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Superconductor (Nb)–charge density wave ($NbSe_3$) point-contact spectroscopy

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Abstract
Measurements of differential current–voltage (I–V) characteristics of point contacts between Nb and the charge density wave (CDW) conductor $NbSe_3$ formed along the conducting chain direction are reported. Below the superconducting transition of Nb, we have clearly observed Andreev reflection of the gapless electrons of $NbSe_3$. Analysis of the spectra obtained indicates that when the energy of injected particles exceeds the superconducting energy gap, the superconductivity near the S–CDW interface is suppressed because of non-equilibrium effects.

1. Introduction

Investigations of contact phenomena in quasi-one-dimensional conductors with a charge density wave (CDW) ground state (for reviews of CDW properties see [1–3]) allow one to obtain rich information about the physical properties of these materials. Thus, it can now be regarded as reliably established that the current conversion process near the electrical contacts to a CDW conductor proceeds via a slippage of the CDW phase propagating a substantial distance away from the contact [4–6]. Recently there has been a study of the mechanism by which electrons penetrate from the normal metal into the CDW. The most interesting experimental configuration is realized when current contacts are oriented along the CDW chain direction. The current–voltage (I–V) characteristics of the normal-metal (N)–CDW interface in such a geometry were experimentally investigated above liquid nitrogen temperature for $K_{0.3}MoO_3$ [7] and $NbSe_3$ [8]. It was found that the N–CDW interface has an excess resistance for normally incident carriers with energy E less than the Peierls energy gap, Δ_P. These results gave a proof of the validity of the proposed mechanism [9, 10] where it was assumed that electron–hole pairs moving from the interface carry away from it twice the momentum of an electron incident normal to the interface. Unpredictable effects may be expected when the

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normal metal at the boundary with a CDW is replaced by a superconductor. Indeed, while the condensate in a superconductor is formed by pairs of electrons with opposite momenta, a CDW can be visualized as a condensate of bound pairs of electrons and holes whose momenta differ by the magnitude of the wavevector of the CDW. Because of charge conservation, a Cooper pair cannot become an electron–hole pair directly. The question that we want to answer in the present work is the following. What is the mechanism of transmission of charge from the superconductor to the CDW?

We have chosen Nb as the superconducting electrode and $NbSe_3$ as the CDW electrode. This latter material exhibits two CDW phase transitions at $T_{P1} = 144$ K and $T_{P2} = 59$ K. The unit cell of $NbSe_3$ in the a^*–c plane is made up of three types of chain. Band calculations [11] for $NbSe_3$ demonstrates that the upper transition below T_{P1} is attributable to a nearly perfect nesting and associated with a first pair of chains. It was conjectured that the lower CDW below T_{P2} occurs on the second and third pairs of chains. But normal carriers still exist at low temperature in small pockets as a result of the lack of perfect nesting between portions of the Fermi surface connected by the distortion wavevector, yielding the semi-metallic low-temperature ground state of $NbSe_3$. The situation is rather unusual because of the very small concentration of these normal carriers at low temperature, $n = 1.1 \times 10^{18}$ cm^{-3}, and, at the same time, their mobility achieves the value $\mu = 3 \times 10^5$ cm^2 V^{-1} s^{-1} [12, 13]. In this specific case, is it possible to observe at temperature below the superconducting transition temperature of Nb a similar picture to that encountered for usual N–S contacts, namely the Andreev reflection [14]? The existence of such an effect would be an indication of a contact with direct conductivity (without a tunnel barrier). Another reason for the choice of $NbSe_3$ in the present work is the substantial reduction of the band bending effect near the N–CDW boundary [15], because the screening by gapless electrons is very effective.

2. Experimental technique

The sizes of the $NbSe_3$ samples selected for the experiment were $L_b \approx 1$–2 mm along the b-axis, $L_c \approx 10$–50 μm along the c-axis and $L_a \approx 1$ μm along the a^*-axis. The very small thickness of the $NbSe_3$ samples makes it practically impossible to form a point contact along the chains with the use of a conventional metallic needle-type tip. Therefore, similarly to the case for the contact geometry investigated in [8], as a tip we used a thin Nb strip with a width of 200 μm and a thickness of 5 μm. The measurements of the I–V characteristic and its first derivative $R_d = \mathrm{d}V/\mathrm{d}I$ have been carried out with standard lock-in techniques for temperatures between 3.6 and 30 K, with the sample in exchange gas. The potential probes were attached at some distance from the point contact. Therefore a small part of the sample ($\sim$100–300 μm) in addition to the point contact was included in the measurements, but its contribution was usually 2–3 orders of magnitude smaller than that of the resistance of the point contact and consequently was neglected. We have investigated nine samples and more than 100 different contacts with contact resistances ranging from 10^2 up to 10^5 Ω.

3. Experimental results and discussion

The I–V characteristics obtained in our point-contact experiments exhibit a number of features that are reproducible for different samples and for contacts with a wide range of resistances. Because we are interested in studying the direct interaction between a superconductor and a CDW, we only describe hereafter low-voltage singularities of magnitude comparable to the superconducting energy gap. The behaviour of the contact at high voltages contains mainly

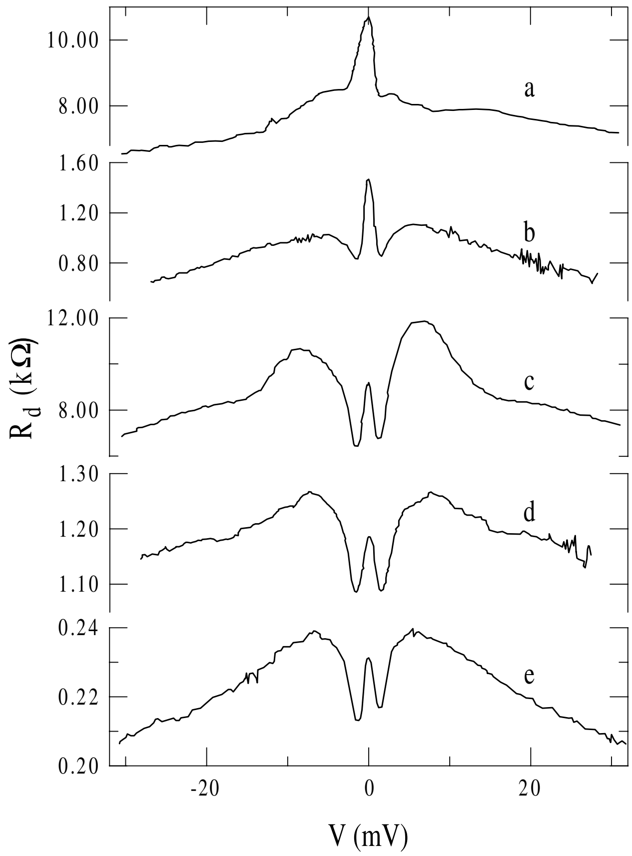

Figure 1. The bias voltage dependence of the differential resistance $R_d(V)$ for superconducting (Nb)–CDW ($NbSe_3$) point contacts of different types measured at $T = 3.6$ K. Curves (a), (b) are for the examples of junctions with insulating tunnel barriers on the S–CDW interface; curves (c)–(e) are for the examples of point contacts with direct conductivity (without insulating barriers).

information about the normal-metal–CDW interaction, which is the subject of the work [16]. Examples of point-contact characteristics of different types measured at 3.6 K are shown in figure 1. For all curves shown, the singularities at $|V| \sim 1.5$ mV corresponding to the superconducting energy gap, Δ_s, of Nb, are clearly seen, but the shapes of the curves exhibit significant differences. Curve (a) is for an example of a tunnel-type junction. Indeed, the large maximum at $V = 0$ is an indication of the usual mirror reflection of injected particles occurring because of the strong barrier at the S–CDW boundary. For curve (b), the height of such a barrier is less, with the result of a relative decrease of the amplitude of the zero-bias maximum. The curves (c)–(e) are for examples of contact characteristics obtained with the lowest barrier. It may be seen that such types have been observed in a very wide range of resistances from 10^2 up to $\sim 10^5$ Ω. In the present study, we are mainly interested in the investigation of contacts of this type because it is claimed that they can be considered as contacts with direct conductivity (without tunnel barriers). The exact determination of the quality of such a contacts needs analysis of the point-contact characteristics below and above the superconducting transition temperature. Typical spectra for one such contact with a zero-bias resistance $R_d(0) \sim 1$ kΩ are shown in figure 2 by a solid curve below, $R_d(V)$, and by a dotted curve above, $R_{dN}(V)$,

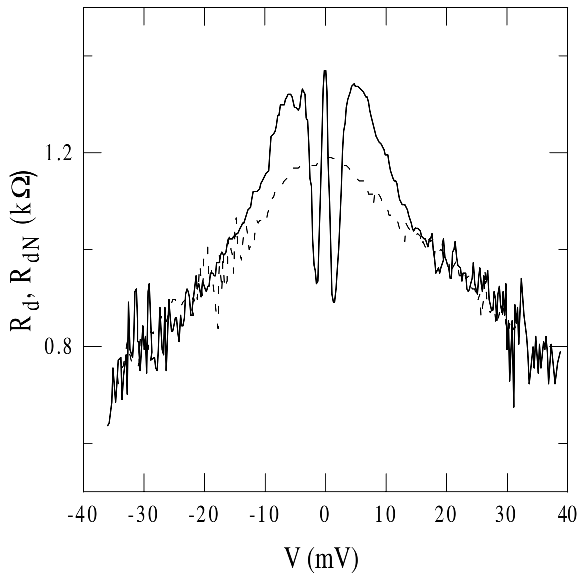

Figure 2. The differential resistance of one Nb–$NbSe_3$ contact revealing the Andreev reflection singularity: the solid curve at $T = 3.6$ K ($R_d(V)$) and the dotted curve at $T = 10.1$ K ($R_{dN}(V)$) are for below and above the Nb superconducting transition temperature, $T_c = 9.2$ K.

the critical temperature, T_c, of Nb. It is interesting to note that $R_{dN}(V)$ strongly decreases with the voltage increase. Such behaviour may be connected with the excess resistance arising from the reflection of normal quasi-particles injected from Nb at the Peierls energy gap barrier of $NbSe_3$ [8]. At the same time, at low bias voltage and at temperature below T_c, the I–V spectra exhibit a double-minimum structure, characteristic of Andreev reflection at N–S point contacts.

The Andreev reflection can be visualized as a given electron having an energy $E < \Delta_s$, under the influence of the pairing potential step at the N–S boundary (proximity effect), joining a second electron, leaving a hole in N with the resulting pair propagation in S. Because most CDW materials have a semiconducting ground state, a CDW–S contact should be considered as a semiconductor–superconductor contact and Andreev reflection, as the effect of transformation of a superconducting current to a one-particle current, is possible only in the case where one-particle states with $E < \Delta_s$ are permitted in the CDW. But for $NbSe_3$, $\Delta_P \gg \Delta_s$ [16–18], and the observation of Andreev reflection from condensed to CDW carriers will only be possible in the case of the suppression of the Peierls energy gap, which is unlikely. Therefore, we can conclude that the observed Andreev reflection may be attributed to the gapless electrons of $NbSe_3$ only, while, as was mentioned above, the concentration of such carriers is very low.

We will analyse the spectra obtained using the formulation of Blonder, Tinkham and Klapwijk [19, 20]. This theory describes the crossover from a metallic to a tunnel junction behaviour. The point contact is modelled as a delta function barrier potential and a step function pair potential separating the metal and the superconductor with an energy gap Δ_s. The height of the barrier is proportional to a dimensionless parameter $Z = [Z_0^2 + (1-r)^2/4r]^{1/2}$ where Z_0 characterizes the normal reflection due to the oxide layer or surface irregularities and r is the ratio of the Fermi velocity for each material of the point contact. For Nb we took $v_F = 1.3 \times 10^8$ cm s^{-1} and for $NbSe_3$ we took $v_F = 3 \times 10^7$ cm s^{-1} [2]. Therefore $r \sim 4.4$ and a pure direct contact ($Z_0 = 0$) will be characterized by the minimum value of Z,

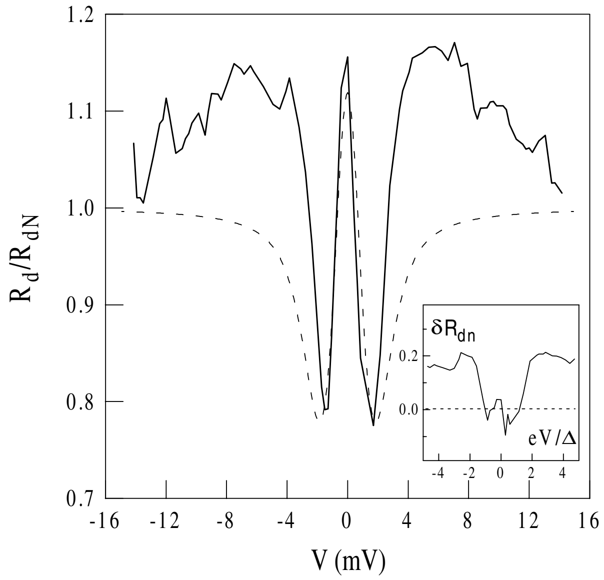

Figure 3. The normalized dependence of the differential resistance $R_{dn}(V) = R_d(V)/R_{dN}(V)$ for the Nb–$NbSe_3$ contact (from figure 2). $R_d(V)$: Nb superconducting, $T = 3.6$ K; $R_{dN}(V)$: Nb normal, $T = 10.1$ K. The dashed curve is the Blonder, Tinkham, Klapwijk [19] fit to the experimental dynamical resistance with fit parameters $\Delta_s = 1.5$ meV and $Z = 0.83$. The inset shows the difference $\delta R_{dn}(V)$ between $R_{dn}(V)$ and the BTK curve.

$Z_{min} \approx 0.8$. Thus, if the I–V curves of the point contacts that we measured can be described by the BTK theory with parameter $Z \approx Z_{min}$, we will be able to investigate the possible direct interaction between a superconducting Cooper pair condensate and a CDW condensate. The voltage dependence of the normalized differential resistance $R_{dn}(V) = R_d(V)/R_{dN}(V)$ for the contact shown in figure 2 is shown in figure 3. The dashed curve is the theoretical curve obtained using the BTK model with fit parameters $\Delta_s = 1.5$ meV and $Z = 0.83$. The good agreement between the experimental curve and the BTK fit at $V \leqslant \Delta_s/e$ is an indication that this contact has a very low barrier which can be attributed to the non-ideal N–CDW boundary; it may be considered as a contact with a direct conductivity.

At $|V| > \Delta_s/e$, as seen from figure 3, the experimental spectrum deviates from the theoretical BTK fit. This may be seen more clearly from the inset in figure 3 which shows the difference $\delta R_{dn}(V)$ between the experimentally observed normalized differential resistance and the theoretical curve. The experimental value of the differential point-contact resistance begins higher than the theoretical one and shows a broad maximum in this range of voltages. We assume that the observed deviation from the BTK theory is related to the suppression of the superconductivity of Nb near the contact when the energy of the injected carriers exceeds the superconducting energy gap. Indeed, the Andreev reflection at the usual N–S interface yields an excess current I_{ex} through the boundary for bias voltages far above the superconducting energy gap, because there is a small, but finite, probability of Andreev reflection at $V > \Delta_s/e$. It was shown in [19] that this excess current $I_{ex} \sim \Delta_s/e$ is independent of the bias voltage and the differential resistance of the contact in this voltage range is equal to R_{dN}. If the energy gap decreases or if the superconductivity is suppressed, the excess current is reduced and the resulting shift in the direct I–V characteristics appears as a maximum of the $R_d(V)$ dependence. Such a resistance maximum connected to the transition of the superconducting electrode at the interface into the normal state at finite bias was observed in the usual N–S configuration [21, 22]. However, in contrast to our results, the resistance peaks were sharper and appeared only at $|V| \gg \Delta_s/e$. In our case, this resistance maximum appears just when the energy of the injected particles exceeds the superconducting energy gap, which may be an indication of a superconducting–normal-metal transition at the surface of the Nb electrode.

The suppression of the superconductivity of Nb at $|V| > \Delta_s/e$ can be qualitatively explained by considering two effects. The first one is the quasi-particle injection of gapless electrons of $NbSe_3$ in the superconducting Nb at $|V| > \Delta_s/e$. However, this effect cannot be significant because of the very small concentration of normal carriers in $NbSe_3$ [12]. The second one is the result of the interaction of quasi-particle excitations of Nb with a CDW at energies less than the Peierls energy gap. According to [16–18] for low-temperature CDW in $NbSe_3$, $\Delta_P/e \approx 30$ mV, which is larger than the voltage range investigated in our case. As was shown in [7–10], for energies less than Δ_P, quasi-particles hitting chains with a CDW distortion are reflected due the Peierls energy gap barrier. The combination of the two processes, quasi-particle injection across the superconducting energy gap and reflection of carriers at the Peierls energy gap, yields non-equilibrium effects: increase in the quasi-particle concentration and a corresponding decrease in the superconducting energy gap (the superconductivity is fully suppressed at some critical concentration of quasi-particles) in a region at the surface of the Nb electrode, the depth of which is equal to the length of diffusion of the quasi-particles into the superconductor.

Thus, we see the following picture of conversion of the superconducting current to the CDW current on the Nb–$NbSe_3$ boundary. If the voltage drop on the contact $V \leqslant \Delta_s/e$, the current conversion proceeds by means of Andreev reflection of gapless electrons of $NbSe_3$. At $V > \Delta_s/e$, because of non-equilibrium effects, the superconductivity near the S–CDW interface is suppressed and the current conversion is the same as in the case of the N–CDW boundary. This phenomenon may be considered as some kind of dynamic proximity effect.

4. Conclusions

In conclusion, we have investigated I–V characteristics of Nb–$NbSe_3$ point contacts formed along conducting chains. Below the superconducting transition temperature of Nb, we clearly observed Andreev reflection from non-condensed to CDW carriers of $NbSe_3$. When the energy of the injected particles exceeded the superconducting energy gap, we observed some kind of dynamic proximity effect with the superconductivity near the S–CDW boundary suppressed because of high quasiparticle injection and reflection of carriers at the Peierls energy gap barrier. As a result, a normal-state buffer layer arises between S and CDW electrodes.

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