180$ Å, compared to $l\simeq 1200$ Å in the bulk.

mal conducting two-dimensional regions force the ac shielding currents to penetrate locally into the material to a depth corresponding to the normal conducting penetration depth λ_{NL} of NbO_x. In the formula for the inductance change $\Delta L = \Delta\lambda(T)G$, the geometry factor G is, therefore, drastically changed at 7 K. This change can be described by $G = G_0(1 + \alpha 2\lambda_{NL})$, where α is the number of, e.g., grain boundaries per unit length. For example at 30 kHz (Fig. 1), the increase of $d\lambda/dT$ by a factor of 2 compared to the slope between 8 and 9 K expected from the BCS theory for $l \approx 1200$ Å is explained by $\lambda_{NL}(NbO_x) \approx 0.03$ cm and $\alpha = 18$/cm. At 7 K this normal conductor becomes superconducting, which leads to a sudden decrease of λ_{NL}. This change in G by a factor of 2 yields a step in $\Delta\lambda$ of $(2-1)\,\lambda\,(T \approx 6.5\ \text{K}) \approx 600$ Å. This agrees with the result $\Delta\lambda \approx 600$ Å shown in Fig. 1. Because $\lambda_{NL} \propto \omega^{-1/2}$ becomes smaller with increasing frequency, the enhanced slope and the step weaken, as observed.

The above discussion showed that, whereas surface roughness alone is insufficient to explain the $\Delta\lambda(T,\omega)$ deviations from the BCS theory, grain boundaries in Nb give a quantitative description. These grain boundaries near the Nb surface become normally conducting at about 7 K due to O and H precipitates.

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