Physica C 152 (1988) 105-110
North-Holland, Amsterdam

DETERMINATION OF THE ENERGY GAP IN A THIN $YBa_2Cu_3O_{7-x}$ FILM BY ANDREEV REFLECTION AND BY TUNNELING

H.F.C. HOEVERS, P.J.M. VAN BENTUM, L.E.C. VAN DE LEEMPUT and H. VAN KEMPEN
Research Institute for Materials, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands

A.J.G. SCHELLINGERHOUT and D. VAN DER MAREL
Department of Applied Physics, Delft University of Technology, Lorentzweg 1, NL-2628 CJ Delft, The Netherlands

Received 15 January 1988
Revised manuscript received 26 January 1988

We have observed for the first time Andreev reflection at the normal metal–superconductor interface in a thin film Ag–$YBa_2Cu_3O_{7-x}$ sample, which indicates a zero-momentum paired state in this high-T_c superconductor. The energy-dependence of the reflection probability indicates a lower limit of the energy gap in the $YBa_2Cu_3O_{7-x}$ equal to $\Delta = 12.5 \pm 2$ meV. Tunneling measurements on the same thin-film samples are in reasonable agreement with this value and yield $\Delta = 14 \pm 2$ meV. Both results are not incompatible with the weak-coupling BCS prediction $2\Delta/k_BT_c = 3.5$.

1. Introduction

The recent discovery of the new high-T_c copper-oxide superconductors [1] has stimulated an international effort to isolate the basic physical interaction that induces the unexpected high critical temperature. At present it appears that a wide spectrum of experimental results, including specific heat data [2–5], d.c. and a.c. [6–9] Josephson effects, quasiparticle tunneling [10–13] and flux quantization [14], can be readily described in terms of the BCS pairing scheme. On the other hand, the absence of an oxygen isotope effect in $YBa_2Cu_3O_{7-x}$ [15,16] indicates that the underlying interaction is possibly not of a phononic nature. One would expect that, in order to obtain a critical temperature in the 100 K range within the original BCS picture, the electron–phonon coupling would be exceptionally strong. The most straighforward indication for such strong-coupling effects is an enhanced value of the gap versus T_c ratio, far above the pedicted weak-coupling BCS value $2\Delta/k_BT_c = 3.5$. Calculations of the electron–phonon spectral density $\alpha^2F(\omega)$ for $La_{1.85}Sr_{0.15}CuO_4$ indicate that a T_c of 35 K for this material can be obtained with reasonable values of the Coulomb pseudopotential μ^* [17]. For this calculated spectral density, a gap-T_c ratio $2\Delta/k_BT_c = 5.3$ was predicted [18], assuming that the superconductive interaction is mediated by phonons. Similar calculations for $YBa_2Cu_3O_7$, assuming phonon-mediated superconductivity, predict a critical temperature in the range 19–30 K [19], and are not able to explain the experimentally observed 90 K.

Far infrared reflection measurements on polycrystalline $YBa_2Cu_3O_{7-x}$ indicate an increase of the normalized reflectivity [20–23] R_s/R_n above unity for frequencies below approximately 200 cm^{-1}. The far infrared results for the $2\Delta/k_BT_c$ value scatter between 2.5 and 3.5. In view of the uncertainty in these values, this is in general not inconsistent with the weak-coupling BCS prediction. More recent results on orientated films and single crystals, however, seem to indicate a somewhat larger gap [24,25]. The far infrared reflection itself is however strongly dominated by the Drude-type character of the metal and by the presence of optical phonons close to the gap frequency. An accurate comparison with the Mattis–Bardeen calculations is in general not possible.

Tunneling measurements, on the other hand, generally yield a larger gap ranging approximately between $3k_BT_c$ and $6k_BT_c$ [10–13]. The interpretation of the tunneling characteristics is unfortunately also not as straightforward as one should like. A quantitative comparison of the tunneling $I-V$ or dI/dV curves with theory is generally not possible, due to Coulomb charging effects of small isolated particles, multiple-peak structures and/or broadening of the peaks.

In this article, we will present an indenpendent determination of the energy gap of a thin evaporated $YBa_2Cu_3O_{7-x}$ film, based on the Andreev reflection of electrons at a normal metal–superconductor interface. The observation of Andreev reflection is a strong indication for zero-momentum $(k,-k)$ pairing in $YBa_2Cu_3O_{7-x}$. The results are compared with tunneling measurements on the same film. The value of the energy gap indicates a weak electron–phonon coupling.

2. Andreev reflection

Consider the configuration shown in the inset of fig. 1. A point contact with a contact radius of approximately 10 nm (Sharvin type [26]) is used to inject electrons with energies up to eV (where V is the voltage over the point contact) above the Fermi energy into the normal metal layer that is backed by a superconductor. When an electron, with energy smaller than the gap energy Δ, reaches the interface, it cannot enter the superconductor as a quasiparticle, since there are no states below $E=\Delta$. Instead, it can condense, together with a second electron of opposite spin and momentum from the normal metal, to form a Cooper pair in the superconductor. The hole, or missing electron, that results in the normal metal will move back in exactly the same direction where the incident electron came from (Andreev reflection [27]). This hole therefore travels back through the point contact and gives rise to the so-called excess current. In other words, for electron energies below Δ, one expects a decrease of the point contact resistance. This Andreev reflection has already been measured using both single [28,29] as well as double [30,31] point-contact techniques.

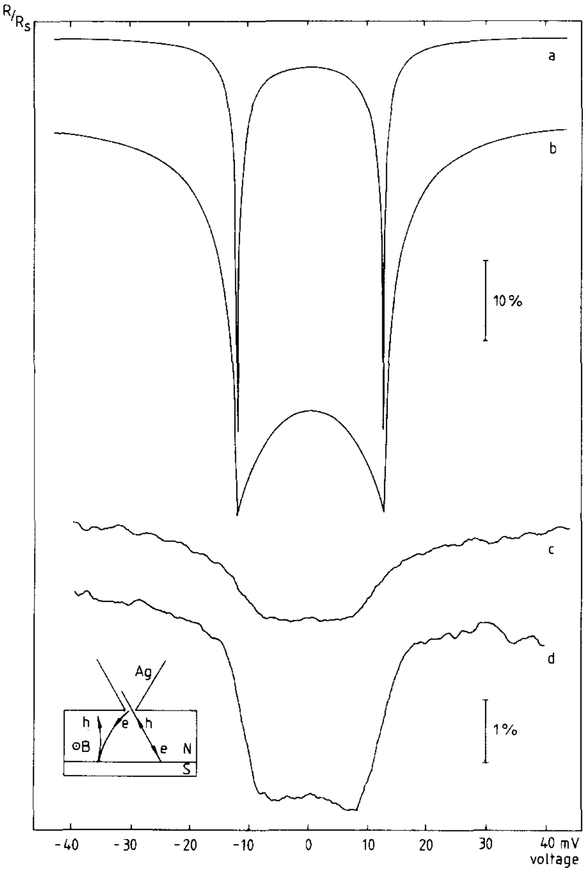

Fig. 1. Differential resistance of a point contact versus voltage. The upper curves (a and b) are calculated using the BTK model and assuming a gap energy of 12.5 meV, the scattering potential is 1.4 and 0.4 for curves a and b, respectively. The lower curves show two measurements with point contact resistances of 25.30 Ω and 5.81 Ω. respectively for curve c and d. The measurements are made on a 0.25–1 μm thick Ag–$YBa_2Cu_3O_{7-x}$ bilayer. Note the different scales for the calculations and the measurements. The inset shows the geometry of the single point-contact experiment with and without a magnetic field.

The sample was evaporated in two steps. First, a 1 μm thick layer of $YBa_2Cu_3O_{7-x}$ was evaporated on a sapphire substrate. The copper, yttrium and barium were evaporated with two electron guns and an effusion cell respectively. The evaporation rate of Ba was 0.3 nm s^{-1} and the rates of the other elements was adjusted to obtain the ratio of 1 : 2 : 3 for Y, Ba, and Cu. During evaporation oxygen was sprayed onto the substrate and a pressure of 2×10^{-4} Pa was obtained. In order to obtain a superconducting film, the sample had to be annealed at 1070 K for four hours, with a slow increase from and towards room temperature. The resistance of these films indicated an onset of superconductivity at 90 K, and a zero resistance state below 60 K. (For a more detailed description of the sample fabrication and characterization see ref. [32]).

Next, before the evaporation of Ag, the sample was kept in an oxygen atmosphere and sputter-cleaned in a glow discharge at room temperature and at a pressure of 10 Pa for 5 minutes. Then the substrate temperature was reduced to 120 K and the Ag film of 250 nm thickness was evaporated with a rate of 1.5 nm s^{-1} at a pressure of 6×10^{-4} Pa. Directly after the evaporation the pressure was increased by O_2 inflow and the sample was allowed to warm up.

The electrical contacts to the sample were made with indium pressure contacts. The point contact was made with a 50 μm diameter Ag wire with a electrochemically etched sharp point. The measurements were done in a pumped helium bath (1.2 K). A differential screw mechanism was used to make proper Sharvin contacts inside the bath. Stable point contacts with resistances between 2 and 100 Ω were obtained. A home-built current source provided a direct current and a small a.c. modulation through the point contact. As in our experiment the thickness of the normal metal layer is much greater than the point contact diameter (a Sharvin resistance of 1 Ω implies for Ag a contact radius of 18 nm), only the Andreev reflected holes return into the point contact, giving rise to an excess current. The excess current is measured as a decrease of point contact resistance using standard phase-sensitive-techniques.

Some typical results are displayed as curves (c) and (d) in the lower part of fig. 1. The curves show an almost symmetrical behaviour around zero voltage. In both curves the point-contact resistance at zero voltage is higher than that at low bias voltages; at voltages higher than approximately 10 mV the resistance starts to increase and finally becomes more or less constant above 15 mV.

This shape can be qualitatively well explained from a simple model of the energy dependence of the Andreev reflection probability, similar to previous results on Ag–Pb bilayers. A positive identification with Andreev reflection can be made by applying a magnetic field. When a magnetic field is applied parallel to the surface of the sample the orbits of electrons and holes are bent (see left side of the inset of fig. 1). The spot where Andreev reflected holes reach the surface will be shifted outside the point contact area, and the number of holes contributing to the excess current is reduced. We have observed that the point contact resistance increased with increasing magnetic field; for a magnetic field of 0.8 T and a point-contact resistance of 2.22 Ω the relative increase was 0.5% at zero voltage. According to a simple ballistical model a relative increase of about 1% is expected. Several models to explain the deviation between measured and calculated change of point-contact resistance are discussed in ref. [33]. Other possible explanations of the observed energy-dependent resistance, like for example electron–phonon scattering, do not depend on the magnetic field.

The theory of the energy dependence of Andreev reflection probability $A(\epsilon)$ at a normal metal–superconductor (N–S) interface is well developed and we follow the approach of Blonder, Tinkham and Klapwijk [34] (BTK). The effect of normal reflection at the N–S interface is represented by a scattering potential Z. The magnitude of Z is determined by elastic scattering and the mismatch of Fermi velocities on both sides of the interface [35]. A high value of Z, indicating a large ordinary reflection, results in a reduction of the excess current (which is proportional to $A(\epsilon)$). The effect of increasing Z is shown in the two upper curves of fig. 1, where the differential resistance $R(\epsilon)$ of a point contact is calculated as a function of voltage, using $R(\epsilon)/R_s=[1+A(\epsilon)]^{-1}$ with R_s the point contact resistance without excess current; the curves are drawn adopting the BTK model and a gap energy Δ of 12.5 meV. Note that at $|E|=\Delta$, $R/R_s=0.5$, independent of Z.

Qualitatively, the measured curves resemble the theoretical curves based on the BTK model. It is clear that the maximum change of differential resistance is much smaller than the factor 0.5 of the ideal case, and that the sharp peaks at the gap energy do not show up.

The magnitude of the differential resistance at zero voltage depends on the thickness of the normal metal layer, the mean free path of the electrons due to impurity scattering, l_{imp}, and the value of Z. In case of thin films, l_{imp} is comparable to d. Adopting 1.4×10^5 m s^{-1} [36] and 1.5×10^6 m s^{-1} as Fermi velocities of $YBa_2Cu_3O_{7-x}$ and Ag respectively, a Z of 1.4 is derived for a perfect N–S interface without elastic scattering. From fig. 1 it can be seen that the measured decrease in resistance at zero voltage is of the same order of magnitude as that calculated for $Z=1.4$. The sharp peaks at the gap energy have, however, disappeared and only small structures at $V\approx 10$ mV remain. Several effects, such as modulation broading, electron–phonon scattering in the Ag, proximity-induced superconductivity, and inhomogeneity of the gap in various crystallites of the film, may influence the shape of the curves. In the following, we will give a brief and preliminary account of these effects.

Since the measurements were made at 1.2 K and with a modulation voltage of 0.1 mV, thermal and modulation broadening can not account for such a considerable smoothing that the peaks would no longer be recognizable. The mean free path $l(\epsilon)$ of the injected electrons in the normal metal consists of an energy independent part l_{imp} and the energy-dependent phonon–emission length $l_{\mathrm{eph}}(\epsilon)$. For energies which become comparable to the gap energy of the $YBa_2Cu_3O_{7-x}$, $l_{\mathrm{eph}}(\epsilon)$ starts to dominate $l(\epsilon)$. Measurements of the energy-dependent electron–phonon coupling constant α^2F of Ag [37] indicate that $l_{\mathrm{eph}}(\epsilon)$ will decrease rapidly and stay almost constant above 20 mV. When $l(\epsilon)$ decreases drastically, the excess current as well as the peaks at $E=|\Delta|$ become smaller. However, model calculations in which a Lorentzian was fitted to the α^2F function of Ag in order to account for the decrease of $l(\epsilon)$, still showed distinct peaks at the gap energy. Therefore, we conclude that the reduction of $l(\epsilon)$ alone is not sufficient. Additional experiments with the Ag replaced by Cu may give information on the effect of $l(\epsilon)$. The advantage of Cu in comparison with Ag is that the electron–phonon coupling in Cu becomes important at higher energies than in Ag.

If the value of Z is lower than 1.4, the peaks are less pronounced (compare the upper curves in fig. 1). However, a lower value of Z can only be obtained if the difference in Fermi velocities in the $YBa_2Cu_3O_{7-x}$ and Ag is smaller. As noted in ref. [35], it is questionable to use a single parameter Z to describe complex Fermi surfaces.

When the energy gap has, due to the proximity effect, a gradual increase from the normal metal to the superconductor instead of the step-like behaviour assumed in the BTK model, a broadening of the peak in combination with a shift to lower energies is found [38]. Although the curves will smooth near the gap energy, the peaks will stay visible due to the large Z. Since the proximity effect at the Ag–$YBa_2Cu_3O_{7-x}$ interface is unknown the effect is difficult to judge. In addition to the former argument when the effect of a gap extending in a direction perpendicular to the interface was considered, the energy gap may also vary in the plane of the N–S interface for the different crystallites. The area of the N–S interface that is probed by Andreev reflection has dimensions comparable to the thickness of the normal metal layer, which implies that a large number of crystallites of $YBa_2Cu_3O_{7-x}$ may be probed. If the gap energy of the crystallites varies, the measured curves will be smoothed. The absence of sharp peaks, and the slope in the resistance is not incompatible with a statistical variation of the energy gap between approximately 10 and 15 meV.

If an onset critical temperature $T_c=90$ K is adopted, the Andreev reflection measurements give a gap-T_c ratio of 3.2 ± 0.6, based on an energy gap of 12.5 ± 2 meV. The latter value may however be a lower limit due to effects of electron–phonon interaction in the normal metal layer.

3. Tunneling

In order to check for a possible inhomogeneity of the energy gap we have performed tunneling measurements on the same film that was measured in the Andreev experiment. The thin-film sample was mounted in a low-temperature scanning tunneling microscope, which allowed us to determine the tunneling I–V characteristic at different spots on the surface of the film. As in the case of sintered polycrystalline $YBa_2Cu_3O_{7-x}$ samples, the best tunneling curves were obtained with the tungsten tip in direct mechanical contact with the film (see also ref. [13]). In fig. 2 we show a typical tunneling I–V curve, taken at a temperature of 1.2 K. The sharp increase of the current is characteristic for superconductor– isolator–superconductor tunneling. We assume that the grain boundaries act as a natural tunneling barrier. This would also explain the relatively low values of the critical current for these samples. The superconducting path between the electrodes is then of a percolative nature with many weak links between

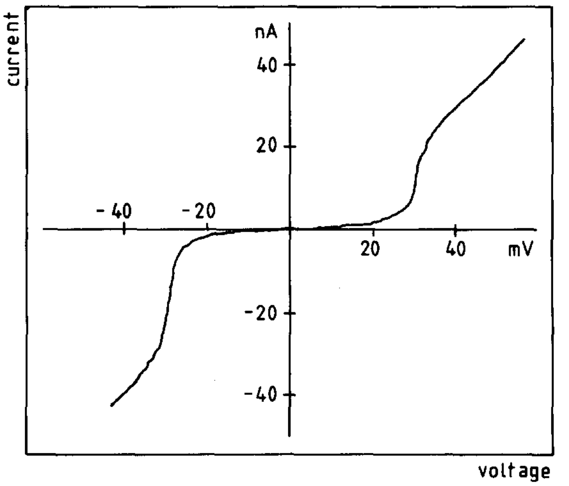

Fig. 2. Tunneling characteristic of a superconductor–isolator–superconductor junction between two grains embedded in the $YBa_2Cu_3O_{7-x}$ film.

adjacent superconductive crystallites, and the critical current is completely determined by the weakest link in the chain.

From the tunneling characteristic in fig. 2, we can deduce a value for the gap $\Delta = 14$ meV. The absence of a tunneling current below $eV = 2\Delta$ indicates that there are no quasiparticle states below $|E| = \Delta$. In the case of p-wave superconductivity one would expect a gapless quasiparticle density of states for at least some directions in k-space [39]. The value of the gap was found to vary slightly from point to point on the surface, roughly between 11 and 16 meV. The I–V curves that showed gap structures near the lower limit were less clear than the one shown in fig. 2. In many cases there were also indications of a Coulomb blockade, related with the electrostatic charging of small isolated grains in the film. These values for the gap are in reasonable agreement with some other tunneling measurments [10,11,13], with most of the far infrared reflection data [20–23], and with the result obtained from the Andreev experiment. Only in one occasion, we found an apparent local gap, which was much larger ($\Delta \approx 22$ meV). This could be either related to the presence of two junctions in series, or to local deformations of the lattice. One should realize that the tunneling probes the superconductor very locally. The fact that tunneling occurs at the grain boundaries already indicates that the crystal structure at these boundaries may differ considerably from the bulk 123 structure.

If we take the onset critical temperature $T_c = 90$ K as a reference, we find a gap-T_c ratio of 3.6 ± 0.6. One could argue that the spread in Δ is comparable to the spread in T_c, determined from the resistive transition, and that the results are not in contradiction with the weak-coupling BCS prediction $2\Delta/k_BT_c = 3.5$. Unfortunately, the present experimental STM set-up does not allow us to measure the energy gap of a single crystallite as a function of temperature.

4. Conclusions

We conclude that we have observed for the first time excess current due to Andreev reflection, with a point contact on a thin film Ag–$YBa_2Cu_3O_{7-x}$ bilayer. The observation of Andreev reflection is in itself a clear manifestation of the fact that the superconducting ground state in $YBa_2Cu_3O_{7-x}$ consists of a paired zero-momentum state. The energy and magnetic field dependence of the measurements agree qualitatively with the BTK model. From these preliminary measurements, a lower limit of $\Delta = 12.5 \pm 2$ meV of the $YBa_2Cu_3O_{7-x}$ is found. Tunneling measurements on the same film indicate a slightly larger gap of $\Delta = 14 \pm 2$ meV. In view of the uncertainties, this overlap may be considered as reasonable. Both results are not incompatible with the weak-coupling BCS value $2\Delta/k_BT_c = 3.5$. It is therefore tempting to assume that the superconductive interaction is not exclusively of a phononic nature. In order to obtain a more definite conclusion we propose similar measurements on Cu–$YBa_2Cu_3O_{7-x}$ bilayers, deposited onto more suitable substrates, like for example $SrTiO_3$.

The combined results from the Andreev reflection and tunneling are compatible with a BCS $(k\uparrow, -k\downarrow)$ pairing.

Part of this work is supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO), and by Philips Research Laboratories.

References

[1] G. Bednorz and K.A. Müller, Z. Phys. B 64 (1986) 189.

[2] K. Kitazawa, T. Atake, H. Ishi, H. Sato, H. Takagi, S. Uchida, Y. Saito, F. Fueki and S. Tanaka, Jpn. J. Appl. Phys. 26 (1987) L748.

[3] A. Junod, A. Bezinge, T. Graf, J.L. Jorda, J. Muller, L. Antognazza, D. Cattani, J. Cors, M. Decreaux, O. Fischer, M. Banozski, P. Genoud, L. Hoffman, A.A. Manuel, M. Peter, E. Walker, M. Francois and K. Yvon, Europhys. lett. 4 (1987) 247.

[4] N.V. Nevitt, G.W. Grabtree and T.E. Klippert, Phys. Rev. B 36 (1987) 2398.

[5] S.E. Inderhees, M.B. Salamon, T.A. Friedmann and D.M. Ginsberg, Phys. Rev. B 36 (1987) 2401.

[6] A.Th.A.M. de Waele, R.T.M. Smokers, R.W. van der Heijden, K. Kadowaki, Y.K. Huang, M. van Sprang and A.A. Menovsky, Phys. Rev. B 35 (1987) 8858.

[7] J. Kuznik, M. Odehnal, S. Safrata and J. Endal, J. Low Temp. Phys. 69 (1987) 313.

[8] J. Niemeyer, N.D. Kataria, M.R. Dietrich, C. Politis, H. Koch, R. Schöllhorn and H. Eickenbusch, Z. Phys. B 69 (1987) 1.

[9] Fan Changxin, Sun Lin, Miao Bocai and Liu Jun, Solid State Commun. 64 (1987) 689.

[10] J.R. Kirtley, R.T. Collins, Z. Schlesinger, W.J. Gallagher, R.L. Sandstrom, T.R. Dinger and D.A. Chance, Phys. Rev. B 35 (1987) 8846.

[11] M.F. Crommie, L.C. Bourne, A. Zettl, Marvin L. Cohen and A. Stacy, Phys. Rev. B 35 (1987) 8853.

[12] J. Moreland, J.W. Ekin, L.F. Goodrich, T.E. Capabianco, A.F. Clark, J. Kwo, M. Hong and S.H. Liou, Phys. Rev. B 35 (1987) 8856.

[13] P.J.M. van Bentum, L.E.C. van de Leemput, L.W.M. Schreurs, P.A.A. Teunissen and H. van Kempen, Phys. Rev. B 36 (1987) 843.

[14] P.L. Gammel, D.J. Bishop, G.J. Dolan, J.R. Kwo, C.A. Murray, L.F. Schneemeyer and J.V. Waszczak, Phys. Rev. Lett. 59 (1987) 2592.

[15] B. Batlogg, R.J. Cava, A. Jayaraman, R.B. van Dover, G.A. Kourouklis, S. Sunshine, D.W. Murphy, L.W. Rupp, H.S. Chen, A. White, K.T. Short, A.M. Mujsce and E.A. Rietman, Phys. Rev. Lett. 58 (1987) 2333.

[16] L.C. Bourne, M.F. Crommie, A. Zettl, H.C. zur Loye, S.W. Keller, K.L. Leary, A.M. Stacey, K.J. Chang, M.L. Cohen and D.E. Morris, Phys. Rev. Lett. 58 (1987) 2337.

[17] W. Weber, Phys. Rev. Lett. 58 (1987) 1371.

[18] M. Schossman, F. Marsiglio and J.P. Carbotte, Phys. Rev. B 36 (1987) 3627.

[19] W. Weber and L.F. Mattheis, to be published.

[20] D.A. Bonn, J.E. Greedan, C.V. Stager, T. Timusk, M.G. Doss, S.L. Herr, K. Kamaras and D.B. Tanner, Phys. Rev. Lett. 58 (1987) 2249.

[21] G.A. Thomas, H.K. Ng. A.J. Milles, R.N. Bhatt, R.J. Cava, E.A. Rietman, D.W. Johnson Jr., G.P. Espinosa and J.M. Vanderberg, Phys. Rev. B 36 (1987) 846.

[22] J.M. Wrobel, S. Wang, S. Gygax, B.P. Clayman and L.K. Peterson, Phys. Rev. B 36 (1987) 2368.

[23] A. Wittlin, L. Genzel, M. Cardona, M. Bauer, W. Köning, E. Carcia, M. Barahona and M.V. Cabanas, submitted to Phys. Rev. B.

[24] R.T. Collins, Z. Schlesinger, R.H. Koch, R.B. Laibowitz, T.S. Plaskett, P. Freitas, W.J. Gallagher, R.L. Landstrom and T.R. Dinger, Phys. Rev. Lett. 59 (1987) 704.

[25] Z. Schlesinger, R.T. Collins, D.L. Kaiser, and F. Holtzberg, Phys. Rev. Lett. (1987) 1958.

[26] Yu.V. Sharvin, Zh. Eksp. Teor. Fiz. 48 (1965) 984 [Sov. Phys.-JETP 21 (1964) 655]. A Sharvin junction is a junction between two metals in the Knudsen limit, i.e. $l \gg b$, where l is the electron mean free path and b the contact radius.

[27] A.F. Andreev, Zh. Eksp. Teor. Fiz. 46 (1964) 1823 [Sov. Phys.-JETP 19 (1964) 1228].

[28] P.A.M. Benistant, A.P. van Gelder, H. van Kempen and P. Wyder, Phys. Rev. B 32 (1985) 3351.

[29] P.C. van Son, H. van Kempen and P. Wyder, Phys. Rev. Lett. 59 (1987) 2226.

[30] S.I. Bozkho, V.S. Tsoi and S.E. Yavkolev, Pis'ma Zh. Eksp. Teor. Fiz. 36 (1982) 123 [JETP Lett. 36 (1982) 152].

[31] P.A.M. Benistant, H. van Kempen and P. Wyder, Phys. Rev. Lett. 51 (1983) 817.

[32] A.J.G. Schellingerhout, R.H.M. van de Leur, D. Schalkoord, D. van der Marel and J.E. Mooij, Z. Phys. B, to be published.

[33] P.C. van Son, H. van Kempen and P. Wyder, to be pubished.

[34] G.E. Blonder, M. Tinkham and T.M. Klapwijk, Phys. Rev. B 25 (1982) 4515.

[35] G.E. Blonder and M. Tinkham, Phys. Rev. B 27 (1983) 112.

[36] M. Gurvitch and A.T. Fiory, Phys. Rev. Lett. 59 (1987) 1337.

[37] A.G.M. Jansen, F. Mueller and P. Wyder, Phys. Rev. B 16 (1977) 1325.

[38] P.C. van Son, H. van Kempen and P. Wyder, Phys. Rev. B, accepted for publication.

[39] T.M. Rice, Z. Phys. B 67 (1987) 141.