Retention of Two–Band Superconductivity in Highly Carbon–Doped MgB₂

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The simple binary compound, MgB₂, appears to be an elegant example of a two–band superconductor with a high $T_c$ of 39 K, in which superconductivity due to strong electron–phonon coupling in the two–dimensional (2D) $\sigma$–bands is induced into the 3D $\pi$–bands by a combination of interband electron–phonon coupling and weak interband quasiparticle scattering. Several key signatures of this include the closing of two energy gaps2,3,4,5,6,7 at the same $T_c$, anomalous features in the specific heat and its field dependence2 and the direct observation of interband scattering in the tunneling spectrum2.

However, two distinct superconducting gaps should only be seen in the clean limit, while in Ref.2 a single intermediate gap with a lower $T_c$ is predicted in the dirty limit. The observed weak dependence of $T_c$ on residual resistivity is not obviously consistent with this latter expectation.10 Mazin et al.16 have used supercell band–structure calculations to conclude that the two gaps can be preserved in the presence of enhanced scattering provided the interband impurity scattering is extremely weak. As will be shown below, introducing additional scattering centers by doping enables us to reduce the mean free path below the coherence length and thereby offers a direct experimental test of the dirty–limit prediction.

In a two–band superconductor the term dirty limit needs to be used carefully, though. The mean free path is reduced by both intra– and interband scattering, but only interband scattering is expected to homogenize the two gaps and result in expected one–band behavior.10 Thus there are two different scenarios for doped MgB₂: (i) impurities strongly enhance interband scattering, in which case the small gap, $\Delta_\sigma$, is expected to increase until it merges with the large gap, $\Delta_\pi$, at an intermediate value, or (ii) interband impurity scattering is minimally affected and two distinct gaps are preserved. In scenario (ii), the ratio $\frac{\Delta_\pi}{\Delta_\sigma}$ for the $\pi$–bands is expected to remain small (~ 1.5 in undoped MgB₂), whereas it would increase in scenario (i). This determination of $\frac{\Delta_\pi}{\Delta_\sigma}$ alone allows us to decide between these scenarios, and in this paper we present tunneling data showing that both $\Delta_\pi$ (the smaller gap) and $T_c$ are simultaneously reduced by about a factor of two upon ~ 10% C–doping. This represents direct experimental evidence for the selective suppression of interband impurity scattering relative to intraband scattering. Several groups3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18 have investigated the doping of MgB₂ with C with conflicting results concerning the C solubility limit, the composition dependence of $T_c$ and the possible presence of phase separation. Much of the discrepancy is possibly a synthesis problem due to the slow kinetics of C incorporation. Mickelson et al.11 and more recently Ribeiro et al.12 have been able to overcome the diffusion problem by using a C containing starting material, B₄C, and obtained samples with sharp diffraction peaks and superconducting transitions. The synthesis using B₄C yields multiphase samples containing another borocarbide, MgB₂C₂, since the solubility limit of C in MgB₂ is less than the 20 atom% present in the starting B₄C.

Our samples were synthesized from high–purity Mg, graphite, and Eagle–Picher ¹¹B enriched to 99.52%. A low carbon content boron carbide sample with a B₀.₈₅C₀.₁₅ composition was first made by arc melting the B and graphite together. This material was ground to a coarse powder, mixed with excess Mg and fired at 1000°C for 5 hr as described in Ref.18. After the excess Mg was removed by heating to 400°C in vacuum, powder neutron diffraction revealed only sharp diffraction peaks (Fig. 1) and the ac susceptibility showed a sharp transition with a midpoint $T_c$ of 21.5 K (Fig. 2). Note the absence of broadening of the diffraction lines precludes phase separation that was reported in Ref.18 for highly C–doped MgB₂. Rietveld analysis of the neutron diffraction data yield lattice constants $a = 3.0528$ Å and $c = 3.5219$ Å with a .07 mole fraction of MgB₂C₂ impurity. The $a$–axis is much reduced from 3.0849 Å for the pure material, while the $c$–axis is relatively unchanged. MgB₂C₂ is still present in our samples (although at a lower concentration then in Refs.11,12) since our starting C content is still larger than the solubility limit of C in MgB₂. From the initial carbon content of the boron carbide sample and the final MgB₂C₂ impurity content, the carbon con-
FIG. 1: Partial neutron powder diffraction pattern for the MgB$_{1.8}$C$_{0.2}$ sample. The solid squares and circle show the diffraction lines for Cd and V, respectively, that are instrumental in nature. The only other extraneous diffraction lines are from MgB$_2$C$_2$, present at about .07 mole fraction.

FIG. 2: (color online) Determination of the bulk–$T_c$ from normalized ac susceptibility (squares), and the junction–$T_c$ from the zero–bias conductance due to Josephson coupling (circles). Excellent agreement precludes reduced surface superconductivity.

The content of the C–doped MgB$_2$ sample is determined to be MgB$_{1.8}$C$_{0.2}$, i.e., a 10 atom% substitution of C for B, with an accuracy of ±2 atom%. This defines the solubility limit that agrees with recent results of Avdeev et al.

Our tunneling data are on superconductor–insulator–superconductor (SIS) break junctions, and they commonly identify the smaller gap in the 3D $\pi$–bands of C–doped MgB$_2$. An example is shown in Fig. 3 where the current–voltage characteristic, $I(V)$, is plotted as the line with open squares along with its differential conductance, $dI/dV$, that was generated numerically and is plotted as open circles. Our tunneling apparatus uses Au tips that readily attach to a piece of MgB$_2$ and afterwards the single tunnel junction formed between this attached piece of MgB$_2$ and the bulk sample predominates the spectra, i.e., has by far the highest resistance. The data exhibit rather sharp coherence peaks near ±3 mV that are characteristic for SIS junctions and an overall spectral shape that is well–reproduced by an SIS fit (solid line in Fig. 3) using $\Delta = 1.45$ meV and $\Gamma = 0.25$ meV. This ratio of $\Gamma/\Delta \sim 20\%$ is consistent with our tunneling data on undoped MgB$_2$.

The Josephson pair–tunneling peak at zero bias is the most prominent difference with the SIS calculation that only considers single–electron, quasiparticle tunneling. Due to the exceptional strength of this feature in lower–resistance tunnel junctions, and its intimate relation to superconductivity, the disappearance of this zero–bias peak at higher temperature is a very accurate test of the junction–$T_c$. We traced this feature to high temperatures in a junction that at 4.2 K showed almost 20 times the normal–state background conductance at zero bias, and find it to merge into a flat background at $T_c \sim 22–23$ K (Fig. 3). This is in excellent agreement with the bulk–$T_c$ from magnetization that for comparison is also shown in the same figure, and allows us to draw two conclusions. First, the zero–bias peak is indeed due to Josephson currents, thereby providing solid corroboration of SIS tunneling. Second, the junction–$T_c$ is equivalent to the bulk value, confirming that the tunneling results are not affected by surface effects. Higher–resistance junctions do not show the Josephson pair tunneling at zero bias, as
reduced from the weak–coupling limit of \( \sim \) samples, the gap ratio, that is crucial experimental evidence for two–band s–nue, that second, larger energy gap, i.e., two–band behavior. We effects. This can only be explained by the presence of a barrier, tunneling currents are generally dominated by the 3D \( \pi \)–plane in a randomly formed junction is highly improbable; thus while all tunneling data on MgB\(_2\) observe the smaller gap in the 3D \( \pi \)–bands, the 2D \( \sigma \)–band is seen only occasionally. When present, contributions from the 2D \( \sigma \)–band are easily distinguished in SIS data but are not seen in the data of Figs. 3 and 4, consistent with our data, although we find that superconductivity persists at 22 K for \( \sim 0.1 \) electrons/B atom.

The retention of two–band superconductivity at such a high doping level is surprising, as it requires the absence of sizable \( \sigma \)-band impurity scattering. Again, there are essentially two scenarios that allow us to understand this behavior: (a) doping does not increase \( \sigma \)-band scattering, or (b) doping increases \( \pi \)-band scattering only, while \( \sigma \)-band scattering is unaffected. In scenario (a) the lack of any scattering implies the C forms a superlattice. Scenarios (b) require the selective suppression of \( \sigma \)-band scattering relative to \( \pi \)-band scattering, and below we will present evidence that supports scenario (b). For impurities as dilute as the 10% C for \( ^{11} \)B in our samples, the possibility of local ordering, e.g., staged replacement of, on average, every 5th B layer with an ordered (BC)\(_{0.5}\) layer cannot be ruled out, but the long–range order needed for scenario (a) would not be expected. Testing for this is difficult since the contrast between C and \( ^{11} \)B is weak by any scattering technique. Electron scattering offers the highest sensitivity to ordering because the diffraction occurs from tiny single crys-
tals in the powder sample. Transmission electron diffraction was performed on crystallites aligned along the [001] and [100] zone axes, and no evidence of any ordering of dopant ions was found. We therefore conclude, that C enters the lattice as randomly distributed impurities, and that the sharp $T_c$ and the narrow powder diffraction peaks (see Fig. 1) are the result of a solubility limit for C in MgB$_2$ (that in the presence of excess C would be expected to result in a homogenous doping just at this limit) rather than a well-ordered C superlattice.

In the absence of C-ordering, the dopant atoms are expected to act as scattering centers, and we may estimate the effective mean free path from the C-concentration. Using a 2 x 2 x 1 MgB$_2$ supercell containing one C atom, equivalent to 1/8 = 12.5% impurities, the average C-C in-plane distance is $\sim$ 0.6 nm, about one order of magnitude less than the anisotropic coherence lengths in undoped MgB$_2$ (that are 4 and 10 nm at). Such a significantly reduced mean free path is borne out by the increase in $\frac{dH_c}{dT}$ ($T_c$) by about a factor of two upon similar C-doping.

We therefore conclude that the retention of two-band superconductivity in the presence of heavy C-doping is a result of the selective suppression of interband impurity scattering, scenario (b). (Note that the absence of sizable interband scattering is a non-trivial prerequisite for the observation of two-band superconductivity even in undoped MgB$_2$.) Mazin et al. studied scattering in MgB$_2$ theoretically and argued that interband impurity scattering would be suppressed due to the disparity between $\sigma$- and $\pi$-wavefunctions. Applied to the case of C-doped MgB$_2$, this suggests that the two-band nature of superconductivity (that requires the absence of sizable interband scattering) can be retained, while at the same time other properties (that depend on intraband scattering) may be suggestive of the dirty limit, e.g., show increased resistivity and $\frac{d\sigma}{dT}$ ($T_c$).

In conclusion, our tunneling results on MgB$_{1.8}$C$_{0.2}$ demonstrate the retention of two-band superconductivity in the presence of significant scattering, consistent with specific heat measurements of Ribeiro et al. We explain this by the selective suppression of interband scattering, as suggested by Mazin et al. Our experiment shows that this suppression is a surprisingly robust feature of MgB$_2$ and strong enough to retain the two-band character even in the presence of a C-doping content sufficient to reduce $T_c$ by a factor of two.

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28. Note the qualitative disagreement with an SIN fit using a gap of 2.6 meV and virtually zero lifetime broadening, $\Gamma$. At 4.2 K, thermal effects alone would broaden the peaks to about half their observed height, as shown by the dashed line in Fig. 4.
29. Note that the SIS calculation reveals a small hump at zero bias due to tunneling of thermally-activated quasiparticles. This is seen in high-resistance, low-$\Gamma$ tunnel junctions in undoped MgB$_2$ but like the Josephson current it is a feature that is only found in SIS junctions. The observed zero-bias peak seen in Fig. 4 is too large to be explained by thermal activation, but agrees with the Josephson pair tunneling that is seen in such low-resistance ($\sim$ 210 $\Omega$ in this case) junctions in undoped MgB$_2$.
30. Note that the zero-bias conductance signal is not proportional to the Josephson current, $J_J$, itself and its temperature dependence is not expected to follow $J_J(T)$. However, the disappearance of both quantities coincides and allows...
for an unambiguous determination of $T_c$. 