# Mechanism of the Size Dependence of the Superconducting Transition of Nanostructured Nb

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A direct measurement of the superconducting energy gap by point contact spectroscopy in nanostructured Nb films shows that the gap decreases with a reduction in the average particle size. The superconducting $T_c$, obtained from transport and magnetic measurements, also decreases with size and scales with the energy gap. The size dependence of the superconducting properties in this intermediate coupling type II superconductor is therefore governed by changes in the electronic density of states rather than by phonon softening. Consistent with the Anderson criterion, no $T_c$ was observed for sizes below 8 nm.

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A fundamental problem in nanoscience research is to provide a conceptual description of the nature of the ground state in confined systems. In particular, despite several decades of active research [1–11], a satisfactory understanding of the modification of superconductivity at reduced length scales is yet to be achieved. Changes in superconducting properties may be expected when the effective size of a superconductor is reduced below its characteristic length scales, such as the London penetration depth $\lambda_L(T)$ or the coherence length $\xi(T)$. Since long-range order cannot persist down to the zero dimensional limit, it is interesting to probe how superconducting properties evolve below these length scales. A complete destabilization of superconducting order is expected when the system size is so small that the electronic level spacing becomes larger than the bulk superconducting energy gap ($\Delta$). Thus, the so-called Anderson criterion [2] suggests that, in principle, superconductivity may persist at length scales much below $\xi$.

Experimental studies of superconductivity in mesoscopic systems fall in two broad categories. The first deals with isolated grains or compacted powders. In weak and intermediate coupling type I superconductors such as Al [1,3,4], In [1,4], and Sn [4,5], $T_c$ is reported to be enhanced for particle sizes below $\approx 100$ nm. In the strong coupling superconductor, Pb [1,4,6], many early reports show no change in $T_c$ down to a few nm. However, a recent study [7] of isolated grains of Pb reports a size-induced decrease in $T_c$ till superconductivity is completely lost below a critical size. The observations are explained on the basis of the discretization of the electronic energy levels [2,12] and softening of the surface phonon modes [13–15]. The calculations predict both an increase and a decrease in $T_c$. The second category of experiments was carried out on quench-condensed, disordered superconducting thin films (Sn, Pb, In, etc.) evaporated on substrates cooled to 4 K [8,10,13]. These films consist of 100–200 nm superconducting islands connected through a two-dimensional network of Josephson junctions. Though the grain size in these films may not be precisely known, superconductivity is gradually destroyed with increasing sheet resistance when the film thickness is below ~5 nm. This has been attributed to rapid phase fluctuations between the grains in the two-dimensional network though the individual grains are believed to remain superconducting [10].

Here, we report the evolution of $T_c$ and the superconducting energy gap ($\Delta$) with decreasing particle size in sputter-deposited nanostructured films of Nb. For Nb ($\Delta \approx 1.6$ meV and $\xi \approx 38$ nm), the electron-phonon coupling strength, $2\Delta/k_BT_c \approx 3.9$, falls between In (3.6) and Pb (4.5) [16]. Films with an average grain size, $D > 25$ nm, show bulk superconductivity with $T_c \approx 9.4$ K. There is a gradual suppression of $T_c$ between 20 and 8 nm. Consistent with the Anderson criterion, no superconducting transition was detected below 8 nm. Also, there is no size-dependent *enhancement* in $T_c$ in nano-Nb. Finally, we demonstrate a direct correlation between the measured values of $\Delta$ and $T_c$ in nano-Nb, which was found to remain in the intermediate coupling BCS regime down to 8 nm. Thus, the evolution of superconductivity with particle size in Nb is quite distinct from that in other weak and strong coupling superconductors studied so far.

Nanostructured films of Nb ($\approx 0.5$ $\mu$m thick) were deposited on oxidized Si substrates by high-pressure magnetron sputtering from elemental Nb targets [17]. The particle size was varied in the 5–60 nm range by controlling the sputtering gas (Ar) pressure, the power, the deposition time, and the substrate temperature. The average particle size and size distribution were determined from x-ray diffraction line profile analysis [18] and transmission electron microscopy. The sample consists of a dense aggregate of nanoparticles separated by a poorly conducting intergranular region [19]. This can be visualized as a network of *weakly connected* superconducting grains. The weak link Josephson junction character of the intergranular regions was established from a study of the current-voltage characteristics. To this extent the nanostructured films are similar to quench-condensed films [8,10], but the similarity ends here since the film thickness does not affect superconducting properties in the essentially 3D nano-Nb films.

 

Magnetization and transport measurements were carried out using a Quantum Design MPMS SQUID magnetometer and a liquid-He cryostat, respectively. The superconducting energy gap ($\Delta$) was measured using a custom-designed point contact spectroscopy setup. A mechanically cut Pt-Ir tip was brought in contact with the film using a differential screw technique, and the resulting conductance spectra were analyzed to determine $\Delta$.

Figures 1(a) and 1(b) show the temperature dependence of the magnetic susceptibility and resistivity for the nano-Nb films with different particle size. The $T_c$s obtained from both measurements coincide for all the samples [Fig. 1(c)], and we observe a monotonic decrease in the $T_c$ from 9.4 to 4.7 K between 20 and 8 nm. Below 8 nm, no superconducting transition was observed down to the lowest measurable temperature of 1.76 K. There is also a steady increase in the lattice parameter with decreasing size [Fig. 1(c)], the origin of which has been discussed elsewhere [17]. Since our measurements were made on nanostructured films with closely packed grains, it is important to establish that the electrons are localized within the grains, before ascribing the observed variation of $T_c$ to finite size effects. The superconducting grains need to be weakly coupled for the film as a whole to behave as a disordered Josephson junction network with a well-defined, macroscopic $T_c$. Quench-condensed films that are known to form such a weakly coupled disordered Josephson junction network [20] display a pronounced hysteresis in the current-voltage ($I$-$V$) characteristics when the current is swept across the critical current. Apart from that with the largest size ($D = 60$ nm, $T_c = 9.4$ K), all other nano-Nb films show a clear hysteresis in the $I$-$V$ characteristics with increasing and decreasing current (Fig. 2), confirming the weakly coupled nature of the grains. The reduction in $T_c$ can therefore safely be attributed to size effects.

The evolution of the superconducting gap ($\Delta$) with particle size was studied by point contact spectroscopy at several temperatures below $T_c$. Several contacts were made for each film and the conductance vs voltage ($G = dI/dV$ vs $V$) characteristics of the junction recorded. Figure 3 shows representative $G$-$V$ spectra for contacts on four films with different particle sizes. The value of $\Delta$ was determined by fitting the spectra with the Blonder-Tinkham-Klapwijk theory [21] with $\Delta$, $Z$ (barrier parameter), and $\Gamma$ (broadening parameter [22]) as fitting parameters [23]. $\Delta$ varies from its bulk value, $\Delta(0) \approx 1.60$ meV for the film with $D = 60$ nm to $\Delta(0) \approx 0.90$ meV for $D = 11$ nm ($T_c = 5.9$ K). Significantly, we observe a direct correlation between $T_c$ and $\Delta$ [Fig. 4(a)]. This confirms that the destruction of superconductivity in these films is an intrinsic property of the grains and not caused by rapid phase fluctuation between adjacent grains as observed in quench-condensed films in which $\Delta$ remains unchanged [10]. The linear relation between $\Delta$ and $T_c$ also indicates that Nb remains in the intermediate coupling limit down to the smallest size [24]. This is confirmed by the observed temperature variation of $\Delta$, which can be fitted well (for all sizes) with the behavior expected from the weak coupling BCS theory [Fig. 4(b)].

It is important to point out that the poorly conducting intergranular region (that leads to localization of the electronic wave function) controls the normal-state resistivity, but should affect neither $T_c$ nor $\Delta$. This is clearly supported by the excellent agreement between the $T_c$ measured by dc magnetization and electrical transport. For the measure-

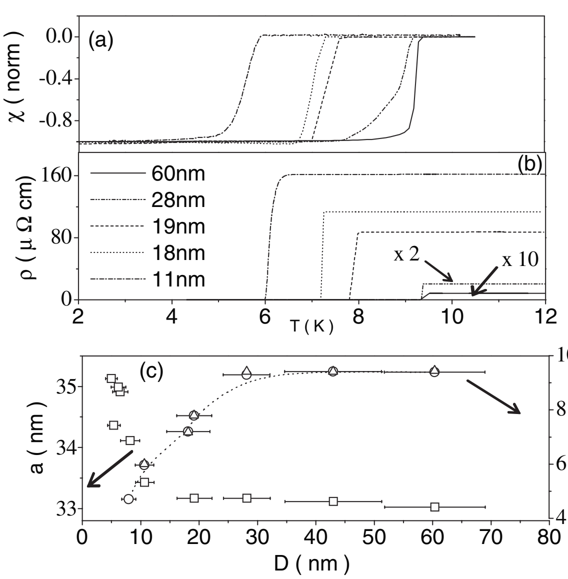


FIG. 1. Temperature dependence of (a) magnetic susceptibility ($M/H$), and (b) resistivity in nanostructured thin films of Nb with different average particle size. (c) Size dependence of the superconducting transition temperature ($T_c$) obtained from magnetization (open circles) and resistivity (open triangles) measurements (scale on right). (c) Also shows the size dependence of the lattice parameter (open squares) in nano-Nb (scale on left). The width of the measured size distribution is indicated by the error bars.

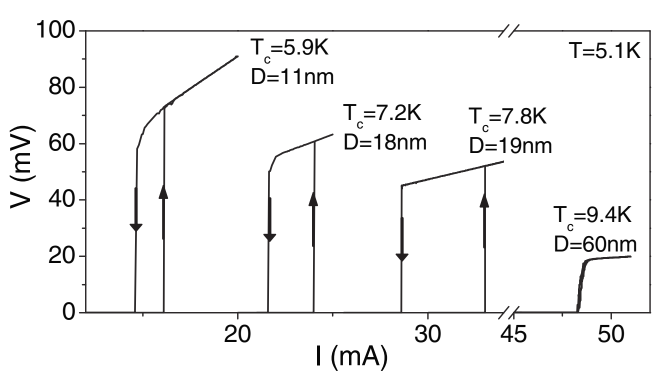


FIG. 2. $I$-$V$ characteristics (with increasing and decreasing current) of the nanostructured Nb samples with $T_c = 9.4$, 7.8, 7.2, and 5.9 K measured at 5.1 K. The sample with an average size ($D$) of 60 nm shows bulklike behavior.

ment of $\Delta$, the contact diameter was a few nm (a condition necessary for the contact to be in the ballistic regime), so that the contact is formed on a single grain. Tunneling through a nonconducting layer would just contribute to the barrier parameter ($Z$) and not affect the value of $\Delta$.

The two mechanisms usually invoked to account for the size dependence of $T_c$ involve the softening of the phonon spectrum [13,14] and the change in the electronic density of states (DOS) due to discretization [12] of the energy bands. The first mechanism assumes that individual grains consist of a surface shell in which the phonon frequency ($\omega$) is reduced from its bulk value. From the McMillan equation [15], $T_c = \frac{\Theta}{1.45} \exp[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}]$, where $\Theta$ is the Debye temperature, $\mu^*$ the Coulomb coupling constant, and $\lambda$ the electron-phonon coupling constant ($\sim 1/\langle\omega^2\rangle$), one can show that a lowering of the phonon frequency results in an increase in the effective electron-phonon coupling, and hence the $T_c$. This is widely believed to be the reason for the $T_c$ enhancement in weak coupling superconductors [3,13]. In strong coupling superconductors or for very small particle sizes, this effect is offset by an increase in the low frequency phonon cutoff arising from quantization of the phonon wave vector, and effectively suppressing the $T_c$ [25,26]. Note that any change in $T_c$ caused by a change in the electron-phonon coupling constant should also be accompanied by a change in $2\Delta/k_B T_c$. In the particular case of strong coupling superconductors, where $T_c$ decreases with decreasing $D$, $\Delta$ is nevertheless expected to show a measurable increase. This is clearly incompatible with our observations. Similarly, the size-dependent lattice expansion observed by us [Fig. 1(c)] would cause an increase in the amplitude and a reduction in the frequency of the ionic vibrations (phonon softening) with decreasing size. This should also lead to an increase in the electron-phonon coupling constant, contrary to our observations.

The second mechanism based on changes in the DOS due to quantization [27] of the electron wave vector was developed [12] to explain the destruction of superconductivity in very small particles. Solving the discrete version of the BCS equation, one can show that the quantization of electronic states leads to a suppression of $\Delta$ through a modification of the DOS, $N(0)$, at the Fermi level. Now, $T_c$ and $\Delta$ are related to $N(0)$ through the same functional form. Thus, for weak coupling superconductors $\Delta(0) = 2\hbar\omega_D \exp[-1/N(0)V]$ and $k_B T_c = 1.13\hbar\omega_D \exp[-1/N(0)V]$. Hence, any variation in the $T_c$ arising from this mechanism should be associated with a proportionate variation [26] in $\Delta$. The linear relation between $\Delta$ and $T_c$ seen in our films strongly indicates that the second mechanism plays a dominant role in nano-Nb while the effect of phonon softening is negligible [28].

It is pertinent to ask why the effect of phonon softening, so ubiquitously claimed to play a dominant role in superconducting nanoparticles, is not observed in Nb. The softening of the surface phonon modes has been typically demonstrated through molecular dynamic simulations for particles with a thickness of a few monolayers [14]. This effect could be compensated if the surface phonon spectrum is qualitatively different from the bulk, e.g., if the surface stabilizes in a crystallographic structure different from the bulk. This is, indeed, a possibility in Nb, in view of the appreciable lattice expansion ($\approx 6\%$) exhibited at

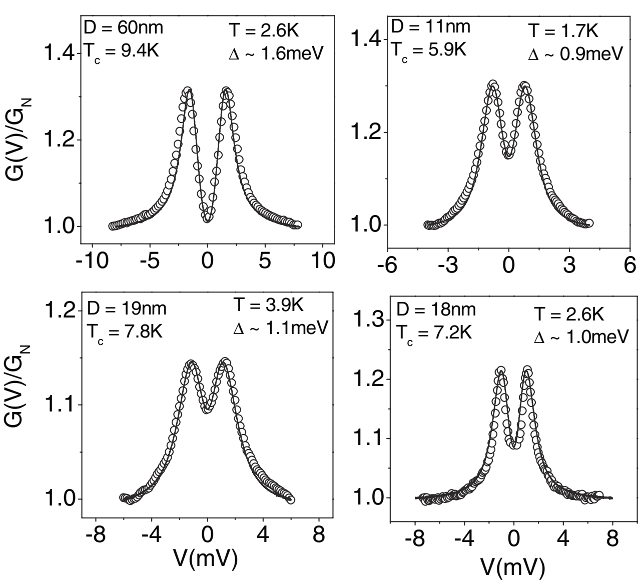


FIG. 3. Point contact Andreev reflection spectra for nanostructured Nb samples with $T_c = 9.4$, 7.8, 7.2, and 5.9 K. The open circles show the conductance data (normalized to the conductance in the normal state) while the solid line is the fit to the Blonder-Tinkham-Klapwijk theory.

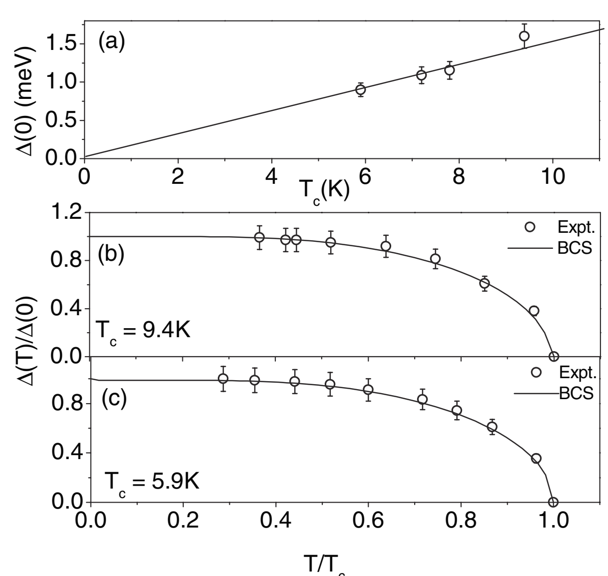


FIG. 4. (a) Variation of superconducting gap $\Delta(0)$ with the $T_c$, and (b) temperature dependence of $\Delta(T)$ with the reduced temperature for two typical samples of nano-Nb, with $T_c = 5.9$ K, and $T_c = 9.4$ K.

small particle sizes [Fig. 1(c)]. This is in sharp contrast with In, Sn, or Al, in which the lattice parameter changes by less than 0.2%. We also point out that an unambiguous proof of the involvement of surface phonon softening in the size dependence of $T_c$ requires direct measurements of $\Delta$ and $T_c$ (such as reported here) to determine if $2\Delta/k_BT_c$ varies with particle size. Measurements on granular Al particles [29] show that $2\Delta/k_BT_c$ increases with decreasing particle size, which is in contrast with our observation in Nb.

In summary, we have reported a detailed investigation of the evolution of superconductivity with particle size in nanostructured films of Nb. We have shown that, contrary to previous expectations, the electron-phonon coupling is not significantly affected by a decrease in the particle size and the superconductor remains in the intermediate coupling limit down to 8 nm. Our results strongly indicate that the size dependence of superconductivity in Nb is primarily governed by the changes in the electronic density of states and not by changes in the electron-phonon coupling due to surface effects, as suggested earlier for In, Sn, and Al. However, in view of the results described here, it would be instructive to confirm, even in those systems, the validity of the surface phonon softening mechanism through a similar study of $2\Delta/k_BT_c$ to estimate the actual change in electron-phonon coupling strength with decreasing particle size.

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