Shape resonances in the superconducting order parameter of ultrathin nanowires

A. A. Shanenko
Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

M. D. Croitoru
EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
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We study the shape-resonance effect associated with the confined transverse superconducting modes of a cylindrical nanowire in the clean limit. Results of numerical investigations of the Bogoliubov–de Gennes equations show significant deviations of the energy gap parameter from the bulk value with a profound effect on the transition temperature. The most striking is that the size of the resonances is found to be by order of magnitude larger than in ultrathin metallic films with the same width.

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Modern rapid miniaturization of electronic circuits requires good understanding of basic mechanisms responsible for the electronic properties of nanoscale structures. The most important point about these structures is that the quantum-confinement effects play the corner-stone role in this case. One can even say in general that recent success in nanofabrication technique has resulted in great interest in various artificial physical systems with unusual phenomena driven by the quantum confinement (quantum dots, nanoscale semiconductors, nanosuperconductors, etc.). The quantum-confined superconductivity is of special interest here due to the macroscopic quantum character: any effect on electron wave functions manifests itself directly in the superconducting order parameter.

An obvious consequence of the confinement in a nanoscale superconducting structure is nonuniform spatial distribution of the superconducting condensate because, as is known since the classical papers by Gor'kov[1] and Bogoliubov,[2] the superconducting order parameter can be interpreted as the wave function of the center-of-mass motion of a Cooper pair. It is also known that the Cooper-pair wave function involves important in-medium terms.[3] In the presence of the electron confinement these terms can result in shape resonances in the energy gap parameter, another confinement effect first found and investigated in the paper by Blatt and Thompson[4] for ultrathin metallic films. A shape resonance in the dependence of the energy-gap parameter on the specimen dimensions can occur any time when an electron subband appearing due to the size quantization passes through the Fermi surface.[4] Strong indications for such behavior are found not only in ultrathin films but also in nanoparticles (see, for example, Refs. 5 and 6) and superfluid nuclei[7,8] (as it had been predicted by Blatt and Thompson). Recently a new technique of electrodeposition into extended nanopores has been developed,[9] which makes it possible to produce single-crystal nanowires of high quality. Thus, the shape resonances in the nanowire superconducting order parameter can be investigated in the clean limit, with a direct link to the microscopic (BSC) theory. In particular, it is of importance to explore the situation where the QPS (quantum phase slips) regime[9–12] is expected to generate a new low-temperature metallic phase with proliferating quantum phase slips of the superconducting order parameter (for radii less than 5 nm).[13] The point is that when calculating the QPS energy barrier[9,13] in ultrathin nanowires, one assumes the superconducting order parameter being uniform in the transverse direction but with the phase slips in the longitudinal one.[13] The absolute value of the order parameter is set to be equal to the bulk one. However, at a resonant point the superconducting condensate shows significant spatial variations in the transverse direction, and its mean absolute value can be much larger than that of the bulk material. Note that the quantum confinement can influence the superconducting state by two channels. The first is due to change in electron wave functions (this is a main reason for the shape-resonance effect) whereas the second is connected with the confined phonons. Both channels were examined for ultrathin metallic films,[14] which make it possible to expect that confinement modifications of the phonon modes can produce quantitative corrections if the nanowire width is less than or about 2 nm. In the present work the first channel is under consideration while the phonons are taken to be the same as in the bulk material. Thus, below we investigate the shape-resonance effect associated with the confined transverse superconducting modes of an ultrathin nanowire in the clean limit.

To explore the superconducting order parameter varying with position, one should use the Bogoliubov–de Gennes (BdG) equations.[15] We are interested in numerical solutions of BdG equations taken in the absence of magnetic field for a superconducting cylinder with the radius R and length L. In all the calculations L remains the same and equal to 2000 nm while R is varied from 1 nm to 10 nm. In the absence of magnetic field the superconducting order parameter $\Delta(\mathbf{r})$ can be chosen as a real quantity (phase effects are beyond the scope of our consideration) and the BdG equations have the form

$$E_n u_n(\mathbf{r}) = \left(-\frac{\hbar^2}{2m^*}\nabla^2 - \mu \right) u_n(\mathbf{r}) + \Delta(\mathbf{r}) v_n(\mathbf{r}), \qquad (1)$$

$$E_n v_n(\mathbf{r}) = \Delta(\mathbf{r}) u_n(\mathbf{r}) - \left(-\frac{\hbar^2}{2m^*}\nabla^2 - \mu \right) v_n(\mathbf{r}), \qquad (2)$$

where E_n stands for the quasiparticle spectrum, μ is the chemical potential, and m^* denotes the electron band mass.

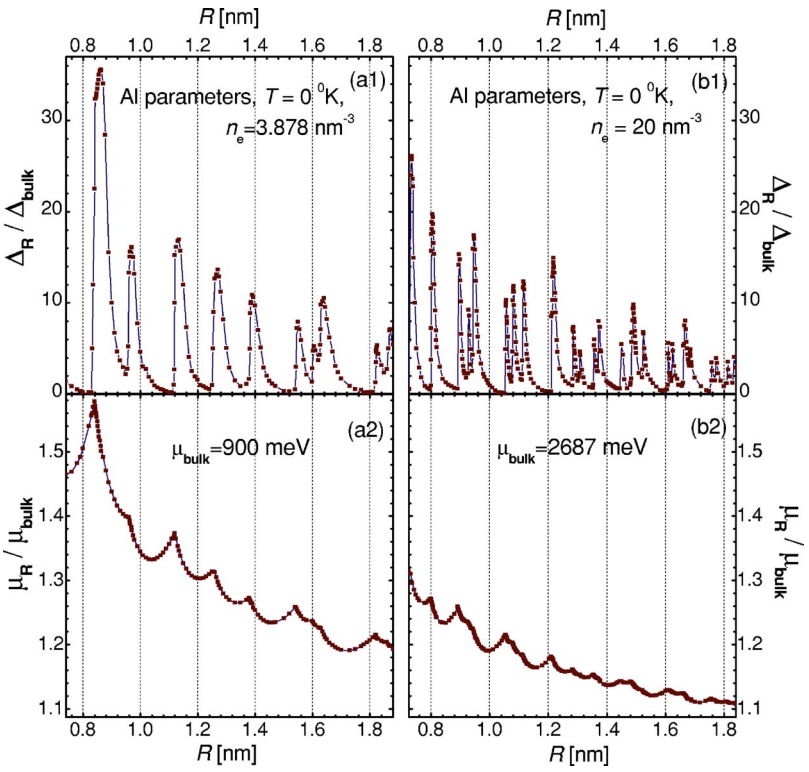

FIG. 1. (Color online) The relative gap of the quasiparticle spectrum $\Delta_R/\Delta_{\rm bulk}$ [panels (a1) and (b1)] and relative chemical potential $\mu_R/\mu_{\rm bulk}$ [panels (a2) and (b2)] vs the nanowire radius R: the panels (a1) and (a2) represent the data calculated for $n_e=3.878$ nm^{-3} (the bulk chemical potential $\mu_{\rm bulk}=900$ meV); panels (b1) and (b2) are the data for $n_e=20$ nm^{-3} ($\mu_{\rm bulk}=2687$ meV). Squares are the results of numerical investigations of the BdG equations, the solid line is the spline interpolation.

The single electron wave functions u_n and v_n make a contribution to the order parameter via the self-consistency relation

$$\Delta(\mathbf{r}) = g\sum_n u_n(\mathbf{r})v_n^*(\mathbf{r})[1-2f(E_n)], \tag{3}$$

where g is the coupling constant and $f(x)$ is the Fermi function $f(x)=1/[\exp(\beta x)+1]$, $\beta=1/(k_BT)$ with T the temperature and k_B the Boltzmann constant. Summation in Eq. (3) is taken over the eigenstates with the kinetic energy (including the chemical potential) within the window $[-\hbar\omega_D,\hbar\omega_D]$, and ω_D is the Debye frequency. The chemical potential is fixed by

$$n_e = \frac{2}{\pi R^2 L}\int d^3r \sum_n \{|u_n(\mathbf{r})|^2 f(E_n) + |v_n(\mathbf{r})|^2[1-f(E_n)]\} \tag{4}$$

with n_e the mean total electron density. Introducing the cylindrical coordinates ρ,φ,z, we can write $\Delta(\mathbf{r})=\Delta(\rho)$ as the periodical boundary conditions are implied in the longitudinal (z) direction. In this case we get

$$u_{jmk}(\mathbf{r}) = \tilde{u}_{jmk}(\rho)\frac{e^{im\varphi}}{\sqrt{2\pi}}\frac{e^{ikz}}{\sqrt{L}}, \quad v_{jmk}(\mathbf{r}) = \tilde{v}_{jmk}(\rho)\frac{e^{im\varphi}}{\sqrt{2\pi}}\frac{e^{ikz}}{\sqrt{L}}, \tag{5}$$

where $n=(j,m,k)$ with j the quantum number associated with the ρ coordinate, m the azimuthal quantum number, and k the wave vector in the z direction. Substituting Eq. (5) into Eqs. (1) and (2), we recast the BdG equations in terms of $\tilde{u}$ and $\tilde{v}$:

$$E_{jmk}\tilde{u}_{jmk}(\rho) = \left[-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{m^2}{\rho^2}-k^2\right)-\mu\right]\tilde{u}_{jmk}(\rho) + \Delta(\rho)\tilde{v}_{jmk}(\rho), \tag{6}$$

$$E_{jmk}\tilde{v}_{jmk}(\rho) = \Delta(\rho)\tilde{u}_{jmk}(\rho) - \left[-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{m^2}{\rho^2}-k^2\right)-\mu\right]\times\tilde{v}_{jmk}(\rho). \tag{7}$$

Due to the electron confinement in the transverse directions we should put

$$\tilde{u}_{jmk}(R) = \tilde{v}_{jmk}(R) = 0. \tag{8}$$

Then, $\tilde{u}$ and $\tilde{v}$ functions are expanded in terms of the Bessel functions, and Eqs. (6) and (7) can be converted into a matrix form convenient for the numerical iteration procedure typical for a self-consistent mean-field treatment.

Numerical investigation of Eqs. (6) and (7) reveals the resonance structure of the energy gap parameter of a cylindrical nanowire in agreement with the results for ultrathin films and nanoparticles. But what is surprising is that the resonance size is now by order of magnitude larger than in ultrathin films of the same width (see the results for ultrathin metallic films with the width 10–20 Å[4]). In Fig. 1 the R-dependent gap of the quasiparticle spectrum Δ_R and the chemical potential μ_R are given for $0.8\ \text{nm}\leqslant R\leqslant 1.8$ nm at zero temperature. The Al-parameter set was used in the calculations: $gN(0)=0.18$ [$N(0)$ is the bulk energy density of states for one spin projection at the Fermi surface] and $\hbar\omega_D/k_B=375$ K.[16] The electron band mass was set to the free electron mass. To have a feeling about influence of the

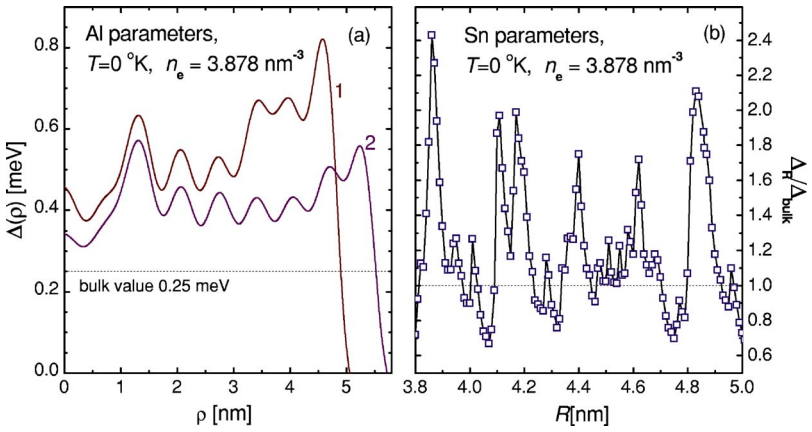

FIG. 2. (Color online) (a) The superconducting order parameter $\Delta(\rho)$ vs ρ at the resonance points $R=5.06$ nm (1) and $R=5.75$ nm (2), and (b) the relative gap of the quasiparticle spectrum $\Delta_R/\Delta_{\text{bulk}}$ for the nanowire radii near $R=4.5$ nm. In (a) the Al parametric set is under consideration, whereas in (b) the Sn parameters are used.

choice of the total electron density on the shape resonances, we performed calculations for the densities $n_e=3.878$ nm^{-3} (with the bulk chemical potential $\mu_{\text{bulk}}=900$ meV) and $n_e=20$ nm^{-3} (with $\mu_{\text{bulk}}=2867$ meV). Any time when the number of the electron subbands (associated with the quantum numbers j and m) below the Fermi level gets less by 1 or 2 with decrease of the wire radius R (1 for the situation of j dropping, 2 for the case of $|m|$ decreasing), a resonance appears in the energy gap dependence on R. The same manifests itself in a sharp change of the chemical potential derivative. At a resonance point the bottom of a subband (or of two degenerate subbands) goes in the Debye window $[\mu-\hbar\omega_D, \mu+\hbar\omega_D]$, which results in an increase in the number of the single electron states belonging in this window. This leads to a sharp and significant rise of the energy gap function together with the mean value of the superconducting order parameter. On the contrary, between two neighboring resonant points, the number of the single electron states making contribution to the superconducting order parameter drops down and a local minimum occurs in the R dependence of the energy gap function. Note that this drop of Δ_R becomes more significant with a decrease in the nanowire radius but even at $R=0.8$ nm the energy gap does not vanish: it is simply very small as compared to its bulk value (about 0.3 Δ_{bulk}). As is seen, there is no essential difference concerning the resonance magnitudes between the panels (a1) and (b1) of Fig. 1. Thus, we can expect that $\Delta_R/\Delta_{\text{bulk}}$ at a given resonant point is not sensitive (to within the accuracy of 10–20 %) to the choice of the mean total electron density in the metallic domain $n_e\approx 10^{21}-10^{23}$ cm^{-3}. However, the larger electron density, the larger density of the resonant points: the distance between neighboring resonances is roughly proportional to $1/k_F$ with k_F the Fermi wave number of the bulk material. Below we limit ourselves to the case $n_e=3.878$ nm^{-3}.

The next important thing about the shape-resonance effect in ultrathin nanowires is that the well-known[16] BCS relation $\Delta_{\text{bulk}}/(k_BT_c)\approx 1.76$ (with T_c the bulk superconducting temperature) is not fulfilled in the presence of the profound shape resonances. The ratio $\Delta_R/(k_BT_{c,R})$ (with $T_{c,R}$ the R-dependent transition temperature) is not constant but oscillates with a change of the nanowire radius: it goes down at the resonant points and rises up to a nearly bulk value between two neighboring resonances. When the nanowire radius increases, the amplitude of these oscillations slowly decreases (together with the magnitude of the shape resonances in the energy gap function) so that for $R>10$ nm we have the bulk relation. For the resonances situated at the points $R=0.86$ and 1.12 nm [panel (a1) of Fig. 1] we have approximately the same result $\Delta_R/(k_BT_{c,R})\approx 1.48$. Hence, to estimate $T_{c,R}/T_c$ for the resonances located in the interval $0.8\text{ nm}\leqslant R\leqslant 1.8$ nm, one can simply multiply the data of Fig. 1 (a1) by a factor of 1.175 (for $n_e=3.878$ nm^{-3}). For the case of the panel (b1) this factor is about 1.66. As is seen, the resonant increase of the superconducting temperature with respect to its bulk value is even more significant than that of the energy gap parameter.

Any profound shape resonance in the quasiparticle-spectrum gap is accompanied by strong spatial variations of the superconducting order parameter $\Delta(\rho)$ and by a giant increase of its mean value (this value is close to the energy gap parameter). For example, the superconducting order parameter calculated at the resonant points $R=5.06$ and 5.75 nm is plotted in Fig. 2, the panel (a). The shape resonances become less pronounced with rise of the nanowire radius [compare the data for the energy gap function in the panels (b) of Figs. 2 and 3]. At $R>4$ nm the electron subbands appearing due to the size quantization are not well separated any more: a new shape resonance appears when the previous one has not yet decayed. This is why we get the irregular pictures of the resonances in the panels (b) of Figs. 2 and 3. Here it necessary to note that the resonance magnitude is quite sensitive to the parameters $\hbar\omega_D$ and $gN(0)$ but the resonance position is not. Indeed, for Cd we have[16] $gN(0)=0.18$, and $\hbar\omega_D/k_B=164$ K, and the value of $\Delta_R/\Delta_{\text{bulk}}$ at the resonance point $R=0.86$ nm is about 57.5. Whereas for the Al parameters, $gN(0)=0.18$, and $\hbar\omega_D/k_B=375$ K, the same resonance appears again at $R=0.86$ nm but with $\Delta_R/\Delta_{\text{bulk}}\approx 34.2$ (see Fig. 2). For Sn we get[16] $gN(0)=0.25$ and $\hbar\omega_D/k_B=195$ K, and the relative energy gap function has the resonance at $R=0.86$ nm with the magnitude 16.8. The data plotted in the panel (a) of Fig. 3 for the Al and Sn parameters can also be a good illustration to this note. As mentioned above, the resonant deviations of the mean value of the superconducting order parameter from its bulk limit go down to zero with an increase of the nanowire radius so that for $R>10$ nm we arrive at the regime investigated in Ref. 17. In this regime there still survive oscillations of $\Delta(\rho)$ with

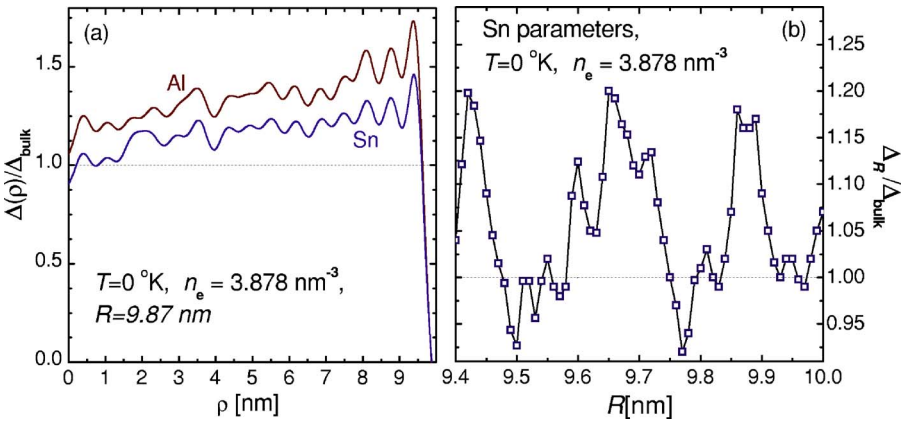

FIG. 3. (Color online) (a) The ratio $\Delta(\rho)/\Delta_{\text{bulk}}$ vs ρ at the resonance point $R=9.87$ nm (Al, the upper curve, and Sn, the lower curve), and (b) the dependence of $\Delta_R/\Delta_{\text{bulk}}$ on the nanowire radius R for the Sn parameters near $R\approx 10$ nm.

the frequency roughly proportional to k_F. As to the mean value of the superconducting order parameter, it is very close to the bulk limit. Note that the BdG equations in Ref. 17 were investigated for the case of the chemical potential independent of the nanowire width. This is reasonable for $R>10$ nm but results in a decrease of the mean total electron density for $R<10$ nm. In this case the BdG equations should be solved together with the relation (4), which leads to the chemical potential depending on the nanowire radius.

Recently the increase of the superconducting temperature by a factor of 1.1 was found for a single-crystalline Sn nanowire with $R=10$ nm.[9] Our investigation suggests that this experimental observation can be explained in terms of the shape-resonance effect. From Fig. 3 [the panel (b)] it is seen that for the Sn parameters the magnitudes of the shape resonances for $\Delta_R/\Delta_{\text{bulk}}$ are about $1.1-1.2$ near the point $R=10$ nm. The same scenario takes place for $T_{c,R}/T_c$ [we get $\Delta_R/(k_B T_{c,R})\approx 1.76$ for $R=10$ nm]. The structure of these resonances makes it possible to expect that the average effect of increase in $\Delta_R/\Delta_{\text{bulk}}$ (and in $T_{c,R}/T_c$) should survive even in the presence of the radius fluctuations.

In summary, we investigated the shape-resonance effect in a cylindrical nanowire at $R<10$ nm in the clean limit. Numerical analysis of the BdG equations revealed a sequence of the profound shape resonances in the dependence of the energy gap parameter (and the superconducting order parameter) on the nanowire width. The resonant deviations of Δ_R from the bulk value turn out to be by an order of magnitude larger than in ultrathin metallic films of the same width. This results in a giant growth of the superconducting temperature of an ultrathin nanowire at the resonance points. Our calculations suggest that the recently observed increase of the superconducting temperature in a single-crystal cylindrical Sn nanowire with $R=10$ nm[9] can occur due to the shape-resonance effect. We expect that the shape resonances are able to survive in dirty ultrathin nanowires. Indeed, if a nanowire is thin enough (when the mean free path of electrons is close to the nanowire width), it can be treated as clean in the transverse direction. In this case the presence of the nonmagnetic impurities in the longitudinal direction can be taken into account in a way of the well-known Anderson theorem.[15] It allows one to expect that the nonmagnetic impurities do not have a serious effect on the transition temperature of the ultrathin superconducting nanowires.

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