Systematic study of the two band/two gap superconductivity in carbon-substituted MgB$_2$ by point-contact spectroscopy

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Point-contact measurements on the carbon-substituted Mg(B$_{1-x}$C$_x$)$_2$ filament/powder samples directly reveal a retention of the two superconducting energy gaps in the whole doping range from $x = 0$ to $x \approx 0.1$. The large gap on the $\sigma$-band is decreased in an essentially linear fashion with increasing the carbon concentrations. The changes in the small gap $\Delta_x$ up to 3.8 % C are proportionally smaller and are more difficult to detect but for the heavily doped sample with $x \approx 0.1$ and $T_c = 22$ K both gaps are still present, and significantly reduced, consistent with a strong essentially linear, reduction of each gap with the transition temperature.

The MgB$_2$ superconductor [1] represents a challenge for both technological relevance and fundamental science. Its relatively high transition temperature is due to the interference effect between the $\sigma$ and $\pi$ bands with respectively strongly and weakly coupled Cooper pairs, and respectively large and small superconducting energy gaps. This theoretical two-gap scenario [2,3] has now been supported by many experiments [4–11]. Prospects for applications of MgB$_2$ depend on a success in increasing the critical parameters such as the upper critical field and critical current. For that the material must be driven from the clean superconducting limit to the dirty one. The possibility of selective tuning of the $\sigma$ and $\pi$ bands with respect to the $\sigma$-band scattering seems to be the way of accomplishing this [12,13]. This can be realized, for example, via the substitution of a constituent element, such as boron by carbon. An undesirable side effect may be a significant increase of the interband scattering, presumably leading to merging of the two gaps and, as consequence, to a substantial decrease of the transition temperature [2]. Previous studies [14–16] on the heavily doped MgB$_2$ by 10 % of carbon ($T_c = 22$ K) have shown a presence of the small energy gap with $2\Delta/k_BT_c \approx 1.6$, the same relative strength as for the gap in the $\sigma$-band of the undoped system, incompatible with the single-gap scenario. $\mu^+$SR experiments have been performed on the carbon doped MgB$_2$ with $T_c$'s from 38.3 K down to 34.8 K [17]. The deduced gaps $\Delta_x$ and $\Delta_{\pi}$ showed a linear decrease with increasing the carbon content and $T_c$, but for the samples with $T_c \leq 36.1$ K the reduced value of the large gap $2\Delta/k_BT_c$ was below the BCS weak-coupling value 3.52.

Here we present a systematic study of the two-gap superconductivity in carbon-doped Mg(B$_{1-x}$C$_x$)$_2$ filaments with the carbon content $x = 0$, 0.021 and 0.038 and additional experiments on the powder sample with $x \approx 0.1$. The Andreev reflection spectra on the filings show two very well resolved superconducting energy gaps. The large gap on the $\sigma$-band is decreased with increasing the carbon concentrations, whereas the changes in the smaller gap are proportionally smaller and, for these low carbon concentrations, difficult to resolve. For the more heavily doped sample with $x \approx 0.1$ and $T_c = 22$ K, the broadening of the Andreev reflection spectra makes a direct detection of the large gap difficult but we succeeded in detecting it by careful measurement at 1.6 K. Our identification of the large gap was confirmed by the use of an in-magnetic field experiment where the small gap contribution can be partially suppressed and the large gap revealed. The large gap can also be extracted from the analysis of the specific-heat data [14]. In the 10 % C doped samples both gaps are detected and both gaps scale linearly with the suppression of $T_c$. The temperature dependences of the large and small gaps indicate that the interband coupling is not significantly changed upon the doping in the whole concentration range.

Wire segments of carbon-substituted MgB$_2$ were synthesized from carbon doped boron filaments made by chemical vapor deposition. The boron and carbon were co-deposited to form a fiber of about 75 $\mu$m diameter. Mg(B$_{1-x}$C$_x$)$_2$ filaments were made by exposing the fibers to Mg vapor. More details about preparation are given elsewhere [12]. X-ray diffraction shows the MgB$_2$ phase and Mg lines. No traces of MgO and B$_4$C have been found. No measurable changes in the $c$-axis lattice parameter were detected, whereas the measured changes of the $a$-axis lattice parameter $\Delta a(x)$ were used to determine the carbon concentration by comparison to Avdeev et al. neutron diffraction [18] on $x \approx 0.1$ samples of Mg(B$_{1-x}$C$_x$)$_2$. The resulting carbon concentrations are $x = 0$, 0.021 and 0.038. The quality of the samples is evidenced by a single step and narrow transitions to superconducting state in magnetization and resistivity with $T_c = 39$, 37.5 and 36.2 K defined at the onset of the superconducting state with $\delta T_c \leq 0.3$ K between 10 and 90.
% of the normal state resistivity. The resistivity of the wires increases from 0.5 $\mu\Omega\text{cm}$ for the undoped system to about 10 $\mu\Omega\text{cm}$ for 3.5 % C. Mg(B$_{0.9}$C$_{0.1}$)$_2$ with $T_c = 22$ K in the form of pellets were prepared following the procedure described in Ref. [14] from magnesium lumps and B$_4$C powder. Traces of B$_2$C were not visible in the XRD patterns. Small amounts of two impurity phases (MgO and MgB$_2$C$_2$) resulted even with optimization of the synthesis.

Point-contact measurements on the wire segments have been performed in a **"reversed"** configuration - with the Mg(B$_{1-x}$C$_x$)$_2$ wire as a tip touching softly a bulk piece of electrochemically cleaned copper. In the experiments on bulk Mg(B$_{0.9}$C$_{0.1}$)$_2$ samples a tip was (electro)chemically formed from copper, platinum or silver wires. 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 10 kHz was used to measure the differential resistance as a function of applied voltage on the point contacts. The microconstrictions were prepared in **situ**. The approaching system enabled both the lateral and vertical movements of the tip by differential screw mechanism.

The point-contact spectrum - **differential conductance versus voltage** between a metal and a superconductor can be compared with the Blonder, Tinkham and Klapwijk (BTK) theory using as input parameters the energy gap $\Delta$, the parameter $z$ (measure for the strength of the interface barrier with transmission coefficient $T = 1/(1 + z^2)$) and a parameter $\Gamma$ for the quasi-particle lifetime broadening [19]. In the case of the MgB$_2$ two-gap superconductor the overall conductance can be expressed as a weighted sum of the partial BTK conductances from the quasi two-dimensional $\sigma$-bands (with a large gap $\Delta_{\sigma}$) and the 3D $\pi$-bands (with a small gap $\Delta_{\pi}$) $\Sigma = \alpha \Sigma_{\pi} + (1 - \alpha) \Sigma_{\sigma}$. The weight factor $\alpha$ for the $\Delta_{\sigma}$ gap contribution can vary from 0.65 for the tunneling/point-contact current strictly in the MgB$_2$ $ab$-plane to 0.99 of $c$-axis tunneling [20]. Indeed, the tunneling experiments on single crystalline MgB$_2$ [10] have proved that the small gap on the $\pi$-band is observed for any tunneling direction while $\Delta_{\sigma}$ is observable only for significant $ab$-plane tunneling component.

Extensive measurements on tens of pieces of wire segments and bulk doped MgB$_2$ have been performed. The point-contacts revealed different barrier transparencies from more metallic interface with $z = 0.4$ up to an intermediate case between metallic and tunneling barrier with $z \sim 1.2$. Crystallites in the wire segments have a size up to tens of microns. For such large crystallites, the point-contacts yield an information on a particular single crystal at the junction, but of unknown orientation. By trial and error we looked for the junctions where the both gaps would be present. A large number of the "two-gap" spectra on Mg(B$_{1-x}$C$_x$)$_2$ wires of $x = 0$, 0.021 and 0.038 carbon concentrations have been recorded. For the presentation and analysis we have chosen those with a small broadening $\Gamma_{\sigma}$, typically less than 10 per cent of respective gap $\Delta_{\sigma}$. In accordance with the previous report [15] the most of the spectra on Mg(B$_{0.9}$C$_{0.1}$)$_2$ revealed apparently only the small energy gap $\Delta_{\sigma}$. The broadening parameter $\Gamma$ was in this case at least 20 per cent of the gap value. Larger scattering rates and inhomogeneities in the heavily doped Mg(B$_{0.9}$C$_{0.1}$)$_2$ are probably the main reason preventing as easy of a direct detection of the large gap, here. Since the point-contact spectroscopy is a surface sensitive technique it is sensitive to a possible surface proximity effect with correspondingly suppressed $T_c$. For most of the junctions the particular $T_c$ has been checked: in all cases the point-contact transition temperature agreed with the bulk $T_c$. In addition, as it will be shown below, both gaps close near the bulk $T_c$.

Figure 1 shows characteristic examples of the normalized conductance-versus-voltage spectra (full lines) obtained on the Mg(B$_{1-x}$C$_x$)$_2$-metal junctions. All displayed point-contact conductances have been normalized to the conductance in the normal state at $T > T_c$. The fits to the spectra by the two-gap BTK formula are shown by open circles. As can be seen the spectra on the wires with the lower carbon-concentrations - up to 3.8 % C reveal very well resolved two superconducting energy gaps with small *intrinsic* broadening. The upper spectrum was obtained on the more heavily doped, 10 % C, powder sample. To achieve better resolution this spectrum is measured at 1.6 K, whereas the others were measured at 4.2 K. A one-gap fit to this spectrum is shown as well (by the open triangles). Obviously, the two-gap formula fits the spectrum better. Thus, the spectrum represents one of a few examples indicating a presence of the large gap in MgB$_2$ with 10 per cent of carbon.

Whereas we are able to detect the larger gap in the 1.6 K tunnelling spectra of the Mg(B$_{0.9}$C$_{0.1}$)$_2$ sample, it is not as unambiguously resolved as in the lower doped samples. Our identification of the larger gap is strongly supported by in-field tunneling measurements. In the Fig. 2 the spectrum on the 10 % C MgB$_2$ sample is shown in magnetic field. In the spectrum recorded at zero magnetic field the shoulder originating from the second large gap is not very pronounced and we have to rely on the fit showing that the two gap formula works better than the one-gap fit. But a finite magnetic field partially suppresses the contribution from the $\pi$-band, with a smaller gap, and makes a presence of the large gap from the $\sigma$-band more conspicuous. This is a well known effect in MgB$_2$ which we detected in our original paper on the two-gap superconductivity in pure MgB$_2$ [6]. Here, in a very similar way it helps to further reveal the existence of the large gap $\Delta_{\sigma}$: appearing as more and more clearly defined shoulder, best seen in the spectrum taken at $B = 0.7$ Tesla. At even higher fields the intensity of the $\pi$-band contribution is suppressed so that the $\pi$ and $\sigma$ peaks interfere to the single maximum, which is located
indeed at higher voltages [21] than the original maximum of the prevailing $\pi$-band spectrum at $B = 0$. Data such as these are further evidence of the clear persistence of two superconducting gaps in Mg(B$_{1-x}$C$_x$)$_2$ even at $x = 0.1$ levels.

To obtain further information on the large energy gap $\Delta_\sigma$ in the heavily doped Mg(B$_{0.9}$C$_{0.1}$)$_2$, an analysis of the electronic specific heat on the data from Ribeiro et al. [14] was performed within the frame work of the $\alpha$-model as proposed for MgB$_2$ by Bouquet et al. [4]. A typical jump at $T_c$ from the large energy gap was seen as well as an excess weight at low temperatures as a hint of the small energy gap $\Delta_x$. Even if this is an indirect method the resulting gaps are indicated as asterisks in Fig. 3 and are in good agreement with the direct point-contact determination of the gaps.

Figure 3 shows the overall statistics of energy gaps which have been obtained from analysis done on about 15 best resolved spectra for each carbon concentration, except for the 10 % C substituted MgB$_2$ sample, where we only two junctions revealed the large gap. The widths of the bars indicates the error in determination of the energy gap associated with the fitting to the BTK model. The double peak distribution of the large and small gaps well covers the gap sizes given by most of the tunneling and point contact data on the pure MgB$_2$ [6,8–10,22]. Due to distribution of the two gaps better comparison can be made with the similar histograms obtained from the MgB$_2$ point-contact data by Naidyuk et al. [23] and Bugoslavsky et al. [24]. Good agreement is found among those measurements. There is also a possibility to make comparison with the distribution of the gaps on the Fermi surface calculated by Choi et al. within the fully anisotropic Eliashberg formalism [3]. Matrinez-Samper et al. [9] even fitted directly their particular tunneling spectra with a distribution of gaps showing two maxima around 2.5 and 7 meV. But recently Mazin et al. argued that to see directly more than two gaps in the spectrum or even whole distribution would require extremely small, unrealistic $\pi$ and $\sigma$ intraband scattering rates [25]. Thus, this particular question of the gap distribution around two maxima asks for further studies. Nevertheless, even with the presented gap distributions one can see clearly the effect of the carbon doping on the gaps.

In Fig. 4 the gap energies as a function of $T_c$ are presented. The circles are positioned at the averaged energies of the gap distributions in Fig.3 and the error bars represent the standard deviations of the distributions. Broadly, the tendency of the evolution of two gaps in MgB$_2$ with carbon doping seems to be almost linear with both gaps disappearing (as extrapolated) simultaneously at $T_c = 0$. More data is needed to address possible non-linearity at low carbon content and to more precisely determine the point where two gaps merge to one or disappear (the error bars on the data presented in Fig. 4 support a merging of the two gaps for 0 K $\leq T_c \leq 10$ K). The inset to Fig. 4 with the reduced gaps $2\Delta/k_BT_c$, shows that already for the small carbon concentrations there is a tendency to merge both gaps. Despite this tendency, on the samples with 10 per cent of carbon doping and $T_c = 22$K the two-gap superconductivity is still clearly retained as presented by the normalized gaps $2\Delta_\sigma/k_BT_c \simeq 3.6$ and $2\Delta_x/k_BT_c \simeq 1.6$.

The temperature dependence of the large and small energy gaps $\Delta_\sigma$ and $\Delta_x$ from the point-contact spectra on Mg(B$_{1-x}$C$_x$)$_2$ samples with different carbon concentrations are shown in Fig. 5. One can notice that the shape of the temperature dependence of both gaps does not show any obvious change due to a different carbon concentration. As mentioned already by Stuhl et al. [26], the shape of the temperature dependence of the small gap is related to the measure of the interband coupling. If it was too small the small energy gap would tend to close at temperatures much below the bulk $T_c$ with a tail to $T_c$. In the case of pure MgB$_2$ the temperature dependence of the small gap slightly undershoots the BCS line [6] in line with the predictions of Liu et al. [2]. Within the shown error bars in Fig. 5 we can conclude that the interband coupling is not changed by the carbon doping.

The theoretical calculations have shown that due to a very different $k$-space distribution of the $\pi$ and $\sigma$ bands, the only route to increase the $\sigma-\pi$ scattering is via intralayer hopping, from a $p_z$ orbital ($\pi$-band) in one atomic layer to a bond orbital ($\sigma$-band) in another layer [27]. But no changes in the $c$-lattice parameter which could help the interlayer charge transfer in carbon substituted samples in comparison with the pure MgB$_2$ were detected [12]. Recent theoretical modelling also corroborates that carbon doping is not favorable for increased interband scattering [28]. What is then the reason for a significant decrease of the transition temperature to $T_c = 22$ K at 10 % C doping? The transition temperature is determined by the characteristic phonon frequency, the strength of the electron-electron coupling and the density of the conduction electrons. Due to hole $\sigma$-band filling the density of states can be decreased by carbon substituting boron. Masui et al. have detected hardening and narrowing the $E_{2g}$ phonon modes by Raman scattering [29] which can have a dramatic effect on the strength of the cooper pairs coupling in the $\sigma$-band. Decrease in the density of states at the Fermi level was suggested by band structure calculations [30] and observed through measurements of heat capacity [14]. Also a significantly lower anisotropy in $H_{c2}$ [14] in heavily carbon doped compound implies that the $\sigma$-band Fermi surface is not nearly so 2D as in the pure MgB$_2$.

In conclusion, we have obtained an experimental evidence for existence of the two-gap superconductivity in the carbon-substituted MgB$_2$ for all C concentrations from 0 to about 10 per cent with $T'_c$'s from 39 down to 22 K. The both gaps are closing near the bulk critical temperature of the respective sample. The temperature
dependence of the gaps indicates no changes in the interband coupling which could eventually lead to definite merging of the gaps.

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[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature (London) 410, 63 (2001).
[2] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. 87, 087005 (2001).
[3] H. J. Choi et al., Nature 418, 758 (2002); Phys. Rev. B 66, 020513 (2002).
[4] P. Bouquet et al., Phys. Rev. Lett. 87, 047001 (2001).
[5] Y. Wang et al., Physica C 355, 179 (2001).
[6] P. Szabó et al., Phys. Rev. Lett. 87, 137005 (2001).
[7] F. Giubileo et al., Phys. Rev. Lett. 87, 177008 (2001).
[8] M. Iavarone et al., Phys. Rev. Lett. 89, 187002 (2002).
[9] P. Martinez-Samper et al., Physica C 385, 233 (2003).
[10] M. R. Eskildsen et al., Physica C 385, 169 (2003).
[11] Review Superconductivity in MgB$_2$: Electrons, Phonons and Vortices, eds. W. Kwok, G. Crabtree, S. L. Bud’ko and P. C. Canfield, Physica C 385, Nos. 1-2 (2003).
[12] R. H. T. Wilke et al., cond-mat/0312235.
[13] A. Gurevich et al., Supercond. Sci. Technol. 17, 278 (2004).
[14] R. A. Ribeiro, S. L. Bud’ko, C. Petrovic and P. C. Canfield, Physica C 384, 227 (2003).
[15] P. Samuely et al., Phys. Rev. B 68, 020505 (R) (2003).
[16] H. Schmidt et al., Phys. Rev. B 68, 060508 (R) (2003).
[17] K. Papagelis, J. Arvanitidis, K. Prassides, A. Schenck, T. Takenobu, and Y. Iwasa, Europhys. Lett. 61, 254 (2003).
[18] M. Avdeev, J.D. Jorgensen, R. A. Ribeiro, S. L. Bud’ko, and P. C. Canfield, Physica C 387, 301 (2003).
[19] A. Plecenik et al., Phys. Rev. B 49, 10016 (1996).
[20] A. Brinkman et al., Phys. Rev. B 65, 180517 (R) (2002).
[21] P. Samuely et al., Physica C 385, 244 (2003).
[22] H. Schmidt, J.F. Zasadzinski, K.E. Gray and D.G. Hinks, Physica C 385, 221 (2003).
[23] Yu. G. Naidyuk et al., Pis’ma Zh. Eksp. Teor. Fiz. 75, 283 (2002); JETP Lett. 75, 238 (2002).
[24] Y. Bugoslavsky et al., cond-mat/0307540.
[25] I. Mazin et al., Phys. Rev. B 69, 056501 (2004).
[26] H. Suhl, B. T. Matthias, L. R. Walker, Phys. Rev. Lett. 3, 552 (1959).
[27] I. I. Mazin et al., Phys. Rev. Lett. 89, 107002 (2002).
[28] S. C. Erwin and I. I. Mazin, Phys. Rev. B 68, 132505 (2003).
[29] T. Masui, S. Lee, and S. Tajima, cond-mat/0312458.
[30] N. I. Medvedeva et al., Phys. Rev. B 64, 020502 (2001).
FIG. 1. Full lines - Mg(B\textsubscript{1-x}C\textsubscript{x})\textsubscript{2} point-contact spectra at $T = 4.2$ K (except for the top spectrum recorded at 1.6 K). Open circles - fitting for the thermally smeared BTK model for two gaps. Open triangles for $x = 0.1$ curve - fit to the one-gap BTK formula. The upper curves are vertically shifted for the clarity. The arrows indicate a development of the gaps with increasing carbon content.
FIG. 2. Mg(B_{0.9}C_{0.1})_{2}-Cu point-contact spectrum at 1.6.K (shown in Fig.1) recorded at different magnetic fields. Partial suppression of the small gap contribution helps in revealing the large gap (see the text). The curves at finite field are shifted down for clarity.
FIG. 3. Distribution of the superconducting energy gaps of Mg(B$_{1-x}$C$_x$)$_2$ as obtained from numerous point-contact junctions on different samples of the particular C concentration. Asterisks - the gaps obtained from analysis of the specific heat [14].
FIG. 4. Superconducting energy gaps from point-contact experiments at lowest temperature as a function of $T_c$. The points - average energy of the particular gap distribution shown in Fig.3. The error bars - the standard deviations in the distributions. Asterisks - deduced from analysis of the specific heat measurement (see text). Lines are guide for the eye.
FIG. 5. Temperature dependence of the energy gaps of Mg(B$_{1-x}$C$_x$)$_2$ determined from the fitting of the point-contact spectra. Full lines represent the BCS prediction scaled to the $\pi$ and $\sigma$ gaps.