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Two-band/two-gap superconductivity in carbon-substituted MgB_2 evidenced by point-contact spectroscopy

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The Andreev reflection measurements of the superconducting energy gap in the carbon-substituted MgB_2 are presented. Despite the strong suppression of the transition temperature by 17 K in comparison with the pure MgB_2, the same reduced value of the small superconducting energy gap with $2\Delta/kT_c \approx 1.7$ has been systematically observed. This indicates that the two-band/two-gap superconductivity is still preserved here.

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MgB_2—a surprising intermetallic superconductor at 39 K (Ref. 1) represents a spectacular example of two-band/two-gap superconductivity.[2] Among many experiments,[3–8] the point-contact spectroscopy based on the Andreev reflection process gave one of the first proofs of such a multigap superconductivity.[9] In line with the theoretical predictions,[10] for the larger gap Δ_σ attributed to the two-dimensional (2D) σ band parallel to the c axis originating from the boron $p_{x\text{-}y}$ orbitals, the reduced gap value $2\Delta_\sigma/k_BT_c \simeq 4$ has been found. The smaller gap Δ_π on the 3D π band of the boron p_z orbitals has the reduced value much below the BCS weak-coupling limit of a one-band superconductor ($2\Delta_\pi/k_BT_c \simeq 1.7$). One of the fundamental consequences of multigap superconductivity is a breakdown of the Anderson's theorem saying that superconductivity is not sensitive to nonmagnetic impurities. Indeed, the theoretical calculations of Liu *et al.*[10] argued that the introduction of strong defects should have fatal consequences for the superconductivity in MgB_2, merging its two distinct gaps to one and decreasing the transition temperature to about 22 K. The substitution of magnesium and boron represents one of the possibilities to introduce such defects. Unfortunately, it appears to be a difficult task. The carbon has been one of the few examples of chemical substitution that MgB_2 accepts. Moreover, the transition temperature can be strongly suppressed when inclusion of carbon at about 10% level drops T_c by about 50%.[11,12] Surprisingly, the specific heat measurements of Ribeiro *et al.* have indicated that the two-gap superconductivity still retains in the $Mg(B_{0.9}C_{0.1})_2$ samples with $T_c = 22$ K. Here we directly show by spectroscopic measurements that the small superconducting energy gap with $2\Delta/k_BT_c \simeq 1.7$ has been systematically observed closing at the bulk $T_c = 22$ K. Its reduced value is very similar to the case of pure MgB_2 indicating that it is Δ_π on the 3D π band and that the two-band/two-gap superconductivity is really preserved here, confirming the speculations from the specific heat data.

Samples of carbon-substituted MgB_2 were synthesized in the form of pellets following the procedure described in Ref. 11 from magnesium lumps and B_4C powder. The nominal stoichiometry was kept as $Mg(B_{0.8}C_{0.2})_2$. Synthesis temperature and time were optimized to 1100 °C and 24 h, respectively. Traces of B_4C were not visible in the x-ray diffraction (XRD) patterns. Small amounts of two impurity phases (MgO and MgB_2C_2) result even with optimization of the synthesis and may well indicate that there is a carbon solubility limit of $x \sim 0.1$ for synthesis at ambient pressure.[11,12] The homogeneity of the sample has been evidenced by a narrow transition in magnetic susceptibility with an onset of diamagnetism at 22 K and electrical resistance with $R = 0$ at 21 K. Recent neutron powder diffraction studies[12] on a sample, made in the same way but with the isotopically enriched ^{11}B, have revealed a stoichiometry of $Mg(B_{0.9}C_{0.1})_2$.

Point-contact measurements have been performed on several pieces coming from two different batches of $Mg(B_{0.9}C_{0.1})_2$ samples with $T_c = 22$ K. A special point-contact approaching system with a negligible thermal expansion allows for temperature-dependent measurements up to 100 K. A standard lock-in technique at 400 Hz was used to measure the differential resistance as a function of applied voltage on the point contacts. The microconstrictions were prepared *in situ* by pressing different metallic (M) tips (copper, silver, platinum, and tungsten formed either mechanically or by electrochemical etching) on different parts of the freshly polished surface of the superconductor. The approaching system enabled both the lateral and vertical movements of the tip by differential screw mechanism.

Transport of charge carriers across a normal-metal/superconductor (N/S) interface involves the process of Andreev reflection. If the N/S interface consists of a ballistic point contact with the electronic mean free path l in the normal metal bigger than the diameter of the contact orifice, the excitation energy eV of charge carriers passing the point contact is controlled by the applied voltage V. A direct transfer of the charge carriers with an excitation energy $eV < \Delta$ is forbidden because of the existence of the energy gap Δ in the quasiparticle spectrum of the superconductor. The Andreev reflection causes the retroreflection of a hole back into the normal metal with the formation of a Cooper pair in the superconductor. At excitation energies above the gap, the transfer of quasiparticles is again allowed. This leads to a two times higher conductance of a N/S contact at $V < \Delta/e$ (zero-temperature limit) for the case of ballistic transport with high transmission probability of the charge carriers, $T = 1$. Surface collisions and/or mismatch of the Fermi velocities in the point-contact forming electrodes lead to the tunneling channel of the carrier transport with $T \ll 1$, where neg-

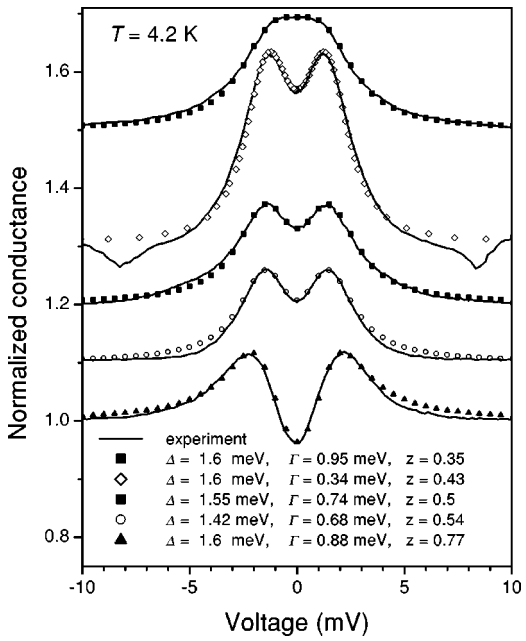

FIG. 1. Metal-Mg$(B_{0.9}C_{0.1})_2$ point-contact spectra at $T=4.2$ K (full lines). The upper curves are vertically shifted for the clarity. Symbols—fitting for the thermally smeared BTK model.

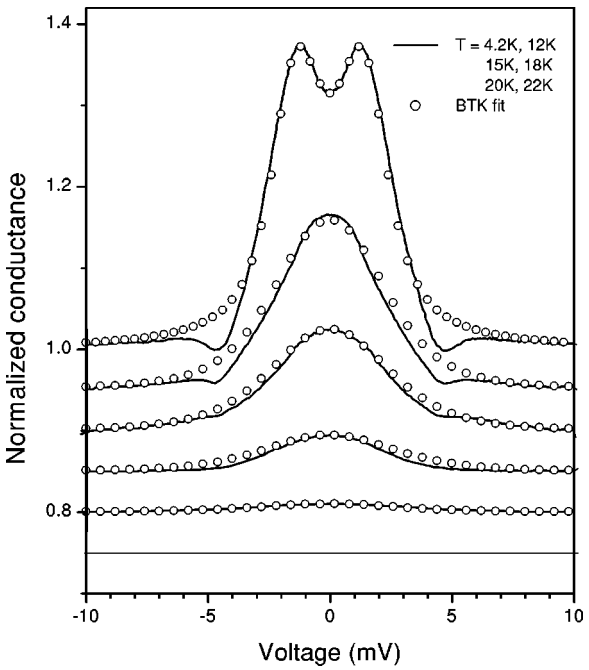

FIG. 2. Differential conductances of Cu-Mg$(B_{0.9}C_{0.1})_2$ point-contact measured (full lines) and fitted (open circles) for the thermally smeared BTK model at indicated temperatures. The fitting parameters $z=0.4$, $\Gamma=0.32$ meV, and Δ (4.2 K) $=1.67$ meV. The lower curves are vertically shifted for the clarity.

ligible conductance is observed inside the gap and a peak at the gap's edge. The general case for an arbitrary transmission T between the normal tip and the superconductor has been treated by Blonder, Tinkham, and Klapwijk (BTK).[13] In any case, the voltage dependence of the conductance of a N/S contact gives direct spectroscopic information on the superconducting order parameter Δ. The conductance data can be compared with the BTK theory using as input parameters the energy gap Δ, the parameter z [measure for the strength of the interface barrier with transmission coefficient $T=1/(1+z^2)$ in the normal state], and a parameter Γ for the quasiparticle lifetime broadening.[14] In the case of the pure MgB_2 for an important contribution of the point-contact current parallel to the a-b plane, both σ and π bands are contributing to the conductance. It can be expressed as a weighted sum of the partial BTK conductances $\Sigma=\alpha\Sigma_\pi+(1-\alpha)\Sigma_\sigma$.

Figure 1 shows typical examples of the normalized conductance-versus-voltage spectra obtained for the various M-Mg$(B_{0.9}C_{0.1})_2$ junctions. All displayed point-contact conductances have been normalized to the conductance background at higher voltages above the energy gap with a smooth interpolation inside the gap voltages. After the first soft touch of the tip, a smooth background conductance of a tunneling character appeared without any gap feature. Increasing the tip pressure allowed for a barrier formation and in some cases, superconducting spectral features appeared. Such an appearance is due to the optimal combination of the good quality of the particular grain under the tip and the barrier. The long term stability of contacts was bad (in comparison with our experience on the pure MgB_2), which was very unfavorable for measurements at different temperatures. The resulting point contacts revealed different barrier transparencies from very metallic interface with $z=0.35$ (upper curve) up to an intermediate case between metallic and tunneling barriers with $z\sim0.8$. Using different metallic tips did not show any influence on the obtained spectra showing the superconducting energy gap. As shown, the four lower curves display symmetric pair of the peaks indicating single but rather small energy gap. The upper curve shows the highest transparency which causes an increase of the conductance inside the gap due to the Andreev reflection without apparent gap peaks due to the tunneling channel. Indeed, the quality of the data is lower than the quality of those taken on the pure and single phase MgB_2, but all these curves could be well fitted by the single BTK conductance with the indicated resulting parameters Δ, Γ, and z. As the most important, the value of the gap little scattered around 1.6 meV, the value twice smaller than the BCS prediction for the superconductor with $T_c=22$ K.

Point-contact spectroscopy is a surface sensitive technique. This gives rise to the possibility that the smaller value of the gap could be caused by a weakening of the superconducting state possibly resulting from a surface proximity effect with the correspondingly suppressed $T_c=2\Delta/3.52k_B\approx11$ K. That is why it is necessary to establish the particular T_c of the point contact with such a small gap. The temperature dependence of the point-contact spectrum of a specific contact is shown in Fig. 2. The spectrum shows a pronounced increased conductance inside the superconducting gap due to the Andreev reflection. The barrier strength $z=0.4$ yields also a well-resolved pair of the gap peaks. Such pronounced spectral features (high conductance due to Andreev reflection and the gap-related peaks) are a result of relatively small smearing parameter $\Gamma=0.32$ meV, which is

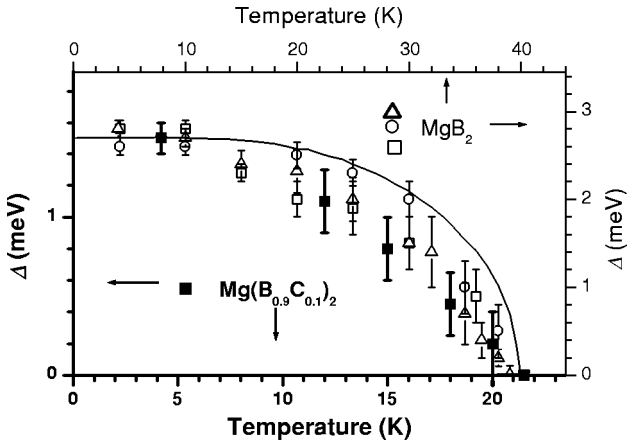

FIG. 3. Bold symbols—temperature dependence of the energy gap in $Mg(B_{0.9}C_{0.1})_2$ determined from the fitting of the point-contact spectrum shown in Fig. 2. Opened symbols—temperature dependence of the small gap Δ_π in the undoped MgB_2 obtained from fitting to three different contacts (Ref. 9). The full line represents the BCS prediction.

less than 20% of $\Delta = 1.67$ meV (similar to the second curve from the top of Fig. 1). It is worth mentioning that also the conductance intensity is well reproduced by the BTK fit without any adjustable parameter. The only spurious feature is a dip outside the gap at ± 5 mV. Such dips could originate from a redistribution of the current path when a critical current is reached in a weak link or a crack near the contact.[15] This effect is hardly avoidable in the powder samples. The dip is not reproducible as can be seen on the junction of comparable quality in Fig. 1.

At elevated temperatures above 10 K, the pair of the gap peaks merge to the one maximum, due to the thermal broadening. Nevertheless, from the smoothly decreasing Andreev reflection maximum it is evident that the spectrum shows the superconducting energy gap still existing near to the bulk critical temperature, when at 20 K it is still not in the normal state. Five temperature dependences have been measured on different junctions, all showing the small gap closing at the bulk transition temperature. Together with the experimental data, the corresponding BTK fits are also shown by opened circles. During the fit, the barrier strength parameter z and the broadening Γ have been fixed once determined at 4.2 K.

The resulting temperature dependence of the energy gap Δ is shown in Fig. 3. Big error bars are caused by two effects. First, there is an uncertainty in the normalization of the data at particular temperature since the background conductance was changing during the temperature measurements. Second, it is the occurrence of the dip interfering with the spectrum. Nevertheless, one can notice that the shape of the temperature dependence shows deviations from the BCS prediction. For comparison, we show in Fig. 3 also the temperature dependence of the small energy gap $\Delta_\pi(T)$ obtained on the three junctions made on pure MgB_2.[9] All dependences show faster decrease with increasing temperature than predicted by the BCS theory, but in line with predictions of Liu *et al.*[10]

The shown data prove that the small energy gap is related to the bulk transition temperature. Obviously, the carbon doped material is not as pure or single phase as the pure MgB_2. The presence of a highly disordered phase cannot be excluded. The special proximity effect could also explain the small energy gap living up to the bulk T_c. But in this case a strong agreement between our spectroscopic finding and the specific heat data of Ribeiro *et al.* showing significant thermal excitations above the small gap for temperatures above 10 K would be very surprising.

The size of the gap as well as its temperature dependence is remarkably similar to that of the small energy gap Δ_π on the π band of pure MgB_2, just rescaled to the reduced transition temperature of 22 K. The absence of the large gap in the measured spectra again resembles the situation in pure MgB_2, where less than 10% of the junctions clearly displayed the large-gap related maximum. While the small gap on the isotropic π band is always contributing to the spectrum, the gap peak from the large gap can be detected only for important contribution from the *a*-*b* plane current. Inhomogeneities in the state-of-art samples of $Mg(B_{0.9}C_{0.1})_2$ cause a relatively large value of the broadening parameter Γ which could hide possible traces of a small contribution of the large gap. But if we could directly see only one gap, it is the smaller one that is more important being significantly out of the size for the one-gap superconductor.

Original theoretical estimates of Liu *et al.*[10] showed that it is only the strong scattering *between* the σ and π bands in MgB_2 which leads to averaging of the two gaps and decreasing of T_c to about 22 K. The *intraband* scattering does not play this role. Later, theoretical and experimental studies have revealed difficulties in realizing the *interband* scattering. MgB_2 samples with very different resistivities at 40 K from 0.38 $\mu\Omega$ cm (Ref. 16) to 25 $\mu\Omega$ cm (Ref. 17) with no significant change in T_c have been prepared. Mazin *et al.*[18] have shown theoretically that introduction of defects such as lattice imperfections and/or nonstoichiometricity in MgB_2 leads to a strong increase of the *intraband* scattering, particularly inside the π-band, rather than an *interband* scattering. The theoretical calculations also showed that due to a very different k-space distribution of the π and σ bands, the only route to increase the σ-π scattering is via interlayer hopping, from a p_z orbital (π band) in one atomic layer to a bond orbital (σ band) in another layer.

Substitution of boron by carbon in the $Mg(B_{0.9}C_{0.1})_2$ samples naturally leads to a heavy increase of the resistivity. Rough estimate with no account for porosity indicates hundreds of $\mu\Omega$ cm at low temperatures.[11] The neutron diffraction studies proved no ordering of carbon. This suggests a large electronic scattering in the system. In our recent experiments,[19] the upper critical field at 1.5 K of about 30 T was found to be much bigger than in the pure MgB_2. It indicates that the doped samples are in a dirty limit with a very short mean free path. On the other hand, both XRD (Ref. 11) and neutron experiments[12] revealed no change in the *c*-lattice parameter in carbon substituted samples in comparison with the pure MgB_2. Then, conditions for interlayer hopping which could increase the σ-π scattering are not more favorable than in MgB_2. The calculations of Erwin and Mazin[20] have proved it. Thus, the dirty limit in our sample is

only due to the strong intraband scattering. The significant suppression of T_c could probably be related to the decreased density of states, the Debye temperature,[11] and/or the E_{2g} breathing mode responsible for the superconductivity in the system, and not due to suppression of the two-gap superconductivity. The transition temperature T_c of 22 K is just coincidentally similar to those proposed by Liu *et al.*[10] for the samples with important interband scattering and should not be confused with it. Later refined calculations of Brinkman *et al.*,[21] within essentially the same two-gap model as proposed in Ref. 10, now based on an extended Eliashberg formalism accounting for the strong-coupling effects, estimate the transition temperature in the limit of strong interband scattering to $T_c = 25.4$ K.

A significantly lower anisotropy in H_{c2}[11] in our carbon doped compound implies that the σ-band Fermi surface is not as 2D as in the pure MgB_2. This can partially suppress the strong electron-phonon coupling in the σ band responsible for T_c. Changes in the Fermi surface are resulting from a different electronic configuration in boron and carbon.

In conclusion, we have obtained an experimental evidence for the existence of the small superconducting energy gap in the carbon-substituted MgB_2 closing at the bulk T_c. The regular observation of this effect in our spectra and the support for it by other measurements demonstrate a survival of the two-gap superconductivity in the carbon-substituted samples with heavily suppressed T_c. During completion of the paper, we noted a preprint of Schmidt *et al.*[22] with the same conclusions on a very similar sample.

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