Local Tunneling Study of Three-Dimensional Order Parameter in the π-band of Al-doped MgB$_2$ Single Crystals

F. Giubileo, F. Bobba, A. Scarfato, and A.M. Cuolo  
CNR-INFM Laboratorio Regionale SUPERMAT e Dipartimento di Fisica "E.R. Caianiello", Università degli Studi di Salerno, via Salvador Allende, 84081 Baronissi (SA), Italy.

A. Kohen and D. Roditchev  
Institut des Nanosciences de Paris, INSP, Université P. et M. Curie Paris 6, CNRS, UMR 75-88, Paris, France

N. Zhigadlo and J. Karpinski  
Solid State Physics Laboratory, ETH Zurich, CH-8093 Zurich, Switzerland

We have performed local tunneling spectroscopy on high quality Mg$_{1-x}$Al$_x$B$_2$ single crystals by means of Variable Temperature Scanning Tunneling Spectroscopy (STS) in magnetic field up to 3 Tesla. Single gap conductance spectra due to c-axis tunneling were extensively measured, probing different amplitudes of the three-dimensional $\Delta_\pi$ as a function of Al content. Temperature and magnetic field dependences of the conductance spectra were studied in S-I-N configuration: the effect of the doping resulted in a monotonic reduction of the locally measured $T_C$ down to 24K for $x=0.2$. On the other hand, we have found that the gap amplitude shows a maximum value $\Delta_\pi = 2.3$ meV for $x=0.1$, while the $\Delta_\pi/T_C$ ratio increases monotonously with doping. The locally measured upper critical field was found to be strongly related to the gap amplitude, showing the maximum value $H_{c2} \simeq 3T$ for $x=0.1$ substituted samples. For this Al concentration the data revealed some spatial inhomogeneity in the distribution of $\Delta_\pi$ on nanometer scale.

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Five years after Nagamatsu et al. \cite{1} reported MgB$_2$ to be superconductor, the huge worldwide experimental and theoretical effort seems to have established the main features of superconductivity in this compound. Indeed, the strong electronic coupling to the high-frequency in-plane boron modes ($E_{2g}$ at the zone centre $\Gamma$) and the number of holes at the Fermi level in the $\sigma$ bands are able to explain a transition temperature $T_C$ as high as 39 K \cite{2, 3}. Moreover, it is now demonstrated \cite{3, 4, 5, 6, 7, 8, 9, 10, 11, 12} that MgB$_2$ is a two-gap superconductor with two distinct energy gaps: a large gap $\Delta_\sigma$ originating from two-dimensional (2D) $\sigma$ bands and a small gap $\Delta_\pi$ originating from three-dimensional (3D) $\pi$ bands. The presence of two bands with distinct superconducting gaps leads to several unusual properties, like the temperature and field dependent anisotropy which dominate the magnetic and transport properties. Anisotropy is related to the intraband and interband electron scattering that can be modified by partial chemical substitutions. In particular, aluminium (replacing magnesium) \cite{13, 14}, and carbon (replacing boron) \cite{14} have successfully entered in the MgB$_2$ structure, doping the material with additional electrons: small variations of the interband scattering have been predicted for C substitutions, while it has been demonstrated that Al doping can realize a considerable out-of-plane distortions of the B atoms \cite{15} causing a significant increase of the interband scattering with consequent increasing of $\Delta_\pi$ and decreasing of $\Delta_\sigma$ \cite{16}.

Experimentally, it has been observed that the superconducting transition temperature of both Mg$_{1-x}$Al$_x$B$_2$ and Mg($B_{1-y}C_y$)$_2$ decreases with doping \cite{13, 17} and in the case of Al (C), superconductivity disappears for $x > 0.5$ ($y > 0.3$) \cite{13, 16}. Recently, measurements of the amplitude of the energy gaps have been performed by means of different techniques (specific heat, point contact, STM) on Al doped \cite{20, 21} as well as on neutron irradiated polycrystals \cite{22, 23} and on disordered thin films \cite{24}. From these studies a quite general trend seems to relate the variation of both energy gaps with $T_C$, however a different behavior of $\Delta_\pi$ has been reported for Al-doped single-crystals, indicating large gap values for doping levels up to 10% and quite small values for higher doping levels \cite{24, 26}. Results on C-doped samples also are controversial and the analysis of the whole set of data resulted in an extended debate \cite{27, 28, 29} still waiting for a definite answer. It is our opinion that in some cases, disagreement arises due to the non-local nature of used experimental techniques and to the high number of fitting parameters necessary to reproduce the experiments.

In this paper we report a systematic study performed by Scanning Tunneling Spectroscopy (STS) on high quality Mg$_{1-x}$Al$_x$B$_2$ single crystals, for different Al concentrations. Directional tunneling along c-axis allowed us to selectively probe the $\pi$ band energy gap, with high spatial and energy resolution. In particular, by measuring the temperature dependence of the tunneling spectra, the local $T_C$ was inferred, corresponding to the energy gap measured in the same location. The magnetic field dependence was also studied to evidence correlations of the locally measured upper critical field $H_{c2}$ with the gap amplitude. Moreover, the high spatial resolution of the STS technique allowed to evidence possible non-homogeneities of the superconducting properties on the sample surface.
to model the experimental data while the temperature finite lifetime of the quasiparticles, as introduced by Dynes
gap value $\Delta$ reproduced by an isotropic BCS state density with a sin-
samples with 10% (x=0.1) and 20% (x=0.2) Al content.

FIG. 1: Left plots: Low temperature spectra measured in
Mg$_{1-x}$Al$_x$B$_2$ for x = 0 (a), x=0.1 (b) and x=0.2 (c). Solid
lines represent the theoretical fittings calculated by consider-
ing a single gap isotropic BCS density of states with a smear-
ing $\Gamma$ parameter. Right plots: corresponding temperature de-
pendence of the superconducting energy gap $\Delta_\pi$ as extracted
from the theoretical fittings. Experimental data are compared
to the theoretical BCS behavior (solid lines).

with variation of $\Delta_\pi$ depending on the doping.

Single crystals of Mg$_{1-x}$Al$_x$B$_2$ were grown by high
pressure method in a cubic-anvil press in the same way
as the pure crystals [30]. The STS experiments were car-
ried out on crystals with nominal 0%, 10% and 20% Al
content by means of an UHV variable temperature STM.
The tunneling junctions were achieved by approaching a
mechanically etched Pt/Ir tip to the c-axis oriented sur-
fase of the crystals. As expected, the STS measurements
revealed only a single gap structure in the dI/dV spectra
at low temperatures because the probability for direct
tunneling into the 3D-sheet of the Fermi surface results
much higher than the probability for tunneling into the
2D-part of the Fermi surface which has no states with
wavevector parallel to the c-axis.

In Fig. 1a,b,c we show the dI/dV characteristics mea-
sured at $T = 6.5K$ respectively on pure MgB$_2$, and on
samples with 10% (x=0.1) and 20% (x=0.2) Al content.
It can be observed that all the tunneling spectra are well
reproduced by an isotropic BCS state density with a sin-
gle gap value $\Delta_\pi$, corresponding to the 3D $\pi$-band, and a
phenomenological smearing factor $\Gamma$, corresponding to fi-
nite lifetime of the quasiparticles, as introduced by Dynes
[31]. These are the only two fitting parameters needed
to model the experimental data while the temperature
was directly measured. The experiments indicated that
pure MgB$_2$ crystals were highly homogeneous with the
sample surface characterized by a superconducting en-
ergy gap $\Delta_\pi = 2.00 \pm 0.05$ meV, i.e. with less than 3%
spread in the values measured in different locations.

The behavior of the doped crystals appeared to be
quite different. For the x=0.1 substituted crystals, the
3D $\Delta_\pi$ resulted to be non-homogeneous in its spatial dis-
tribution on nanometer scale, with values varying be-
tween 1.5 meV $< \Delta_\pi < 2.3$ meV, as observed in Fig. 1b
referring to different locations of the same sample. The
spectrum signed (I) for which we found $\Delta_\pi = 2.3$ meV,
was the statistically most present in about 90% of the
locations. However, in few cases, we have measured dif-
ferent gap amplitudes as observed in curve (II) with $\Delta_\pi$
= 2.0 meV and in curve (III) with $\Delta_\pi = 1.7$ meV. The en-
ergy gap variations in the x=0.1 substituted samples, can
be due to different local Al concentrations arising during
the crystal growth process. Indeed, structural changes
can occur in crystals when the Al content is increased
beyond a critical value $x \simeq 0.1$. These changes include
the segregation of a non-superconducting, Al-rich phase
and the formation of superstructures along the $c$-axis
[20]. We notice that the most satisfactory agreement between
theory and experiments was obtained for the spectra sta-
itionally more present characterized by the largest value
of the energy gap, $\Delta_\pi = 2.3$meV, corresponding to a 15%
increase of the superconducting energy gap compared to
the case of pure MgB$_2$. For the x=0.2 substituted crys-
tals, statistic in several locations showed quite homoge-
neous superconducting properties on the sample surface.
The measured spectra evidenced single gap features (Fig.
1c) with $\Delta_\pi = 1.8$ meV, with less than 6% spread in the
measured values. We notice that this last estimation re-
sults much higher than what previously reported for sim-
ilar doping levels [23].

For all samples, we have performed complete measure-
ments of the temperature dependence of the tunneling
spectra in the range between 5K and 40K. In Fig. 1d,e,f,
the gap amplitude as inferred from the theoretical fit-
ings is plotted as a function of the temperature. In the
case of pure MgB$_2$ (Fig. 1d), a BCS dependence (solid
line) of the data (scattered symbols) is found indicating
a local $T_C = 39$K. In the case of 10% Al-doping (Fig.
1e), gaps of different amplitudes all vanish at the same
critical temperature $T_C \simeq 35$ K indicating that varia-
tions of the 3D order parameter in the $\pi$-band occur on
a scale less than the superconducting coherence length.
For samples with higher doping level, x=0.2 (Fig. 1f), a
local $T_C=24$K is found.

We also performed a complete analysis of the local re-
sponse to external magnetic fields up to 3 T, with the
tunneling current and the applied field parallel to the
$\pi$-band of the crystal. The samples were cooled in zero
magnetic field. At low temperature, the field was slowly
increased from zero up to 3 T and then reduced to zero
again, to evidence any hysteretic behavior. Since the re-
ported spectra were averaged over many vortices passing
In Fig. 2 we show a complete set of data recorded in magnetic field for x=0 (Fig. 2a,d,g), x=0.1 (Fig. 2b,e,h), and x=0.2 (Fig. 2c,f,i). In the first column we show the evolution of the normalized tunneling conductance spectra as measured at $T \simeq 6.5$K. The field dynamics of the DOS at the Fermi level is reported in the second column where the evolution of the Zero-Bias Conductance (ZBC) is presented. We notice that for pure crystals (Fig. 2d), the ZBC rapidly rises for low fields and reaches a value of about 80% of the normal state ZBC around 0.4 T. As the field further increases, the filling of states becomes much slower, the two different dynamics being separated by an almost flat crossover region. Finally, the gap fills completely around 2.2 T. By lowering the field we observed a similar behavior, with the crossover region slightly shifted to higher fields. We speculate that the crossover region can be associated to the rotation of the vortex lattice in the pure MgB$_2$ [32], while the hysteretic behavior seems to indicate different vortex dynamics for increasing and decreasing fields, which may be due to geometrical barriers, vortex pinning, and/or lattice re-arrangements.

Under the tip [32], the main effect of the magnetic field was, as expected, the progressive filling of states inside the energy gap.

In the case of 10% Al doping (Fig. 2c), the data refer to locations with $\Delta_\pi = 2.3$ meV. The field dynamics of the DOS at the Fermi level again shows a rapid rising of the ZBC for low magnetic fields. However, for increasing fields, the filling of states tends to saturate and, at 2.5T, it is still possible to distinguish the presence of the superconducting energy gap in the measured spectra. Extrapolation of the data in this region leads to $H_{c2} \simeq 3$ T, corresponding to a value 30% higher than that observed in the case of pure MgB$_2$. For x=0.2, the ZBC evolution in magnetic field indicates a reduced $H_{c2} \simeq 1.8$ T. We notice that, for both substitutions, the ZBC doesn’t show any hysteretic behavior. Finally, in Fig. 2c,f,i we show the magnetic field dependence of $\Delta_\pi$ for the three samples as inferred from the theoretical fittings. We observe a clear reduction of the gap amplitude for fields up to 0.5 T followed by a region between 0.5 T and 1.0 T, in which no significant variations occur, while pair-breaking continuously increases due to the applied magnetic field. This observation seems to suggest that around 0.5T the contribution to the superconductivity due to the phonon mediated electron-electron interactions in the $\pi$-band itself is not efficient anymore, while for higher fields the energy gap survives due to both the phonon exchange
with $\sigma$-band $\Delta_\pi$ and/or to the quasiparticle interband scattering.

Finally, in Table I we summarize our results that in Fig. 3 are compared with the literature. The significant spread of the data reported by different groups is at the origin of the recent, hot debate $^{27,28,29}$, nevertheless a quite general trend (full lines) for both the $\pi$-band $\Delta_\pi(0)$ and the $2\Delta_\pi(0)/K_BT_c$ ratio as a function of $T_c$, compared with data in literature. Same symbols have been used in both plots and the full lines are guides to the eye.

In conclusion, we have performed a systematic study of the local temperature and magnetic field dependence of the 3D energy gap $\Delta_\pi$ in Mg$_{1-x}$Al$_x$B$_2$ single crystals by means of Scanning Tunneling Spectroscopy. By working with high quality single crystals we succeeded in selectively measure the behavior of the only $\Delta_\pi$, and due to the high spatial resolution of the STS technique, we were able to relate the local values of $T_c$, $\Delta_\pi$ and $H_{c2}$. We have found a reduction of $T_c$ for increasing doping, corresponding to a monotonous rising of the BCS ratio but not of the absolute amplitude of the energy gap. In agreement with recent theoretical models, we have measured the largest gap value ($\Delta_\pi = 2.3$ meV, 15% larger than in pure MgB$_2$) in samples with $x=0.1$, corresponding to a local $H_{c2}^{loc} \approx 3T$ (30% higher than in pure MgB$_2$).

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**TABLE I: Summary of our STM results.**

| $x$ | $T_c$(K) | $\Delta_\pi$(meV) | $H_{c2}$(T) | $2\Delta_\pi/K_BT_c$ |
|-----|-----------|-------------------|-------------|---------------------|
| 0   | 39        | 2.0               | 2.2         | 1.17                |
| 0.1 | 35        | 2.3               | 3.0         | 1.52                |
| 0.2 | 24        | 1.8               | 1.8         | 1.74                |

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**FIG. 3:** (a) $\Delta_\pi(0)$ and (b) $2\Delta_\pi(0)/K_BT_c$ as function of $T_c$, compared with data in literature. Same symbols have been used in both plots and the full lines are guides to the eye.

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[1] J. Nagamatsu et al., *Nature (London)*, 410, 63 (2001).
[2] H.J. Chol et al., *Nature (London)*, 418, 758 (2002).
[3] J.M. An, W.E. Pickett, *Phys. Rev. Lett.* 86, 4366 (2001).
[4] J. Kortus et al., *Phys. Rev. Lett.* 86, 4656 (2001).
[5] S.L. Budko et al., *Phys. Rev. Lett.* 86, 1877 (2001).
[6] A.Y. Liu et al., *Phys. Rev. Lett.* 87, 087005 (2001).
[7] F. Giubileo et al., *Europhys. Lett.* 58, 764 (2002).
[8] F. Giubileo et al., *Phys. Rev. Lett.* 87, 177008 (2001).
[9] P. Szabo et al., *Phys. Rev. Lett.* 87, 137005 (2001).
[10] R.S. Gonzelli et al., *Phys. Rev. Lett.* 89, 247004 (2002).
[11] M. Iavarone et al., *Phys. Rev. Lett.* 89, 187002 (2002).
[12] For a review, see: *Physica C: Superconductivity*, Volume 385, Issues 1-2 (2003), edited by G. Crabtree, W. Kwok, S.L. Bud’ko and P.C. Canfield.
[13] J.S. Slusky et al., *Nature (London)*, 410, 343 (2001).
[14] R. A. Ribeiro et al., *Physica C*, 384, 227 (2003).
[15] S. C. Erwin, I. I. Mazin, *Phys. Rev. B*, 68, 132505 (2003).
[16] A. Bussmann-Holder, A. Bianconi, *Phys. Rev. B*, 67, 132509 (2003).
[17] A. Bianconi et al., *Phys. Rev. B*, 65, 174515 (2002).
[18] P. Postorino et al., *Phys. Rev. B*, 65, 020507 (2002).
[19] B. Renker et al., *Phys. Rev. Lett.* 88, 067001 (2002).
[20] M. Putti et al., *Phys. Rev. B*, 68, 094514 (2003).
[21] M. Putti et al., *Phys. Rev. B*, 71, 144505 (2005).
[22] Y. Wang et al., *J. Phys. Condens. Matter*, 15, 883 (2003).
[23] M. Putti et al., *Phys. Rev. Lett.* 96, 077003 (2006).
[24] M. Iavarone et al., *Phys. Rev. B*, 71, 214502 (2005).
[25] D. Daghero et al., *Phys. Stat. Sol.*, 2, 1656 (2005).
[26] J. Karpinski et al., *Phys. Rev. B*, 71, 174506 (2005).
[27] J. Kortus et al., *Phys. Rev. Lett.* 94, 027002 (2005).
[28] P. Samuely et al., *Phys. Rev. Lett.* 94, 099701 (2005).
[29] J. Kortus et al. Reply, *Phys. Rev. Lett.* 94, 099702 (2005).
[30] J. Karpinski et al., *Supercond. Sci. Technol.*, 16, 221 (2003); J. Karpinski et al., *Physica C*, 385, 42 (2003).
[31] R.C. Dyres et al., *Phys. Rev. Lett.*, 41, 1509 (1978).
[32] A. Kohen et al., *Appl. Phys. Lett.* 86, 212503 (2005).
[33] R. Cubitt et al., *Phys. Rev. Lett.* 91, 047002 (2003).
[34] H. Suhl et al., *Phys. Rev. Lett.* 3, 552 (1959).