Evidence of surface superconductivity in $2H$-$NbSe_2$ single crystals

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We have probed the differential resistance in $2H$-$NbSe_2$ single crystals at very low currents. For fields applied perpendicular to the sample and in the range $B_{c2}<B<(1.6–1.7)B_{c2}$, the differential resistance is Ohmic but well below the usual normal-state differential resistance observed at high currents. This deviation from the normal-state differential resistance is ascribed to surface superconductivity on the lateral surfaces. [S0163-1829(96)06433-8]

The cores of the vortices in a type-II superconductor overlap at the second upper critical field B_{c2}. Below B_{c2}, the electric resistance results from the motion of the vortices under the effect of the Lorentz force. Above B_{c2} the resistance is the one of the normal state. However, deviations from the normal-state resistance above B_{c2} can appear in a superconductor for two intrinsic reasons: (1) the boundary conditions at the surface can favor the existence of superconductivity within a sheath of thickness ξ, where ξ is the coherence length, for fields below a third critical field B_{c3} (*surface superconductivity*);[1] (2) the excess conductivity attributable to superconducting pairs created by thermal fluctuations (*paraconductivity*).[2]

We were able to probe the transport properties of high quality $2H$-$NbSe_2$ single crystals with current densities orders of magnitude lower than used up to now. In this low current regime and for fields applied perpendicular to the sample we detected an Ohmic resistance below the usual normal-state resistance in the range $B_{c2}<B<(1.6–1.7)B_{c2}$. In low-T_c superconductors the critical fluctuation region is extremely small, and paraconductivity has to be discarded as explanation of our results. We shall conclude that the data are compatible with a surface superconductivity picture in which the current flows partially along the lateral surfaces of the sample. Our model brings evidence that surface superconductivity exits for $2H$-$NbSe_2$, and that the flow of very weak currents in layered superconductors can be complex, giving rise sometimes to surprising effects.

Our samples were $2H$-$NbSe_2$ crystals of very large dimensions, grown according to the methods described in Ref. 3. These kinds of crystals are usually used for small angle neutron scattering experiments,[4] and are of high quality. The main sample was a regular parallelepiped with length of 16 mm, width of 5.2 mm, and thickness (along the c axis) of 0.6 mm. Samples of the same batch, but less regular, were also used. Voltage and current contacts, in two different geometrical configurations, were placed on the upper face of the sample (a-b face), by evaporating a gold layer with gold wires then attached with indium-gallium solder. One configuration is the classical four-point contact, in which four parallel gold strips completely traverse the upper face. The other is a Corbino geometry, in which the current is injected into a central dot and collected by a rectangular gold frame along the edges of the upper surface (see inset of Fig. 1). The results shown in this paper were obtained with the applied field perpendicular ($\parallel c$) or parallel ($\perp c$) to the c axis of the crystal. We used low current densities, between 1 mA/cm^2 and 35 A/cm^2. For the main sample, the resistive transition temperature in zero field is $T_c=7.36$ K. The transition is very sharp, typically $\Delta T_c/T_c\approx 0.5\%$. We have measured T_c at different ac currents, and there is no indication of a current dependence of T_c. The critical current density is $J_c\approx 10$ A/cm^2 in perpendicular field at a field of 1 T and a temperature of 4.2 K. We report differential resistance measurements. In the technique, the differential resistance is measured by superimposing an ac current (33 Hz) on top of the dc current and the response at the ac frequency is measured with a phase-sensitive detector.

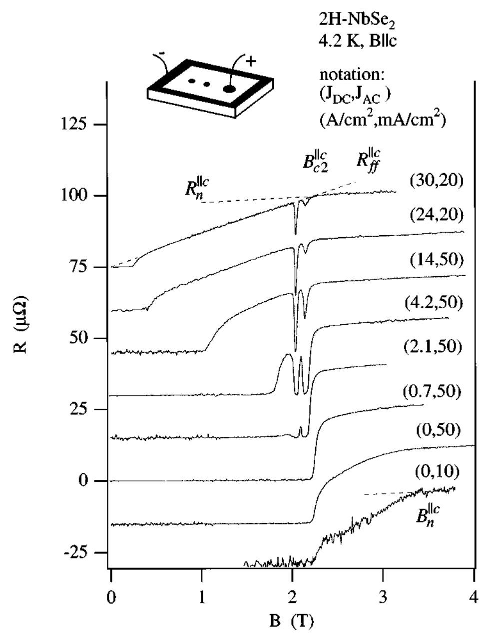

FIG. 1. The differential resistance R versus the field B, at 4.2 K, for different dc and ac currents. The curves are shifted along the vertical axis for clarity. $R_n^{\parallel c}(B)$ is the normal-state resistance. The second critical field is about $B_{c2}^{\parallel c}=2.26$ T. At high dc current density a typical flux-flow resistance $R_{ff}^{\parallel c}(B)\propto B$ is observed below $B_{c2}^{\parallel c}$ interrupted by a double peak effect. For very low current densities superconductivity is observed above $B_{c2}^{\parallel c}$ and below $B_n^{\parallel c}\approx 3.5$ T (see text for details). Inset: the configuration of voltage and current contacts used (Corbino configuration).

Shown in Fig. 1 is the differential resistance (noted R) at a fixed temperature of 4.2 K versus applied field, for different dc and ac currents, measured in the Corbino geometry. The field is perpendicular to the sample ($\|c$). This figure shows the effect of changing the current amplitude over many orders of magnitude. Before discussing our results obtained at very low current densities, let us describe the usual behavior observed at high current densities, for example, the curve obtained at $J_{\rm dc}=30$ A/cm^2 and $J_{\rm ac}=20$ mA/cm^2, noted (30,20) in Fig. 1. This result is essentially similar to recently published transport data on $2H$-NbSe$_2$,[5,6] but our dc current density is still comparatively low. By decreasing the field from a high value, the resistance R is the normal-state resistance $R_n^{\|c}$ which is found to decrease slowly with the field according to a linear law $R_n^{\|c}(B)=R_{n0}^{\|c}+K_n^{\|c}B$, with $R_{n0}^{\|c}=21\ \mu\Omega$ [which corresponds to a conductivity along the layer of $\sigma_n=2.9\times10^5\ (\Omega\ {\rm cm})^{-1}$] and $K_n^{\|c}=1.5\ \mu\Omega$/T. At about 2.26 T, the resistance R deviates from $R_n^{\|c}(B)$. At the same field, magnetization measurements on samples of the same batch show the onset of diamagnetism. Therefore we identify this field as $B_{c2}^{\|c}$. Decreasing the field below 2.26 T, the resistance follows the empirical expression $R_{ff}^{\|c}=BK_{ff}^{\|c}$, with $K_{ff}^{\|c}=R_n^{\|c}(B_{c2}^{\|c})/B_{c2}^{\|c}\approx10.9\ \Omega$/T. This is the characteristic flux-flow resistance in the mixed-state. It is produced by the dissipative motion of vortex lines subject to the Bardeen-Stephen viscous drag.[7] The observed resistance R below 2.26 T deviates from $R_{ff}^{\|c}(B)$ at about 2.14 and 2.04 T, indicating a sharp double "peak effect."[8] A double peak effect is observed in all thick samples. We will not discuss the peak effect in this paper, but notice that at high current the sharp minima tend to disappear in an asymmetric manner. The observed resistance R deviates from $R_{ff}^{\|c}(B)$ also when the field reaches a low level [about $B=0.23$ T for the high current under question (30,20)] where R goes rapidly to zero. This indicates that the vortex-line motion is stopped by the bulk pinning, and the used dc current density (30 A/cm^2) coincides with the critical current density at $B=0.23$ T and $T=4.2$ K. At even higher current densities than shown in Fig. 1, the zero-field critical current is overcome and the resistance follows the empirical flux-flow law $R_{ff}^{\|c}(B)$ down to $B=0$ T.

A completely different behavior appears, however, in the very low current regime, for example, $J_{\rm ac}=10$ mA/cm^2 and $J_{\rm dc}=0$, noted (0,10) in Fig. 1. Measurements in this regime reveal superconductivity effects above $B_{c2}^{\|c}$. Now the deviation from the normal-state resistance occurs at about 3.5 T, well above $B_{c2}^{\|c}$. For low currents the field at which the deviation occurs is independent of the current (see Fig. 2 below), so we can use this field as criterion to define a "critical" field, noted $B_n^{\|c}$. We have to stress that there is no change in the magnetization at this field. By decreasing the field below 3.5 T, the observed resistance R is below the resistance observed in the high current regime. At about 2.26 T, that is at $B_{c2}^{\|c}$, the resistance drops to zero.

Figure 2 shows measurements obtained at very small currents in more detail. The inset of Fig. 2 shows the differential resistance R versus the applied dc current at the same temperature of 4.2 K and a field of 2.5 T, for increasing and

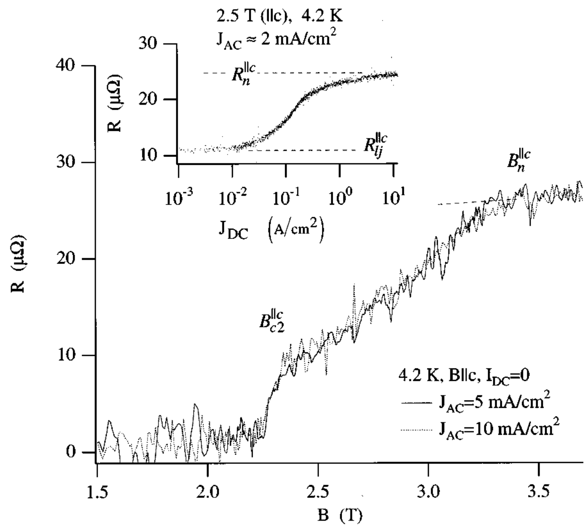

FIG. 2. The differential resistance R versus the field B, at 4.2 K, for small current densities. The response is linear between $B_{c2}^{\|c}$ and $B_n^{\|c}$. At $B_{c2}^{\|c}$ a drop of the resistance is observed. Inset: The differential resistance R versus the dc current density, showing the transition from a low-current Ohmic resistance $R_{lj}^{\|c}$ to the (high-current) normal-state resistance $R_n^{\|c}$.

decreasing dc current. There is no hysteresis in the R-I curve. These data show that for low enough currents the resistance between $B_n^{\|c}$ and $B_{c2}^{\|c}$ is independent of the current and below the normal-state resistance. This Ohmic resistance in the low-current regime has not been previously observed, although an inspection of some published data in thin $2H$-NbSe$_2$ crystals does show a current-dependent deviation from the normal-state resistance well above B_{c2} in the same perpendicular field orientation [for example, see Fig. 3 in Ref. 5 and Fig. 3(a) in Ref. 6].

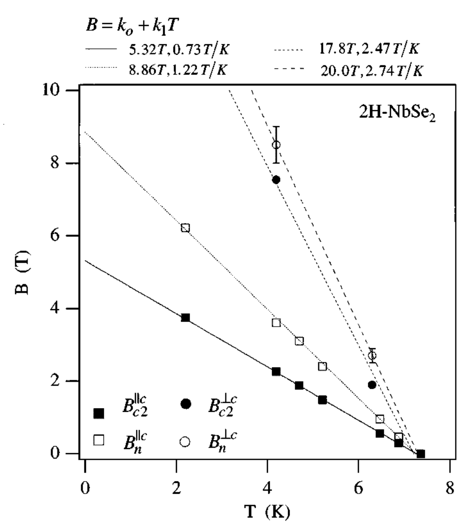

FIG. 3. B_{c2} and B_n versus the temperature for perpendicular and parallel field. Considerable imprecision exists in determining $B_n^{\perp c}$. The anisotropy is $B_{c2}^{\perp c}/B_{c2}^{\|c}\approx3.3$, and one obtains the ratio $B_n^{\|c}/B_{c2}^{\|c}\approx1.6$–1.7. The zero field transition temperature is $T_c=7.36$ K and the transition width $\Delta T_c=0.05$ K. Data are fitted by lines; the parameters are indicated in the figure.

Results shown in Figs. 1 and 2 are obtained in the Corbino configuration. When the four-point contact configuration is used, differences appear only in the low current regime above $B_{c2}^{\parallel c}$. In particular one detects the Ohmic behavior but the differential resistance goes to zero at $B_{c2}^{\parallel c}$, and the drop is absent. The role of the contact configuration will become clear in the discussion.

A last experimental point concerns the results of investigations in parallel field ($\perp c$). In this orientation and in the high current regime we observe the usual normal-state resistance above $B_{c2}^{\perp c}$ and the flux-flow resistance, interrupted by a double peak effect, below $B_{c2}^{\perp c}$. However, in contrast to perpendicular field, for parallel field in the low current regime the deviation from the normal-state resistance occurs only at about $1.2B_{c2}^{\perp c}$. Moreover, an Ohmic resistance and the drop, as in Fig. 2, have not been observed, and the determination of $B_n^{\perp c}$ is approximate. Data for the two orientations are summarized in Fig. 3, which shows the fields B_{c2} and B_n in the B-T diagram. The second upper critical fields coincide with the ones reported in the literature.[6,8–10] The measured anisotropy in the second critical field at 4.2 K is $B_{c2}^{\perp c}/B_{c2}^{\parallel c}\approx 3.3$ which is also accordance with the values observed by other authors. The ratio of B_n and the second critical fields is $B_n^{\perp c}/B_{c2}^{\perp c}>1.2$ and $B_n^{\parallel c}/B_{c2}^{\parallel c}\approx 1.6$–$1.7$.

Up to now we have intentionally adopted a neutral presentation of our results. We shall construct below a model of surface superconductivity consistent with our data. But, first, we will show how our data cannot be explained by sample inhomogeneities or by fluctuation effects. There are two indications that sample inhomogeneities can be excluded: (1) we measure a single zero-field critical temperature over all the range of available currents; (2) there is no change in magnetization above B_{c2}. Moreover, previous studies of similar samples have shown that they are high-quality homogeneous crystals.[3,4] Paraconductivity can also be excluded. The region of critical fluctuations is determined by the Ginzburg number $Gi=[T_c/H_c^2(0)\varepsilon\xi^3(0)]^2/2$.[11] The width of the critical region is $|T_c-T|<T_cGi\approx 7\times 10^{-3}$ K in $2H$-$NbSe_2$. We have to conclude that paraconductivity *cannot explain* the deviation from the normal-state resistance of up to $1.7B_{c2}$ that we observe, as well as the less pronounced deviations observed by other authors.[5,6,12]

The observed ratio $B_n^{\parallel c}/B_{c2}^{\parallel c}$ of about 1.7, as well as the general behavior of our measurements above $B_n^{\parallel c}$ suggest surface superconductivity.[1,13] A supporting element is that magnetization measurements do not reveal B_n, only the onset of diamagnetism at B_{c2} is observed. This supports surface superconductivity because the superconducting current on the surface cannot screen the applied field, as shown for example, by Abrikosov.[14] But there is a strong theoretical limitation which seems in contrast to our data: the angular dependence of $B_{c3}(\theta)$, where θ is the angle between the field direction and the surface, is such that $B_{c3}(0)=1.69B_{c2}$ for parallel fields, and diminishes to $B_{c3}(\pi/2)=B_{c2}$ for perpendicular fields.[15,16] Surface superconductivity does not exist for perpendicular fields and we have to conclude that the current flow has to find a path along the lateral surfaces of our samples, that is along faces parallel to the c axis.

With this point of view one can estimate[17] the total resistance taking into account a ''bulk path'' with a normal resistivity ρ_n in parallel to a ''surface path'' with a surface resistivity ρ_s. Considering a *homogeneous* surface superconducting sheath with a resistivity $\rho_s(J)$ which is strongly nonlinear near a field-dependent surface critical current density $J_c(B)$ (as is usual in explaining transport experiments on surface superconductivity), one can explain the current-dependent deviation from the normal-state resistance, but not the *field-dependent Ohmic* behavior that we observe at very low current density in all the range of fields $B_{c2}<B<(1.6$–$1.7)B_{c2}$, and certainly not the drop at $B_{c2}^{\parallel c}$.

However, a more realistic model should consider the surface superconducting sheath on the lateral faces as *inhomogeneous.* We expect the surface superconducting sheath to develop a ''pattern'' of normal and superconducting regions related to the local angle between the applied field and the surface, according to the angular dependence of $B_{c3}(\theta)$ (see, for example, in Ref. 18). As the field is decreased, an increasing fraction of the surface comes into favorable condition for the nucleation of surface superconductivity. In the limit of very small current densities, the fraction $0\leqslant p\leqslant 1$ of superconducting and normal regions on the surface depends on the applied field only. In particular at the second upper critical field $p(B_{c2})=1$, and near the third critical field $p(B_{c3})$ is the fraction of the surface exactly parallel to the applied field. The total resistance can be crudely estimated considering a circuit formed by a series of bulk elements with normal-state resistivity, intercalated by elements with a bulk path in parallel to a surface path.[19] The total resistance is then approximately $R_{\text{tot}}\approx R_n[1-p(1+r)^{-1}]$, where $r\approx\rho_s h/\rho_n\xi_0$, and h is the thickness of the sample. At low current, in each surface superconducting region one has $\rho_s(J)=0$, and the total resistance, $R_{\text{tot}}\approx R_n(1-p)\leqslant R_n$, is Ohmic. The field dependence of this Ohmic resistance results from the field dependence of $p(B)$, that is from the angular dependence of $B_{c3}(\theta)$ and the detailed distribution of the local angle between the field direction and the surface. By increasing the current, the current starts to destroy part of the superconducting regions on the surface, and p depends now on the current as well as on the field. At sufficiently high currents the entire surface is in the normal state, $p=0$ and $R_{\text{tot}}\approx R_n$. Notice that just above $B_{c2}^{\parallel c}$ the low-current Ohmic resistance can be either equal to or different from zero. When it is different from zero, it indicates that the current crosses some part of the sample for which there is no alternative superconducting surface path above $B_{c2}^{\parallel c}$ (i.e., $p<1$). This situation arises, in particular, when the current is required to flow over the flat upper a-b surface in perpendicular field, for example, from the dot to the frame in the Corbino contact geometry. As a consequence the drop observed at $B_{c2}^{\parallel c}$ in Figs. 1 and 2 is an artifact related to the particular contact configuration. This artifact, however, supports our model. Roughly speaking, a low current in the Corbino geometry prefers to flow along the lateral surfaces until it reaches the point of smallest distance between the frame and the central dot, which minimizes dissipation.

The model is quite satisfactory for perpendicular fields, but it remains for us to understand why in parallel fields we have not succeeded in observing a deviation from the normal-state resistance above more than $\approx 1.2B_{c2}^{\perp c}$ even at very low current densities. This is surprising at first sight since the large a-b surface is expected to be very flat, the surface superconducting sheath to be very homogeneous, and the nucleation of superconductivity to occur over most of the surface very close to $1.69B_{c2}$. The natural explanation is that the surface critical current density J_c, which enters in the nonlinear surface resistivity $\rho_s(J)$, is *much smaller* for the a-b faces than for the lateral faces parallel to the c axis. As a consequence a vanishing surface resistivity cannot be attained even with the lower current density used. The origin of the surface critical current is quite a controversial matter. One point of view associates J_c with the pinning of surface vortices.[16,20] If the surface vortices are pinned by imperfections on the surface so that they cannot move, current flow in the superconducting surface sheath will then be subjected to a vanishing resistance. At a sufficient driving current, above J_c, the surface vortices become unpinned and move, giving rise to dissipation. In this picture one has to conclude that the large a-b surface of the layered $2H$-$NbSe_2$ sample is flatter and cleaner than lateral faces, which is reasonable.

In conclusion, we have shown that the surface superconducting picture can explain our data. In order to do that, we had to construct a model involving the flow of current on the lateral surfaces, across a pattern of normal and superconducting regions. This pattern results form the distribution of the local angle between the surface and the direction of the applied field. Our analysis provides evidence that surface superconductivity exists in the $2H$-$NbSe_2$ compound. It shows also the complicated scenario which can appear at low current in layered superconductors, sometimes giving rise to effects which can easily been misinterpreted.

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[17] Notice that because the surface path is restricted to a thickness of the order of ξ, changes on the order of the bulk resistance appear only when ρ_s/ρ_n is of the order of $\xi/h \approx 10^{-6}$, where h is the thickness of the sample, that is only when the current flow in the surface superconducting sheath occurs with practically vanishing resistivity.

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