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 inter-metallic superconductor at 39 K [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 multi-gap superconductivity [9]. In line with the theoretical predictions [10], for the larger gap $\Delta_\sigma$, attributed to the two-dimensional $\sigma$-band parallel to the $c$-axis originating from the boron $p_{x−y}$ orbitals, the reduced gap value $2\Delta_\sigma/k_BT_c \simeq 4$ has been found. The smaller gap $\Delta_\pi$ on the 3D $\pi$-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 non-magnetic 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 the one and decreasing the transition temperature to about 22 K. $T_c$ of 22 K is exactly the transition temperature of the carbon-substituted Mg(B$_{0.9}$C$_{0.1}$)$_2$ which have been recently synthesized [11,12]. Here we show that despite the strong suppression of the transition temperature by 17 K due to the replacement of boron by carbon in comparison with the pure MgB$_2$ 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 $\Delta_\pi$ on the 3D $\pi$-band and that the two band/two gap superconductivity is still preserved here.

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$_4$C powder. The nominal stoichiometry was kept as Mg(B$_{0.9}$C$_{0.1}$)$_2$. Synthesis temperature and time was optimized to 1100 °C and 24 hours, respectively. Traces of B$_4$C were not visible in the XRD patterns. Small amounts of two impurity phases (MgO and MgB$_2$C$_2$) 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 micro-constrictions 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 $\Delta$ 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 leads to the tunneling channel of the carrier transport with $T << 1$, where negligible conductance is observed inside the gap and peak at the gap’s edge. The general case for 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 $\Delta$. The conductance data can be compared with the BTK theory using as input parameters the energy gap $\Delta$, 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 $\Gamma$ for the quasi-particle lifetime broadening [14]. In the case of the pure MgB$_2$ for an important contribution of the point-contact current parallel to the $ab$-plane the both $\sigma$ as well as $\pi$ bands are contributing to the conductance. It can be expressed as a weighted sum of the partial BTK conductances $\Sigma = \sigma \Sigma_{\pi} + (1 - \alpha) \Sigma_{\sigma}$.

Figure 1 shows typical examples of the normalized conductance-versus-voltage spectra obtained for the various M-Mg(56.5%Co,4.1%Cu)$_2$ 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 very 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 barrier with $z \sim 0.8$. Using of different metallic tips did not show any influence on the obtained spectra showing the superconducting energy gap. As shown, the three 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. All these curves could be fitted by the single BTK conductance with the indicated resulting parameters $\Delta$, $\Gamma$ 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 correspondingly suppressed $T_c = 2\Delta/3.52k_B \approx 11$ 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 less than 20 % of $\Delta = 1.67$ meV. 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 $\pm 5$ 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 nearby the contact [15]. This effect is hardly avoidable in the powder samples.

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. Together with the experimental data also the corresponding BTK fits are shown by opened circles. During the fit the barrier strength parameter $z$ and the broadening $\Gamma$ have been fixed once determined at 4.2 K.

The resulting temperature dependence of the energy gap $\Delta$ 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 a 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 the temperature than predicted by the BCS theory, but in line with predictions of Liu et al. [10].

The shown data unequivocally prove that the small energy gap is related to the bulk transition temperature. The size of the gap as well as its temperature dependence is remarkable similar to that of the small energy gap $\Delta_{\pi}$ on the $\pi$ 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 percent of the junctions clearly displayed the large-gap related maximum. While the small gap on the isotropic $\pi$-band is always contributing to the spectrum, the gap peak from the large gap can be detected only for important contribution from the $ab$-plane current. Inhomogeneities in the state-of-art samples of Mg(B$_{0.9}$C$_{0.1}$)$_2$ cause a relatively large broadening $\Gamma$-parameter which could hide possible traces of a small contribution of the large gap.

Our spectroscopic finding is in agreement with the temperature dependent specific-heat data by Ribeiro et al. [11] showing significant thermal excitations above the small gap for temperatures above 10 K.

Original theoretical estimates of Liu et al. [10] showed that important scattering between the $\sigma$ and $\pi$ bands in MgB$_2$ should lead to averaging of the two gaps and decrease of $T_c$ to about 22 K. Later theoretical and experimental studies have revealed difficulties in realizing such scattering. MgB$_2$ samples with very different resistivities at 40 K from 0.38 $\mu$Ωcm [16] to 25 $\mu$Ωcm [17] with no significant change in $T_c$ has been prepared. Mazin et al. [18] has shown theoretically that introduction of defects like lattice imperfections and/or nonstoichiometricity in MgB$_2$ leads to a strong increase of the interband scattering particularly inside the $\pi$-band rather than to an interband scattering. It is only the latter one which should reveal a proposed pair-breaking effect leading to a one-gap superconductivity with depressed $T_c$. The theoretical calculations also showed that due to a very different $k$-space distribution of the $\sigma$ and $\pi$ bands, the only route to increase the $\sigma - \pi$ scattering is via interlayer hopping, from a $p_z$ orbital ($\pi$-band) in one atomic layer to a bond orbital ($\sigma$-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 the porosity indicates hundreds of $\mu$Ωcm 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 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 the both XRD [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 $\sigma - \pi$ scattering are not more favorable than in MgB$_2$. The significant suppression of $T_c$ could probably be related to the decrease density of states and Debye temperature in the system [11] and not due to suppression of the two-gap superconductivity. A significantly lower anisotropy in $H_{c2}$ [11] in the carbon doped compound implies that the $\sigma$-band Fermi surface is not nearly so 2D as in the pure MgB$_2$. This can partially suppress the strong electron-phonon coupling in the $\sigma$-band responsible for $T_c$. Changes in the Fermi surface are resulting from 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 * demonstrates a survival of the two-gap superconductivity in the carbon-substituted samples with heavily suppressed $T_c$.

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*During completion of the paper we noted a preprint of Schmidt et al. [20] with similar conclusions.
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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 $\Delta (4.2 \text{ K}) = 1.67$ meV. The lower curves are vertically shifted for the clarity.
FIG. 3. Bold symbols - temperature dependence of the energy gap in Mg(B₀.₉C₀.₁)₂ determined from the fitting of the point-contact spectrum shown in Fig. 2. Opened symbols - temperature dependence of the small gap $\Delta_\pi$ in the undoped MgB₂ obtained from fitting to three different contacts [9]. Full lines represent the BCS prediction.