Evidence for Single-gap Superconductivity in Mg(B_{1-x}C_x)\textsubscript{2} Single Crystals with \(x = 0.132\) from Point-Contact Spectroscopy

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We report the results of the first directional point-contact measurements in Mg(B_{1-x}C_x)\textsubscript{2} single crystals with 0.047 \(\leq x \leq 0.132\). The two-gap superconductivity typical of MgB\textsubscript{2} persists up to \(x = 0.105\). In this region, the values of the gaps \(\Delta_\sigma\) and \(\Delta_x\) were determined by fitting the Andreev-reflection conductance curves with a two-band Blonder-Tinkham-Klapwijk (BTK) model, and confirmed by the single-band BTK fit of the \(\sigma\)- and \(\pi\)-band conductances, separated by means of a magnetic field. At \(x = 0.132\), when \(T_c = 19\) K, we clearly observed for the first time the merging of the two gaps into one of amplitude \(\Delta \simeq 3\) meV.

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In the last three years, the great experimental and theoretical efforts of the scientific community have led to a clarification of most features of the intermetallic superconductor MgB\textsubscript{2}. These features are mainly related to the presence of two band systems (\(\sigma\) and \(\pi\)) and of the relevant gaps \(\Delta_\sigma\) and \(\Delta_x\). Point-contact spectroscopy (PCS) has proved particularly useful in measuring both the \(\sigma\)- and \(\pi\)-band gaps at the same time and determining the temperature dependency of these gaps with great accuracy. Very soon after the discovery of superconductivity in MgB\textsubscript{2}, substitutions of Al for Mg and of C for B were tried, in order to introduce impurities in the compound and modify its superconducting properties. In particular, nearly single-phase Mg(B_{1-x}C_x)\textsubscript{2} polycrystals with 0.09 \(\leq x \leq 0.13\) were obtained by starting from Mg and B\textsubscript{4}C\textsuperscript{1, 2, 3}, which showed a linear dependence of the cell parameter \(a\) on the C concentration. More recently, C-substituted MgB\textsubscript{2} single crystals were grown and many of their structural, superconducting and transport properties were measured. The first STM and PCS measurements on polycrystalline Mg(B_{1-x}C_x)\textsubscript{2} have shown the persistence of the two gaps up to \(x = 0.1\) and \(x = 0.13\). Up to now, the predicted achievement of single-gap superconductivity at a very high impurity level has never been observed.

This Letter presents the results of PCS measurements in Mg(B_{1-x}C_x)\textsubscript{2} single crystals with 0.047 \(\leq x \leq 0.132\), in the presence of magnetic fields up to 9 T either parallel or perpendicular to the \(c\) axis. These measurements gave us the dependence of the two gaps (\(\Delta_\pi\) and \(\Delta_x\)) on the carbon content \(x\) and showed that, up to \(x \simeq 0.10\), the two-gap superconductivity typical of unsubstituted MgB\textsubscript{2} is retained. At \(x = 0.132\), we clearly and reproducibly observed for the first time the merging of \(\Delta_\pi\) and \(\Delta_x\) into a single gap \(\Delta = 3.2 \pm 0.9\) meV which shows a ratio \(2\Delta/k_B T_c\) very close to the standard BCS value.

The high-quality Mg(B_{1-x}C_x)\textsubscript{2} single crystals were grown at ETH (Zurich) with the same high-pressure technique adopted for unsubstituted MgB\textsubscript{2}, and by using either graphite powder or silicon carbide as a carbon source. Details on the structural and superconducting properties of these crystals can be found in a recent paper. The 7 different carbon contents of our crystals were estimated from the lattice parameter \(a\), assuming its linear dependence on \(x\). The resulting \(x\) values range between \(x = 0.047\) and \(x = 0.132\), corresponding to bulk critical temperatures between 35 K and 19 K.

We performed PCS measurements with the current mainly injected along the \(ab\)-planes of the crystal, since in unsubstituted MgB\textsubscript{2} this is the most favourable configuration for the contemporaneous measurement of both gaps. The point contacts were thus made on the flat side surface of the crystals (not thicker than 80 \(\mu\)m) spot of Ag conductive paint. This “soft” version of the PCS technique yields greater contact stability on thermal cycling and greater reproducibility of the conductance curves. By applying short current or voltage pulses to the junctions, we were able to tune their characteristics and achieve in most cases a normal-state resistance between 50 and 300 \(\Omega\). Since the in-plane mean free path in these single crystals ranges from \(\ell \simeq 17.5\) nm to \(\ell \simeq 13\) nm for \(x\) between 0.05 and 0.095, these junctions result in the ballistic regime. The formation of parallel micro-junctions explains the very few cases in which ballistic conduction is observed in low-resistance contacts.

Fig. 1 reports some experimental conductance curves (\(dI/dV\) vs. \(V\)) of point contacts on crystals with different C contents (symbols). The curves are normalized as explained in Ref. 4. As already shown by PCS in Mg(B_{1-x}C_x)\textsubscript{2} polycrystals, when \(x \geq 0.047\) the experimental curves do not show the clear four-peak structure typical of \(ab\)-plane contacts on unsubstituted MgB\textsubscript{2}. Hence, the proof of the presence of the \(\sigma\)-band gap

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and its determination require a fit with the two-band BTK model \[3, 4, 11, 12, 13\] and/or the selective sup-
pression of the \[\pi\]-band contribution to the conductance, e.g. by applying a suitable magnetic field \[4, 13\]. In
the following we will present and discuss both these ap-
proaches.

First of all, let us discuss the fit of the zero-field con-
ductance curves reported in Fig. 1. In the two-band BTK model the normalized conductance of a point contact is
given by the two-band (upper curve) or single-band (lower
curves) BTK model. A detailed discussion of the applicability of
the BTK fit of Andreev reflection curves in the presence
of magnetic fields is given in Ref. 13.

Fig. 2 shows how this works in crystals with \(x = 0.055\) (a) and \(x = 0.100\) (b). In both panels, the zero-field con-
ductance \(\sigma_0\) (circles) is compared to the relevant two-
band BTK fit (solid line). Triangles represent instead the conductance peaks.

The reliability of the determination of \(\Delta_\sigma\) and \(\Delta_\pi\) by
means of a 7-parameter fit may be questioned. We thus tried to apply here the procedure we already used in un-
substituted MgB\(_2\), that consists in separating the partial \(\sigma\) and \(\pi\)-band contributions to the total conductance
\((\sigma_\sigma, \sigma_\pi)\) by means of a suitable magnetic field, and in
fitting each of them with the standard, three-parameter
BTK model. A detailed discussion of the applicability of
the BTK fit of Andreev reflection curves in the presence
of magnetic fields is given in Ref. 13.

For any \(x\) between 0.047 and 0.105, the two-band BTK model fits very well the experimental data, as shown in
Fig. 1 (solid lines). The best-fitting parameters are listed in Table I. In the crystals with the highest C content, i.e. \(x = 0.132\), the two-band BTK fit requires gap values very
close to each other and, practically, interchangeable (in
the sense that their error bars largely overlap). Actually,
a fit with the standard single-band BTK model works
even better. The solid line superimposed to the conduc-
tance curve at \(x = 0.132\) in Fig. 1 is indeed obtained with
only one gap of amplitude \(\Delta = 2.8 \pm 0.2\) meV.

The reliability of the determination of \(\Delta_\sigma\) and \(\Delta_\pi\) by
by taking contribution to the conductance and can thus be fitted with the irreversibility field $|16|$. B indicates that $\sigma = 0$ and $\pi$ remains as adjustable parameters. Finally, the difference $\sigma_{\text{diff}} = \sigma_0 - \sigma_{\text{BTK}} + 1$ (triangles) contains only the $\pi$-band contribution to the conductance and can thus be fitted by taking $\sigma_\pi = 1$ in the two-band BTK model. Since $w_\tau$ is reasonably field-independent, only $\Delta_\sigma, \Gamma_\sigma$ and $Z_\sigma$ remain as adjustable parameters. Finally, the difference $\sigma_{\text{diff}} = \sigma_0 - \sigma_{\text{BTK}} + 1$ (triangles) contains only the $\pi$-band conductance and can thus be fitted by taking $\sigma_\pi = 1$ in the two-band BTK model $|3|$. The separate fit of $\sigma_\pi$ and $\sigma_\sigma$ gives the following results: (a) $\Delta_\pi = 5.45$ meV, $Z_\pi = 0.475$, $\Gamma_\pi = 2.4$ meV and $\Delta_\sigma = 2.30$ meV, $Z_\sigma = 0.488$, $\Gamma_\sigma = 4.85$ meV; (b) $\Delta_\sigma = 4.9$ meV, $Z_\sigma = 0.525$, $\Gamma_\sigma = 4.55$ meV and $\Delta_\sigma = 3.28$ meV, $Z_\sigma = 0.42$, $\Gamma_\sigma = 2.07$ meV. In the case of $x = 0.055$, a slight reduction in $\Delta_\sigma$ (smaller than the gap distribution width, see Fig. 3) is present with respect to the two-band fit (that gave $\Delta_\sigma = 6.05$ meV and $\Delta_\pi = 2.35$ meV), possibly because $B^* = 2$ T is already comparable to $B^*_{\text{c2}} \geq 8$ T $|3|$. For the case of $x = 0.100$, the parameters coincide with those reported in Table 1. Similar agreement was found for any C content up to $x = 0.105$, and in all the junctions we studied, showing that this procedure has a high level of internal consistency and gives precise and reliable results, as in unsubstituted MgB$_2$ $|4|$. In the crystals with $x = 0.132$, the same procedure gives quite different results and further confirms the presence of a single gap. Fig. 3(a) reports an example of magnetic-field dependence of the raw conductance curves, for B || ab. Contrary to what happens at lower C contents, there is no clear shift of the conductance maxima towards higher energy (which is the hallmark of the suppression of the $\pi$-band contribution at $B = B^*$) at any field between 0 and 9 T. Rather, the peaks approximately remain in the same position, as indicated by vertical dashed lines. In Fig. 3(b) the curves at B=0 (circles), B=6 T (diamonds) and B=9 T (triangles) are shown after normalization. Similarly, Fig. 3(c) reports the normalized conductance curves of another contact, measured at the same fields but in the B || c configuration. In both (b) and (c), the experimental curves are compared to their single-band BTK fit, whose parameters are reported in the caption. The good quality of the fit and the magnetic-field dependence of the conductance curves strongly indicate that, at $x = 0.132$, Mg(B$_{1-x}$C$_x$)$_2$ is an anisotropic single-gap superconductor with $B^*_{c2} > B^*_{c1} > 9$ T. Further support to the presence of a single gap in crystals with $x = 0.132$ comes from the temperature dependence of the conductance curves, shown in Fig. 4. All the experimental curves (symbols) can be fitted by the single-band BTK model (solid lines), and the resulting gap values (inset, open circles) follow very well the BCS $\Delta(T)$ curve (inset, line). A comparison of $\Delta(T)$ with the ZFC magnetization (inset, filled squares) shows that the critical temperature of the junction coin-

![FIG. 3: (a) Raw conductance curves at T=4.2 K in a crystal with x = 0.132, in a magnetic field B || ab. (b) Some of these curves after normalization (symbols). Solid lines are the single-band BTK fits. On increasing the field from 0 to 9 T, the best-fit parameters vary as follows: $\Delta = 4.0 \rightarrow 3.5$ meV, $\Gamma = 0.8 \rightarrow 3.8$ meV, $Z = 0.60 \rightarrow 0.53$. (c) Same as in (b), but with B || c. Here, the parameters vary as follows: $\Delta = 4.0 \rightarrow 2.0$ meV, $\Gamma = 3.6 \rightarrow 4.6$ meV, $Z = 0.52 \rightarrow 0.42$. In (a), (b) and (c), dashed lines indicate the conductance peaks.](image-url)

![FIG. 4: An example of temperature dependence of the normalized conductance curves for x=0.132 (symbols) with the relevant fit (solid lines). The gap given by the fit (inset, open symbols) follows very well the BCS $\Delta(T)$ curve (inset, line). Filled symbols in the inset represent the ZFC magnetization.](image-url)
cides with the bulk $T_c$ and that the magnetic transition is complete at 5 K.

The dependence of the gaps on the carbon content and on the bulk $T_c$ is reported in Fig. 5 (a) and (b), respectively. Each point results from an average of various gap values (usually 4-8) obtained in different contacts. Hence, error bars indicate the maximum spread of measured values, and give an idea of the good reproducibility of our results. The value of the single gap at $x = 0.132$, $\Delta = 3.2 \pm 0.9$ meV, and the bulk $T_c = 19$ K give a gap ratio $2\Delta/k_BT_c \sim 3.9$ close to the BCS value. Despite the large uncertainty on $\Delta$, all the curves at $x = 0.132$ were best-fitted by a single gap BTK model. Note that the gap merging at $x = 0.132$ is perfectly consistent with the regular and smooth trend of the gaps for lower C contents. The decrease in $\Delta_\pi$ and the slight increase in $\Delta_\sigma$ shown in Fig. 5 suggest an increase in interband scattering, as predicted by the two-band model [1]. However, interband scattering alone would make the gaps merge in an isotropic gap $\Delta \simeq 4$ meV when $T_c = 26$ K. Clearly, other effects are playing a role, such as the changes in the electronic structure due to electron doping [17] and the hardening and narrowing of the $E_{2g}$ phonon mode [14]. By taking into account these effects, the observed $\Delta_\sigma(x)$ and $\Delta_\pi(x)$ curves in Mg(B$_{1-x}$C$_x$)$_2$ single crystals (included their merging at $T_c = 19$ K) can be well explained within the two-band Eliashberg theory as resulting from the band filling, plus a decrease in the Coulomb pseudopotential and an increase in interband scattering [18, 19] – even though this contrasts with the theoretical prediction that C substitution should have negligible effects on the $\sigma - \pi$ scattering [20].

In Fig. 5 (b), our gap values are compared to data from PCS in polycrystals by Holanová et al. [12]. Apart from a small systematic shift, their $\Delta_\sigma(T)$ curve is in good agreement with our results in the whole doping range, while their value of $\Delta_\pi$ at $x = 0.10$ ($T_c = 22$ K), is much smaller than ours. This disagreement is probably related to the greater amount of interband scattering in our crystals, which might be due to microscopic defects (also acting as pinning centers [8]) or to the existence of micro-domains with ordered C distribution [10]. Both possibilities are compatible with the presence of local C-content inhomogeneities on a scale comparable to $\xi$ [8].

Finally, notice that the evidence of single-gap superconductivity at $x = 0.132$, accompanied by an anisotropic band structure (see Fig. 6) is consistent with the extrapolation at $x > 0.10$ of recent measurements of $B_{c2}$ and Hall effect in single crystals up to $x = 0.10$ [14].

In conclusion, we have presented the results of the first directional point-contact measurements in Mg(B$_{1-x}$C$_x$)$_2$ single crystals with $0.047 \leq x \leq 0.132$, that allowed us to obtain the dependence of $\Delta_\sigma$ and $\Delta_\pi$ on the carbon content $x$. This dependence was confirmed by applying to the junctions a suitable magnetic field $B^*$ able to remove the contribution of the $\pi$-band gap to the total conductance, thus allowing the separate determination of the gaps via a single-band BTK fit. Up to $x \sim 0.10$, the two-gap nature of superconductivity characteristic of unsubstituted MgB$_2$ is retained. At $x = 0.132$ we clearly and reproducibly observed for the first time the merging of the two gaps into a single gap $\Delta \simeq 3$ meV with a gap ratio $2\Delta/k_BT_c$ close to the standard BCS value and a critical field greater than 9 T.

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