Temperature and junction-type dependency of Andreev reflection in MgB$_2$

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We studied the voltage and temperature dependency of the dynamic conductance of normal metal-MgB$_2$ junctions obtained either with the point-contact technique (with Au and Pt tips) or by making Ag-paint spots on the surface of MgB$_2$ samples. The fit of the conductance curves with the generalized BTK model gives evidence of pure s-wave gap symmetry. The temperature dependency of the gap, measured in Ag-paint junctions (dirty limit), follows the standard BCS curve with $2\Delta/k_BT_c = 3.3$. In out-of-plane, high-pressure point contacts we obtained almost ideal Andreev reflection characteristics showing a single small s-wave gap $\Delta = 2.6 \pm 0.2$ (clean limit).

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An enormous interest has been aroused by the recent discovery of superconductivity in magnesium diboride by Nagamatsu et al. [1]. The critical temperature ($T_c$) of this intermetallic compound is about 40 K. Many papers have recently appeared in literature concerning the determination of the energy gap $\Delta$ from tunneling [2, 3, 4, 5, 6], Andreev reflection [6, 7, 8] and many other measurements. The results are still controversial, since the measured values of $\Delta$ range between 2 and 7.5 meV. Many authors found a temperature dependency of the gap following rather well the BCS curve for a pure s-wave superconductor [2, 3, 5]. On the other hand, very recent tunnel and Andreev reflection measurements have suggested the presence in MgB$_2$ of two different gaps, both having a BCS-like temperature dependency and the same $T_c$ [3, 5]. According to a recent theoretical work [11], the small gap $\Delta_1$ would appear on the sheets of the Fermi surface arising from 3D $p_z$ bonding and antibonding bands, while the larger one $\Delta_2$ would be related to the nearly-cylindrical hole sheets around the Γ-A line arising from quasi-2D $p_{x,y}$ B bands.

At the present moment, it is of primary importance to understand whether these two gaps are really present (e.g., by possibly measuring each of them separately and independently of the other) and to try to explain why various experiments have so far observed such a large spread of gap values. To do so, in this paper we present and discuss Andreev reflection results obtained in normal metal – MgB$_2$ junctions made either with the point-contact technique (by using sharp platinum or gold tips) or by making small silver-paint spots on the surface of the samples. We will show that the fit of the normalized experimental conductance curves of the junctions with the Blonder-Tinkham-Klapwijk (BTK) model generalized by Y. Tanaka and S. Kashiwaya [12] gives evidence for a s-wave symmetry of the order parameter and shows that, when the tip is almost perpendicular to the B planes, a single small gap is measured. The results of the fit also suggest that the superconducting properties of this compound are strongly influenced by impurities.

The polycrystalline MgB$_2$ starting material, of high density (2.4 gr/cm$^3$), was produced at EDISON S.p.A. by means of a reaction sintering, for 3 hours at 950 °C, of elemental B and Mg, in a sealed stainless steel container, lined with a Nb foil. More details on the preparation are given elsewhere [13]. X-ray powder diffraction showed the presence in the material of spurious phases (mainly MgO and unreacted Mg). Both AC susceptibility and resistivity measurements indicate that $T_c = 38.8$ K with $\Delta T_c = 0.5$ K as determined by the full width at half maximum of the $d\chi'/dT$, where $\chi'$ is the real part of the susceptibility [14]. These values, together with the rather small residual resistivity ($\rho_0 \approx 4 \mu\Omega$-cm) prove that the high quality of the bulk material is not spoilt by the presence of spurious phases. The samples, of about $2 \times 1 \times 0.5$ mm$^3$, were cut from the very hard bulk MgB$_2$ material with a fine diamond circular saw. Their surface was polished with fine diamond tools and then etched with a solution of 1% HCl in pure ethanol. The resulting samples, observed by a metallographic microscope, clearly show the presence of small (50-70 µm) single crystals (with random orientation) immersed in a more amorphous matrix. Figure 1 shows a photograph of a sample surface, taken by an optical microscope at 98×, where the MgB$_2$...
crystals are clearly visible.

The point-contact junctions were obtained by pressing very sharp metallic tips against the surface of the samples. We used three kinds of tips, obtained by electrochemically etching in an HCl-HNO$_3$ solution thin Au and Pt wires (with diameter $\varnothing = 0.2$ mm) and of a thicker Pt wire ($\varnothing = 0.5$ mm), respectively. As a consequence, we could apply different pressures in the contact area of the sample surface.

Junctions of a different kind were obtained by directly gluing thin ($\varnothing = 25\mu$m) Au wires on the etched surface of the sample by using small spots of silver paint [8]. The conductance vs. voltage curves showed that many of these contacts were actually S–N junctions.

We measured the $I - V$ characteristics of the various S–N junctions and calculated the dynamical conductance curves ($dI/dV$ vs. $V$), which were then normalized so that $dI/dV \simeq 1$ for $|V| \gtrsim 15$ meV. In doing this we considered only the data sets for which $dI/dV$ was reasonably constant at $|V| > 15$ mV and did not show sensible variations at the change of temperature.

None of the conductance curves showed effects of heating phenomena. In fact, the values of the normal-state point-contact resistance we obtained clearly indicate that all the junctions are in the Sharvin limit (mean free path larger than the size of point contact) [15]. The contact radius $a$, evaluated from the contact resistance, is always less than 100 Å. Since the mean free path for MgB$_2$ is estimated in 600 Å [14], the conditions for energy-resolved spectroscopy are totally fulfilled.

Figure 2 reports two examples of the best-quality normalized conductance curves (open circles) obtained at $T = 4.2$ K with the point-contact technique by using a Pt tip made starting from the thicker Pt wire. A maximum pressure of the order of 0.6 GPa is applied to the sample by this kind of tips, as we independently measured from the tip deformation. The conductance curves show classical Andreev reflection features. The maximum value of the normalized conductance is very high in comparison with previous data present in literature [8, 10], being equal to the theoretical one for an ideal S–N junction with a very low barrier height according to the BTK model [12]. Notice that contacts of such a high quality were actually obtained in a small percentage of measurements. We fitted these conductance curves by using the generalized BTK model [12], and we found that the best results (see for example the solid lines in Fig. 2) were obtained with a pure $s$-wave gap symmetry. Let us remind that the free parameters of an $s$-wave fit are: the parameter $Z$, which takes into account the barrier height and the mismatch between the Fermi velocities in the superconductor and in the normal metal, the lifetime broadening $\Gamma$, and the value of the gap $\Delta$. Actually, curves such as those reported in Fig. 2 can be fitted very well by using null or very small values of $\Gamma$. The resulting gap values are consistent with one another and give an average value $\Delta = 2.6 \pm 0.2$ meV [8, 10].

Figure 3 shows two examples of the best point-contact normalized conductance curves (open circles) obtained with Pt (a) and Au (b) tips made by starting from the thinner wires ($\varnothing = 0.2$ mm), together with the relevant $s$-wave best fit curves (solid lines). Here, the maximum pressure applied by the tips on the sample surface is about 0.4 and 0.1 GPa for Pt and Au tips, respectively.

It can be clearly seen by comparing Fig. 3 (a) and (b) to Fig. 2 that, at the decrease of the tip pressure, the
maximum value of the normalized conductance decreases from $\sim 1.8$ (Pt tip made from thick wire) to $\sim 1.35$ (Pt tip, thin wire) and $\sim 1.25$ (Au tip, thin wire). The corresponding best-fit parameters (shown in the legends) indicate a slight increase of $Z$ and $\Delta$ (up to $Z \sim 0.38$ and $\Delta \sim 3.2$ meV, respectively) but especially a more remarkable increase of the lifetime broadening (up to $\Gamma = 0.69$ and 1.25 meV for Pt and Au tip, respectively) which seems to indicate a progressive increase of the disorder in the junction at the decrease of the tip pressure.

We also obtained good and reproducible Andreev reflection characteristics in the MgB$_2$/Ag-spot junctions. The great stability of these contacts allowed us to study the temperature dependency of the conductance curves. In figure 4 (a) we report the normalized conductance curves obtained at different temperatures between 4.2 K and the temperature at which the Andreev features disappear, $T_2 \simeq 34.5$ K (open symbols). For clarity, only some of the measured curves are shown. It is evident from the comparison of these curves with those of the previous figures that the Andreev features are largely broadened and the maximum normalized conductance at low $T$ is reduced to values of the order of 1.15. The fit of the curves with the generalized BTK model is very good for any temperature up to $T_2$ if an $s$-wave gap symmetry is used. The best-fit curves are reported in figure 4 (a) (solid lines). The fact that $T_2$ is smaller than $T_c^{\text{bulk}}$ could be due to the presence of a modified layer at the surface of the polycrystalline samples.

Figure 4 (b) reports the temperature dependency of the order parameter $\Delta$ (solid circles) determined by the fit of the curves in Fig. 4 (a), together with the $\Delta$ vs. $T$ standard BCS behaviour (solid line) calculated with $T_2 = 34.5$ K and $\Delta = 4.9$ meV, from which a ratio $2\Delta/k_BT_c^{\text{bulk}} = 3.3$ is obtained. The agreement between experimental data and theoretical curve is rather good for $T > 12$ K. Notice that both the theoretical BCS low-temperature gap $\Delta = 4.9$ meV and the experimental one (which is slightly lower) reported in Fig. 4 are very different from the gap determined with the point-contact technique on the same samples (about $\Delta = 2.8 \pm 0.4$ meV if all the point-contact results are averaged).

At a first glance, the results collected in the different sets of junctions appear inconsistent: very different gap values have been obtained and a large broadening dominates the Andreev curves in the Ag-spot junctions, while it is totally absent in the high-pressure point-contact ones and partially present in the low-pressure ones. The situation can be clarified by carefully analyzing the different measurement conditions and the probable state of the sample surfaces.

In the point-contact junctions the tip touched the sam-
ple perpendicularly to a surface such as that shown in Fig. 1. Due to the presence of rather large MgB$_2$ crystals (the darker islands in the figure) and to the small tip dimensions (a few microns), it is very likely that the best Andreev curves we have shown in Figs 2 and 3 are due to contacts with the surface of a single crystal. Further support to this hypothesis comes from the inspection of the tip position at the end of the experiments.

The crystal surface, even shortly after the etching, is likely to be modified by the presence of impurities (e.g. MgO whose formation is due to the contact with air), grain boundaries or, maybe, by intrinsic surface phenomena of relaxation or reconstruction. If the tip applies a rather large pressure on the sample surface (as in the case of the tips obtained from the thick Pt wire, see Fig. 2) it is possible to remove or perforate this modified surface layer. This allows us to obtain ideal contact with the crystal surface in the clean limit. In this conditions we have evidence of a single small gap $\Delta_1 \approx 2.6$ meV with a pure $s$-wave symmetry and without any broadening. The experimental detection of a small single gap (of about the same amplitude as that we observed) is predicted in the case of tunneling perpendicular to the honeycomb B planes in a recent paper by Liu et al. [1], where the small gap $\Delta_1$ and a larger one $\Delta_2 \sim 3\Delta_1$ are associated to the 3D parts and to the quasi-2D sheets of the FS, respectively. The strong directionality of the tunneling experiments can be explained by the point-contact measurements, where the carriers are actually injected in the whole half-space. Nevertheless, the probability of normal injection is still maximum and therefore the electronic properties are mainly probed along the direction perpendicular to the surface. Then, our results could be compatible with the predictions of Ref. [1] if the tip is within a certain solid angle around the out-of-plane direction. Taking into account the random distribution of grain orientation and the small percentage of conductance curves such as those reported in Fig. 2, this hypothesis is definitely plausible.

At the decrease of the tip pressure (see Fig. 3), the modified surface layer plays a more and more important role giving rise to a larger $Z$ value but, especially, to a large increase of the lifetime broadening. If we roughly interpret $\Gamma$ as a measure of the disorder of the surface, we can argue that the disorder is rather large in the modified surface layer.

In the MgB$_2$/Ag-spot junctions, due to the very large apparent contact area (the Ag spots have $\varnothing = 150 - 250\mu m$, as can be seen from Fig. 1), we probably measure an effective average of the properties of many crystals with different orientation, of their surfaces and also of the intergrain material, possibly having different composition. Therefore, the directionality of the contact is completely lost. Moreover, the absence of pressure in the contact region makes it impossible to remove the probable modified surface layer, which is therefore expected to play a major role in these junctions (proved by the very large $\Gamma$ values) and we can argue that we are actually measuring the Andreev reflection properties of MgB$_2$ surfaces in the dirty limit. In this conditions the paper of Liu et al. [1] predicts the presence of a single gap with a low-temperature value $\Delta \approx 0.6\Delta_{BCS}$, a reduced $T_c$ and a BCS-like temperature dependency. The results shown in Fig. 4 (b) seem quite compatible with these predictions.

The previous argument can also help to interpret the results of many other groups who observed, together with $\Delta$ values similar to that we measured in the dirty limit, Andreev reflection features with rather small amplitude [2, 3] or largely broadened STM tunneling curves [4]. Incidentally, if we simulate the tunneling curves that can be obtained by using $\Delta = 4.9$ meV and $\Gamma \approx 3$ meV (approximately the values we obtained in MgB$_2$/Ag spot junctions) and $Z \approx 5$, we get $dI/dV$ curves very similar to those shown in [5].

Of course, the previous discussion opens some questions concerning the role of impurities in MgB$_2$. Contrary to what is expected for a superconductor in pure $s$-wave symmetry, here the nonmagnetic impurities seem to have a big effect on the superconducting properties of the material.

In conclusion, even if a complete temperature and magnetic field dependency of the small out-of-plane 3D gap and the independent observation of the large in-plane quasi-2D gap still have to be done, we suggest that the Andreev reflection results obtained in high-quality single-crystal-like samples are compatible with the two-gap model of superconductivity in MgB$_2$ [1], with the presence of a modified layer at the surface of the crystals and with an important and non-conditional role of the impurities in this material.

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