A Point-Contact Study of the Superconducting Gaps in Al-Substituted and C-Substituted MgB$_2$ Single Crystals

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We present the results of directional point-contact spectroscopy in state-of-the-art Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ single crystals produced at ETH, Zurich. Fitting the conductance curves of our point contacts, that always feature Andreev reflection structures, we obtained the doping dependence of the gap amplitudes. The results are discussed in comparison with other experimental findings and relevant theoretical predictions. We conclude that the physics of Al-substituted crystals at $x \geq 0.09$ might be governed by phase segregation, while C-substituted crystals unexpectedly show a doping-induced transition to single-gap superconductivity at $y = 0.132$.

Magnesium diboride, MgB$_2$, represents a unique and lucky combination of different physical properties that make it the highest-$T_c$ intermetallic compound, the only superconducting diboride and the clearest example of a two-band superconductor ever discovered. As a matter of fact, most of its physics has been explained rather well within the two-band model in either the BCS or the Eliashberg formulation. Much effort has been made in order to understand whether the peculiar properties of MgB$_2$ can be in some way tuned and controlled, both in view of applications (where, for example, higher critical fields or smaller anisotropy are required) or for fundamental reasons (to test the predictions of the two-band models concerning the effects of variations in some of the physical quantities that describe MgB$_2$). In other words, most of the present research work is devoted to investigate the “neighborhood” of MgB$_2$, that is all the systems that can be obtained from MgB$_2$ by means of pressure, irradiation, lattice stress, disorder and, over all, chemical substitutions.

Obtaining partial substitution of Mg or B atoms in MgB$_2$ is a difficult task. Even in the (few) cases of success, e.g. with aluminum and carbon, there are problems of solubility, phase segregation, inhomogeneities and structural transitions. Most of the substituted samples presently available are polycrystalline, of quality good enough to allow various kinds of experimental investigations that have led to highlight many structural, electronic and superconducting properties of these compounds. However, only a few determinations of the doping dependence of the energy gaps have appeared in literature, both for Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ single crystals, and none in single crystals.

In the following, we will present the results of the first systematic study of the energy gaps in Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ single crystals as a function of Al and C contents, by means of directional point-contact spectroscopy (DPCS). We will show that the doping dependence of the gaps is completely different in Al-substituted and C-substituted samples. In Mg$_{1-x}$Al$_x$B$_2$ crystals there is no evidence of gap merging and the small gap strongly decreases on increasing $x$, to become as small as 0.4 meV at $x = 0.21$, while the large gap saturates at about 4 meV at high Al contents. In Mg(B$_{1-y}$C$_y$)$_2$ crystals, instead, the $\pi$-band gap remains practically unchanged (at most, it shows a small increase), while the $\sigma$-band gap decreases and, at $x = 0.132$, the two gaps merge into one of amplitude $\Delta \approx 3$ meV. The results will be discussed in comparison with other experimental findings as well as with theoretical predictions.

Both the Mg$_{1-x}$Al$_x$B$_2$ and the Mg(B$_{1-y}$C$_y$)$_2$ single crystals were grown at the Solid State Laboratory, ETH-Zurich (Switzerland) by using a high-pressure technique in a cubic-anvil press, in the same way as the unsubstituted crystals. The partial substitution of Al in...
MgB$_2$ was obtained by replacing part of the Mg precursor with Al$^{[4]}$. As evidenced by HRTEM, at high doping levels there is a strong tendency to the precipitation of a second phase, in the form of Al-rich layers (probably MgAlB$_4$), perpendicular to the $c$ axis, while no defects are shown in the $ab$ plane. The Mg(B$_{1-x}$C$_x$)$_2$ crystals were grown at 1900-1950°C by starting from magnesium, amorphous boron and graphite powder or SiC as a carbon source. In the latter case, no trace of Si was found in the final material$^{[7]}$.

The crystals used for our DPCS measurements had Al contents $x$ (measured with EDX) ranging from 0.02 up to 0.21, and C contents $y$ (evaluated from the cell parameter $a$) between 0.055 and 0.132. Figure 1 reports the doping dependence of the critical temperature $T_c$, given by DC magnetization measurements, for both Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ crystals. Very surprisingly, the two curves turn out to be rather similar if plotted versus the atomic content of Al and C ($x$ and $2y$, respectively).

Directional point-contact measurements were performed by using the pressure-less (“soft”) technique described elsewhere$^{[15,16]}$ that consists in using a small ($\varnothing \leq 50 \mu$m) drop of Ag conductive paint as the counter-electrode, instead of the usual metallic tip pressed against the sample surface. This ensures greater contact stability on thermal cycling and allows making the contacts on the side of the (very thin) crystals, so as to inject the current mainly parallel to the $ab$ planes. In unsubstituted MgB$_2$, this is the best configuration for a contemporaneous measurement of both the gaps$^{[2,15]}$. The experimental conductance curves ($dI/dV$ vs. $V$) of our point contacts were normalized to the normal-state conductance to allow comparison with the Blonder-Tinkham-Klapwijk (BTK) model for superconductor/normal metal interfaces$^{[17]}$. All our contacts were in the ballistic limit and had small potential barrier. Indeed, the conductance curves show clear Andreev-reflection features. In particular, they present clear maxima at energies roughly equal to the small gap, $\Delta_x$, but in spite of the current injection along the $ab$ plane$^{[15]}$ only smooth shoulders at energies corresponding to the large gap, $\Delta_y$.

Figure 2 reports some normalized experimental conductance curves (symbols) measured in single crystals with different Al contents. All the curves were recorded at 4.2 K apart from the last two ($x = 0.18, 0.21$) that were measured at 1.8 K because the thermal smearing at 4.2 K was already comparable to the energy width of the Andreev-reflection structures. Even at a first glance, two distinct doping regimes can be identified. For $x < 0.09$, the conductance peaks corresponding to $\Delta_x$ slightly move outwards with respect to the undoped case. For $x > 0.09$, instead, the peaks shrink very fast on increasing $x$ and finally merge in a single sharp maximum at zero bias, indicating a fast decrease in $\Delta_x$. The clear narrowing of the whole conductance curves in passing from the low-$x$
to the high-\(x\) regime indicates that also \(\Delta_{\pi}\) undergoes a significant (and sudden) change around \(x = 0.09\).

A quantitative evaluation of the gap amplitudes can be given by fitting the conductance curves with the BTK model generalized to the two-band case, that has been shown to work well in pure MgB\(_2\) \cite{13,18}. The best-fitting curves, that agree well with the experimental data, are shown as solid lines in Fig 2. The fitting function contains 7 parameters: the gaps \(\Delta_{\sigma}\) and \(\Delta_{\pi}\), the barrier parameters \(Z_{\sigma}\) and \(Z_{\pi}\), the lifetime broadening parameters \(\Gamma_{\sigma}\) and \(\Gamma_{\pi}\), plus the weight of the \(\pi\) band in the total conductance, \(w_{\pi}\). Hence, one could object that the fitting procedure should give rather large uncertainties on the gap values. Actually: i) the value of \(\Delta_{\pi}\) is quite well determined by the energy position of the conductance peaks, and thus its uncertainty is necessarily small; ii) the values of both \(\Delta_{\sigma}\) and \(\Delta_{\pi}\) were confirmed, up to \(x = 0.09\), by the independent, three-parameter fit of the \(\sigma\) and \(\pi\)-band contributions to the conductance, whose separation was possible by applying a suitable magnetic field to the junction, as explained elsewhere \cite{12,13}. This was not possible for \(x > 0.09\), where even weak fields depress the \(\sigma\)-band gap and leave \(\Delta_{\pi}\) almost unchanged.

Fig 3 reports a subset of the conductance curves measured at 4.2 K in various Mg(B\(_{1-x}\)C\(_y\))\(_2\) single crystals with different \(y\). In this case there are no dramatic changes in the amplitude of the small gap \(\Delta_{\sigma}\), while the constant narrowing of the Andreev-reflection features indicates a decrease in the \(\sigma\)-band gap. As in Fig 2, solid lines represent the two-band BTK best-fitting curves. In various cases, we were able to separate (and fit separately) the partial \(\sigma\) and \(\pi\)-band conductances by applying a suitable magnetic field, thus achieving a higher-precision determination of the gap amplitudes. (Actually, the effect of the field on the conductance curves of the Ag/Mg(B\(_{1-x}\)C\(_y\))\(_2\) point contacts is rather complex and will be the subject of a forthcoming paper).

The gap values extracted from the fit of the conductance curves are reported in Fig 4 for Mg\(_{1-x}\)Al\(_x\)B\(_2\) (upper panel) and Mg(B\(_{1-x}\)C\(_y\))\(_2\) (lower panel). The trends are roughly indicated by dashed curves that are simply guides to the eye. The \(x\) dependence of the gaps in Mg\(_{1-x}\)Al\(_x\)B\(_2\) clearly reflects the aforementioned distinction between two regimes, delimited by the “threshold” value \(x = 0.09\). In the low-\(x\) regime, the behaviour of \(\Delta_{\sigma}\) and \(\Delta_{\pi}\) is compatible with an increase in interband scattering \cite{1}. Within the two-band model in the Eliashberg formalism, the gaps measured in the \(x = 0.08\) sample (\(\Delta_{\pi} = 3.1\) meV, \(\Delta_{\sigma} = 6.1\) meV) can indeed be obtained from those of MgB\(_2\) by only increasing the interband scattering up to \(\Gamma_{\pi\sigma} \approx 1.55\) meV. If one also takes into account all the other effects of Al substitutions (i.e. the changes in the DOS due to electron doping, \cite{10} and the stiffening of the \(E_{2g}\) phonon mode \cite{24}), the experimental trend of the gaps in the low-\(x\) regime is qualitatively reproduced \cite{21}. Things change completely above \(x = 0.09\), where the experimental data contrast with all present theoretical models. For high doping levels a merging of two gaps into one is predicted either by simply increasing the interband scattering \cite{1} or by including all the effects of Al substitution in the Eliashberg theory \cite{21}. In the first case, a BCS gap \(\Delta \approx 4.1\) meV and a critical temperature \(T_c \approx 26\) K are expected in the so-called “dirty”, isotropic limit \cite{1}; in the second case, the gap merging is predicted to occur around \(x \approx 0.3\), when \(\Delta_{\sigma} = \Delta_{\pi} \approx 3\) meV and \(T_c \approx 20\) K \cite{21}. However, the experimental results show no evidence of gap merging: \(\Delta_{\pi}\) decreases down to 0.4 meV at \(x = 0.21\) (with \(T_c = 20\) K) while \(\Delta_{\sigma}\) seems to saturate at about 4 meV. The failure of the simple “interband scattering” picture is not really surprising, since electron doping and phonon stiffening cannot be neglected \cite{24}. The failure of the more complete Eliashberg two-band model is much more interesting. One possible explanation is that phase segregation (indeed occurring in our crystals at \(x \geq 0.10\)) plays a major role in our result, causing an unpredicted transition to a substantially different physical system. However, it is worth saying that also recent gap measurements in segregation-free Mg\(_{1-x}\)Al\(_x\)B\(_2\) polycrystals by means of PCS \cite{10} have given no evidence of gap merging up to \(x = 0.3\), when \(T_c\) is as low as 24 K. Instead, the values \(\Delta_{\sigma} = 2.0\) meV and \(\Delta_{\pi} = 0.5\) meV have been found,
that agree rather well with those given by specific-heat measurements in the same samples but contrast with the predictions of all present theories \cite{1,21,22}.

The dependence of the gaps in Mg(B_{1-y}C_y)_2 on the carbon content \(y\), reported in the lower panel of Fig.\ref{fig:fig1}, is much more regular. While \(\Delta_\sigma\) slightly increases, \(\Delta_\pi\) decreases monotonically until, at \(x = 0.132\), only one gap of amplitude \(\Delta = 3.2 \pm 0.9\) meV is observed \cite{23}. Each point is the average of different gap values measured in different contacts, whose spread is indicated by the error bar. The large uncertainty at \(x = 0.132\) may arise from carbon-content inhomogeneity on a length scale of the order of \(\xi\) \cite{23}, that unfortunately can be detected by PCS. The overall gap trend does not differ much from that predicted by the two-band Eliashberg model for Al substitutions. Despite the different lattice sites occupied by Al and C, some effects of the C substitution are indeed very similar to those of Al doping: the decrease in \(T_c\) (see Fig.\ref{fig:fig1}), the filling of the \(\sigma\) bands due to electron doping \cite{24}, the stiffening of the \(E_{2g}\) phonon mode and the consequent decrease in the electron-phonon coupling \cite{24}. It is thus possible that, with suitable input from experimental data, the two-band model can reproduce the results presented here. As far as the “interband scattering” picture is concerned, let us just remind that, in principle, carbon substitutions should not increase the interband scattering \cite{23}. On the other hand, critical field measurements in C-doped single crystals have evidenced a reduction in the superconducting anisotropy \cite{24}. The extrapolation of this result above \(y = 0.10\) would lead to almost isotropic superconducting properties accompanied by anisotropic bandstructure, as would be expected for strong interband scattering.

As we did in the case of Mg_{1-x}Al_xB_2, it is worth comparing our results with other gap measurements in Mg(B_{1-y}C_y)_2 reported in literature. Early \(\mu^+SR\) studies of Mg(B_{1-y}C_y)_2 polycrystals in the extreme low-doping region \((y \leq 0.03)\) \cite{18} showed a fast linear decrease of the gaps on increasing \(y\) (with the same slope for \(\Delta_\sigma\) and \(\Delta_\pi\)), in such a way that, at \(y = 0.03\), \(\Delta_\sigma = 4.8\) meV and \(\Delta_\pi = 1.3\) meV. These values are much smaller than ours, and also disagree with those determined, in polycrystalline samples, by PCS \cite{11} and tunneling \cite{12}. In these last papers, the retention of two-gap superconductivity was observed (as in our case) up to \(y = 0.1\), where \(T_c = 22\) K. In the recent paper by Holanová \textit{et al.}, a linear decrease of the gaps vs \(T_c\) (with different slopes for \(\Delta_\sigma\) and \(\Delta_\pi\)) was claimed. The trend they evidenced for \(\Delta_\sigma\) is in very good agreement with ours, despite a systematic difference in the absolute values (that are all smaller than ours by 0.8 meV). On the contrary, the linear decrease in \(\Delta_\pi\) contrasts with our findings. These disagreements might be due to the different nature and quality of the samples, but further investigations are required to clarify this important point.

In conclusion, we have presented the results of the first systematic investigation of Mg_{1-x}Al_xB_2 and Mg(B_{1-y}C_y)_2 single crystals by directional point-contact spectroscopy. We have shown that the dependence of the gaps on the AI content contrasts will all present theories and is probably affected by phase segregation above \(x \approx 0.10\). In C-substituted crystals, instead, we have found the first evidence of gap merging, predicted theoretically as a result of the doping-induced changes in the DOS and in the phonon frequency and/or by the increase of interband scattering. This finding might provide the longed for, final test of the theoretical models for two-band superconductivity.

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