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Two superconducting states of $HoNi_2B_2C$ as seen by Andreev reflection in point-contacts

L. F. Rybaltchenko[1,2], I. K. Yanson[1,2], A. G. M. Jansen[1], P. Mandal[1]
P. Wyder[1], C. V. Tomy[3] and D. McK. Paul[3]

[1] *High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung Centre National de la Recherche Scientifique - B.P. 166, F-38042 Grenoble Cedex 9, France*
[2] *B. Verkin Institute for Low Temperature Physics and Engineering 47 Lenin Avenue, 310164 Kharkov, Ukraine*
[3] *Department of Physics, University of Warwick - Coventry CV4 7AL, UK*

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Abstract. – Andreev-reflection spectra of superconducting-normal contacts with $HoNi_2B_2C$ show a continuous increase of the superconducting order parameter at the antiferromagnetic phase transition $T_N = 5$ K without re-entrant behaviour below the superconducting critical temperature $T_c = 9$ K. A change is found in the superconducting ground state at $T_c^* = 6.5$ K (zero magnetic field), and the magnetic-field–temperature phase diagram corresponding to the two superconducting states is reconstructed.

Among the recently discovered superconducting rare-earth nickel boride carbides RNi_2B_2C (R = Lu, Y, Tm, Er, Ho) [1], the Ho-compound is one of the most interesting, showing the (incomplete) re-entrant-to-normal-state transition of magnetization [2] and resistance [3] in a narrow temperature range close to the antiferromagnetic phase transition ($T_N = 5$ K), and well below the superconducting transition temperature ($T_c \simeq 9$ K). This re-entrant transition from the superconducting into the normal state is supposed to be tightly connected with the incommensurate magnetic ordering which evolves on the way to a simple commensurate antiferromagnetic phase while lowering the temperature [4], [5].

We investigated the superconducting order parameter in $HoNi_2B_2C$ as a function of temperature and magnetic field by means of Andreev reflection of the charge carriers from the normal-superconducting boundary in point-contacts. Surprisingly, we have not found a suppression of the superconducting order parameter probed in the Andreev-reflection spectra which might evidence the re-entrance into the normal state near $T_N = 5$ K. Instead, we discovered the appearance of a uniform, homogeneous superconducting state below $T_c^* = 6.5$ K, with a continuous increase of the order parameter while crossing the antiferromagnetic transition

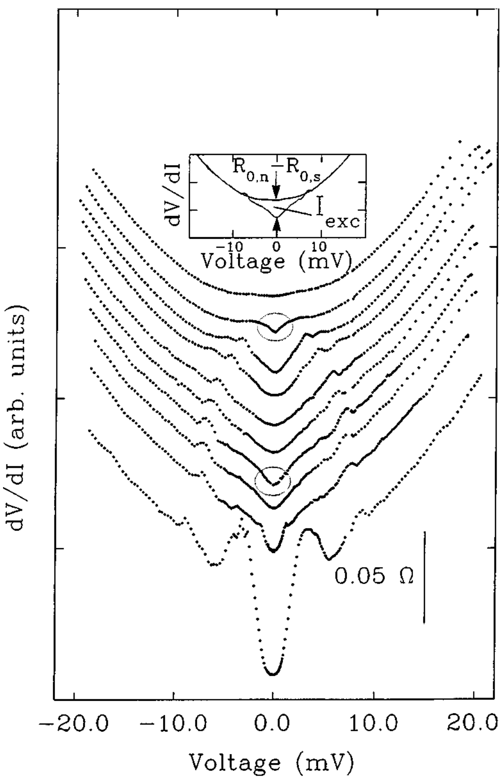

Fig. 1.

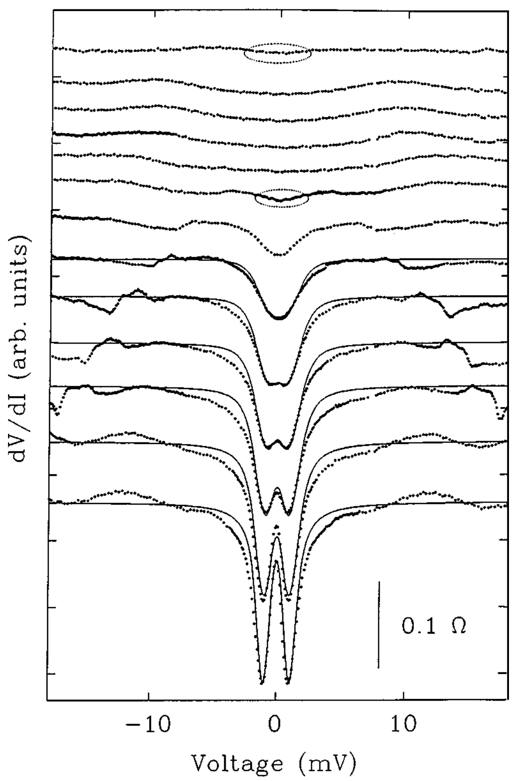

Fig. 2.

Fig. 1. – dV/dI characteristics for a $HoNi_2B_2C$-Ag point-contact with $R_0 = 0.87\ \Omega$. Temperatures from bottom to top are 5.0, 6.0, 6.2, 6.4, 6.8, 7.2, 8.0, 8.4, 8.8, 9.0 K. The inset shows the construction for the parameters used in fig. 3.

Fig. 2. – $dV/dI(V)$ characteristics for a contact with $R = 2.65\ \Omega$ after subtraction of a polynomial fit of the 8.6 K data. The appearance of superconducting order parameter features of states A and B are shown encircled at 8.6 and 6.6 K, respectively. Temperatures from bottom to top are: 2.2, 3.5, 4.2, 4.8, 5.2, 5.8, 6.2, 6.6, 6.8, 7.6, 8.0, 8.4, 8.6 K. BTK fits are shown with a scaling factor from 0.16 and 0.29 between 2.2 and 5.8 K.

around $T_N = 5$ K. Presumably, this superconducting state emerges below the lower critical temperature T_c^* from a microscopically inhomogeneous superconducting state which appears at the upper critical temperature T_c. We argue that the re-entrant behaviour seen in the current-carrying sensitive measurements (resistivity, magnetization) is most probably related to strong phase fluctuations of the superconducting order parameter in the vicinity of the antiferromagnetic transition.

In susceptibility measurements of the investigated polycrystalline Ho compounds the superconducting transition was centred at $\simeq 7.8$ K with a 10–90 % width of 1.5 K and the onset of superconductivity at 8.7 K. At 5 K the re-entrant peak was clearly seen, suppressing at the maximum about 16 % of the full diamagnetic signal.

By the lateral displacement of a sharpened Ag needle many places of the sample surface, freshly broken before mounting, could be probed with a point-contact during one cycle of measurements. The current-voltage characteristics and their first derivatives $dV/dI(V)$ were recorded with the standard lock-in techniques at different temperatures and magnetic fields applied perpendicularly to the contact axis.

The typical contact resistance R was around 1 Ω. Higher resistances showed the same characteristics as discussed below but were not long-living. Using the bulk resistivity $\rho \simeq 10\ \mu\Omega\,\mathrm{cm}$ at low temperatures and the free-electron approach $\rho\ell \simeq 10^{-15}\ \Omega\,\mathrm{m}^2$ for the product of resistivity ρ and mean free path ℓ, we obtain the following values for the contact diameter:

$$d = \rho/R \simeq 10^{-7}\ \mathrm{m} \quad \text{and} \quad d = (\rho\ell/R)^{1/2} \simeq 3 \times 10^{-8}\ \mathrm{m}, \tag{1}$$

from, respectively, the dirty ($d > \ell$) and clean ($d < \ell$) limit expressions of the contact resistance [6]. The contact size is larger than or comparable to the superconducting coherence length ($\xi \simeq 10^{-8}$ m), and the magnetic field penetrates the contact region easily (penetration depth $\lambda \simeq 10^{-7}$ m). Since the typical size of the crystallites ($\simeq 0.1$ mm) is much greater than d, our point-contact measurements probe a single crystal, though of uncontrolled orientation. It is quite well possible that pressures above 10 kbar are attained in the contact region. Pressure has a strong influence both on T_c (increase 0.07 K/kbar) and on T_N (increase 0.25 K/kbar) [7]. Because we have observed no systematic change of the critical temperatures in the point-contact experiments upon changing the contact area, we ignored these pressure effects.

Among the characteristics observed, only those contacts were chosen for further detailed study whose $\mathrm{d}V/\mathrm{d}I$ curves at low temperatures show the well-known double-minimum gap structure related to the Andreev-reflection process [8]. In fig. 1 $\mathrm{d}V/\mathrm{d}I$ curves recorded at different temperatures are shown for a junction with normal-state resistance at zero bias $R_{0,\mathrm{n}} = 0.87\ \Omega$. The inset illustrates the two parameters which have been used below for the description of the temperature evolution of the superconducting properties. The first is the area between the $\mathrm{d}V/\mathrm{d}I$ curves in the normal and superconducting state, proportional to the excess current $I_\mathrm{exc}(T)$ in the N-S contact. Irrespective of the type of superconductivity, *i.e.* gaped or gapless superconductivity, the excess current is a measure for the order parameter probed by the Andreev-reflection process. The second is the difference between the zero-bias resistance in the normal and superconducting state, which is more sensitive to the density of states at the Fermi level and is more closely related to the excitation gap in the quasiparticle spectrum.

In order to compare the point-contact data with the Blonder-Tinkham-Klapwijk (BTK) model [8], we have plotted in fig. 2 for another point-contact with $R_{0,\mathrm{n}} = 2.65\ \Omega$ the experimental $\mathrm{d}V/\mathrm{d}I$ curves after subtraction of a smooth polynomial fit to the highest-temperature curve. In the following, we focus on the voltage range of about the energy gap around zero bias since the features seen at voltages larger than the order parameter are contact-resistance dependent and most probably due to non-equilibrium effects of partial suppression of superconductivity near the constriction.

At voltages up to corresponding gap energies (few meV), the data in fig. 1 and 2 show reproducible features also encountered in other contacts. In the temperature dependence of the $\mathrm{d}V/\mathrm{d}I$ two characteristic temperatures can be recognized for the onset of superconducting structure as indicated by the dashed ellipses in fig. 1 and 2. At the bulk critical temperature $T_\mathrm{c} = 9$ K a dip develops around zero bias. With lowering the temperature this feature deepens and widens, but, evidently, cannot be fitted by any reasonable model due to the large width which exceeds by an order of magnitude the energy gap expected for the given T_c. With further lowering the temperature, a new superconducting structure appears around $T_\mathrm{c}^* = 6.5$ K as a small dip at zero bias which quickly evolves into the usual BTK structure due to Andreev reflections of quasiparticles from the N-S boundary of the point-contact [8] where the voltage positions of the minima roughly correspond to the superconducting order parameter.

Figure 2 demonstrates how the BTK fit done for the lowest temperature 2.2 K matches quite satisfactorily the curves of higher temperatures, for the same order parameter Δ_0 and dimensionless barrier strength Z, proving the existence of a uniform (homogeneous) superconducting

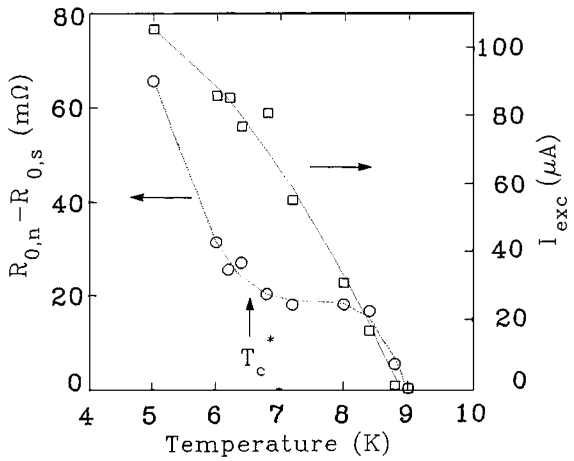

Fig. 3. – Temperature dependences of excess current (squares) and zero-bias contact resistance difference (circles) for the junction whose characteristics are shown in fig. 1. The dotted lines are a guide to the eye.

state with a well-defined energy gap having the standard (BCS) temperature dependence. However, one should note that the intensity of the BTK structure is quite low (at 2.2 K about 8 % compared to the expected 50 % of $R_{0,\mathrm{n}}$), and the vertical-scaling factor is not constant increasing 1.8 times from 2.2 K to 5.8 K for a given junction. The BTK fits for different contacts with the Ho compound yield a zero-temperature energy gap $\Delta_0 = 1.04 \pm 0.06$ meV. For the BCS ratio $2\Delta_0/k_\mathrm{B}T_\mathrm{c}$ one has to take as a critical temperature the lower transition temperature $T_\mathrm{c}^* = 6.5$ K, since the upper one gives an unreasonable low value $2\Delta/k_\mathrm{B}T_\mathrm{c} = 2.8$. The same value $2\Delta/k_\mathrm{B}T_\mathrm{c} = 3.7$ has been found for the Er- and Y-compounds [9] pointing to a quite moderate (electron-phonon) coupling for the superconducting pairing.

The appearance of the structure around zero bias just below T_c is anomalous and cannot be explained within the standard BTK theory. The structure has some resemblance with the "horn-structure" observed for point-contacts with Bi and Sb [10], of which examples can also be seen in fig. 1 and 2 in the form of the wiggles at higher bias voltages. These structures have been related to the suppression of superconductivity in microscopically inhomogeneous regions of the contact. This suppression is driven by the applied current leading to contact-resistance-dependent features in the spectra (note the differences in the data of fig. 1 and 2 around zero bias close to T_c). In our case, however, the microscopically inhomogeneous state is of intrinsic origin because the critical temperature corresponds to bulk single-crystal properties. The large broadening is probably due to strong magnetic scattering of conduction electrons by the disordered Ho magnetic moments preferentially oriented along the basal plane [2].

In fig. 3 we have plotted the temperature dependences of two parameters described above for the contact whose characteristics are presented in fig. 1. The excess current $I_\mathrm{exc}(T)$ increases monotonously and crosses the T_c^*-boundary between two different superconducting states without showing any significant anomaly, while the flattening of the resistance difference $(R_{0,\mathrm{n}} - R_{0,\mathrm{s}})$ in the range from T_c to T_c^* and the subsequent steep rise of this quantity mirrors the appearance of a new superconducting state. In a qualitative interpretation of these two dependences, the temperature-dependent excess current corresponds to a continuous rise of the order parameter below T_c, while the temperature-dependent resistance change at the superconducting transition T_c^* traces the behaviour of the quasiparticle excitation spectrum close to the Fermi energy.

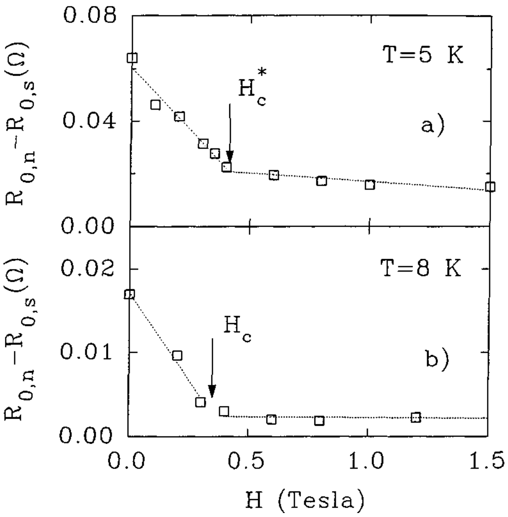

Fig. 4.

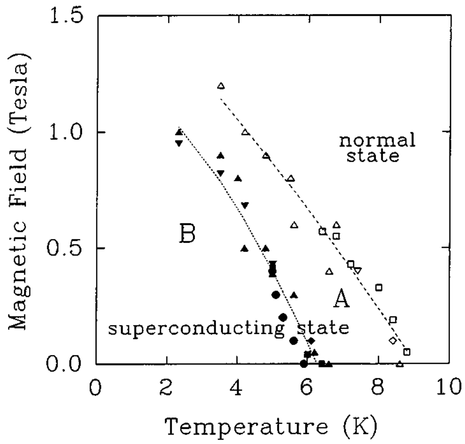

Fig. 5.

Fig. 4. – Zero-bias resistance difference as a function of magnetic field for two different temperatures close to $T_c^*(a))$ and to $T_c(b))$ for the junction of fig. 1. The arrows mark the positions of the deduced critical fields $H_{c2}(T)^*$ and $H_{c2}(T)$, respectively. In fig. 5 this critical-field data belong to the contact with the square symbols.

Fig. 5. – H-T phase diagram constructed from data taken from 5 junctions as indicated by the different symbols. The open and closed symbols correspond to the two transitions to the two states indicated by A and B.

The disappearance of two superconducting states has also been observed in an applied magnetic field by measuring the $dV/dI(V)$ curves at various magnetic fields H and temperatures T. Although these transitions can be clearly observed in the full voltage dependence of the dV/dI curves, we have summarized the results by plotting the difference $R_{0,n} - R_{0,s}$ as a function of the magnetic field. The points of saturation in the $R_{0,n} - R_{0,s}$ plots *vs.* magnetic field (fig. 4) determine the transition points in the phase diagram. Because of the reduced spectral resolution in a magnetic field, both transitions could not always clearly be observed in one field scan below T_c^* (see fig. 4 *a*)). Moreover, for fields greater than about 1.5 T the contact resistance changed often irreversibly. These effects limited our magnetic-field–dependent measurements to temperatures not far from T_c^* and T_c.

From the above-described procedure, the reconstructed phase diagram of $H_{c2}(T)$ for $HoNi_2B_2C$ is given in fig. 5 with the phase regions A and B as indicated. In this diagram there is no place for a re-entrant normal state below the upper critical temperature T_c. The corresponding $H_{c2}(T)$ dependences approach the critical temperatures linearly with slopes of about 0.25 T/K and 0.34 T/K for states A and B, respectively. The absolute values of H_{c2} extrapolated to zero temperature through the formula $H_{c2}(0) = 0.7(dH_{c2}/dT)_{T_c}T_c$ are about 1.5 T which is about 4 times greater than $H_{c2}(0)$ obtained from resistance measurements on polycrystals [3] and single crystals [2]. Anisotropic (magnetic) properties could explain this difference. Our estimate for $H_{c2}(0)$ for the Ho compound fits well to those for the Er and Y compounds found in point-contact experiments [9] showing the expected scaling with T_c^2.

The state B appears on the background of state A, which eventually weakens with further temperature decrease. This proves that the observed A-B phase transformation occurs within the same sample volume and is not due to an inhomogeneous composition of the material in the contact region. If two or more phases were present under the contact due to material inhomogeneity, the different structures related to these superconducting phases would be clearly visible in the $\mathrm{d}V/\mathrm{d}I$ curves at low temperatures.

The re-entrance into the normal state around $T_{\mathrm{N}} = 5$ K observed in resistance and magnetic-moment measurements [2], [3] might be due to the following reasons. As seen from the broadening of the superconducting order-parameter structure while approaching T_{c}^* and T_{N} from above (fig. 1), the spatial inhomogeneity of state A increases for lower temperatures. Magnetic fluctuations in the vicinity of T_{N} may locally create ferromagnetic order along the c-axis with corresponding π-phase shifts of the superconducting order parameter of phase B between adjacent Ni-B layers [4], [11]. This picture would describe the apparent re-entrant-to-normal-state behaviour as being due to the fluctuations of the phase of the modulus-uniform superconducting order parameter, but not to the suppression of the order parameter by magnetic fluctuations (which would be immediately seen in the Andreev-reflection spectra). The superconducting order parameter does not have a minimum, neither around T_{N} nor in the vicinity of T_{c}^*.

In conclusion, in the first experimental Andreev-reflection study of S-N contacts with rare-earth nickel boride carbides an internal structure has been found in the H-T phase diagram of superconducting $\mathrm{HoNi_2B_2C}$. This phase diagram contains a sharp borderline between two superconducting states at $T = 6.5$ K (at $H = 0$), probably related to the anti-ferromagnetic phase transition. Below the bulk superconducting transition temperature $T_{\mathrm{c}} = 9$ K the spectra show an anomalous broadened structure of an unknown superconducting state, and only below $T_{\mathrm{c}}^* = 6.5$ K a superconducting state develops with all the features in the Andreev-reflection spectra of a conventional BCS-type superconductor. The modulus of the superconducting order parameter shows a continuous increase below T_{c} with no sign of a suppression related to the re-entrant behaviour seen in resitivity and magnetization measurements. We argue that this re-entrant behaviour is most probably due to fluctuations of the phase of the superconducting order parameter. We note that nothing similar to this behaviour has been observed in Y- and Er-based junctions using compounds prepared with the same procedure [9].

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