Local tunneling study of three-dimensional order parameter in the π band of Al-doped MgB_2 single crystals

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We have performed an extensive study of the temperature and magnetic field dependencies of local tunneling spectra measured by means of variable temperature scanning tunneling spectroscopy on high quality $Mg_{1-x}Al_xB_2$ single crystals. Single gap conductance spectra due to *c*-axis tunneling were measured, probing different amplitudes of the three-dimensional Δ_π as a function of Al content (i.e., as a function of the critical temperature T_C). We give clear evidence that the locally measured energy gap, as well as the upper critical field, reach maximum values $\Delta_\pi = 2.4$ meV and $H_{c2} \geqslant 3$ T around $x \simeq 0.1$ ($T_C = 33$ K) regardless of the monotonous fall of T_C as a function of doping. Our results strongly suggest that different interband scattering occurs for different gap amplitudes.

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A few years after Nagamatsu *et al.*[1] reported MgB_2 to be a superconductor, the huge world-wide 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 center Γ) and the number of holes at the Fermi level in the σ bands are able to explain a transition temperature T_C as high as 39 K.[2,3] Moreover, it is now demonstrated[4–15] that MgB_2 is a two-gap superconductor with two distinct energy gaps: a large gap Δ_σ originating from two-dimensional (2D) σ bands and a small gap Δ_π originating from three-dimensional (3D) π bands. The presence of two bands with distinct superconducting gaps leads to several unusual properties, such as 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),[16] and carbon (replacing boron)[17] 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 distortion of the B atoms[18] causing a significant increase of the interband scattering with consequent increasing of Δ_π and decreasing of Δ_σ.[19]

Experimentally, it has been observed that the superconducting transition temperature of both $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ decreases with doping[16,20] and in the case of Al (C), superconductivity disappears for $x > 0.5$ ($y > 0.3$).[21,22] Recently, measurements of the amplitude of the energy gap have been performed by means of different techniques (specific heat, point contact, STM) on Al doped[23,24] as well as on neutron irradiated samples[25–27] and on disordered thin films.[28] From these studies a quite general trend seems to relate the variation of both energy gaps with T_C: Δ_σ decreases continuously with decreasing T_C, however Δ_π appears much less affected. Moreover, for Al-doped single crystals, a different behavior of Δ_π was reported indicating relatively large gap values for doping levels up to 10% and severely depressed values for higher doping levels.[29,30] Results on C-doped samples also are controversial and the analysis of the whole set of data has resulted in an extended debate[31–33] still waiting for a definite answer. It is our opinion that disagreement arises due to both the intrinsic, nonuniform distribution of the substituted species into the original crystal lattice and to the high number of fitting parameters often necessary to reproduce the experiments on a double-gap superconductor (that also implies double smearing parameters, weight factor, intraband and interband scattering, etc.).

The effort of using a local probe technique on a highly controlled series of doped samples to obtain an accurate set of measurements appears to be a unique opportunity for clarifying the remaining controversial aspects in the behavior of the MgB_2 system.

In this paper we report a systematic study performed by scanning tunneling spectroscopy (STS) on high quality $Mg_{1-x}Al_xB_2$ single crystals, for different Al concentrations. Directional tunneling along the *c* axis allowed us to selectively probe the π-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 in a local way: An estimation for upper critical field H_{c2} was inferred from the evolution of the tunneling spectra with

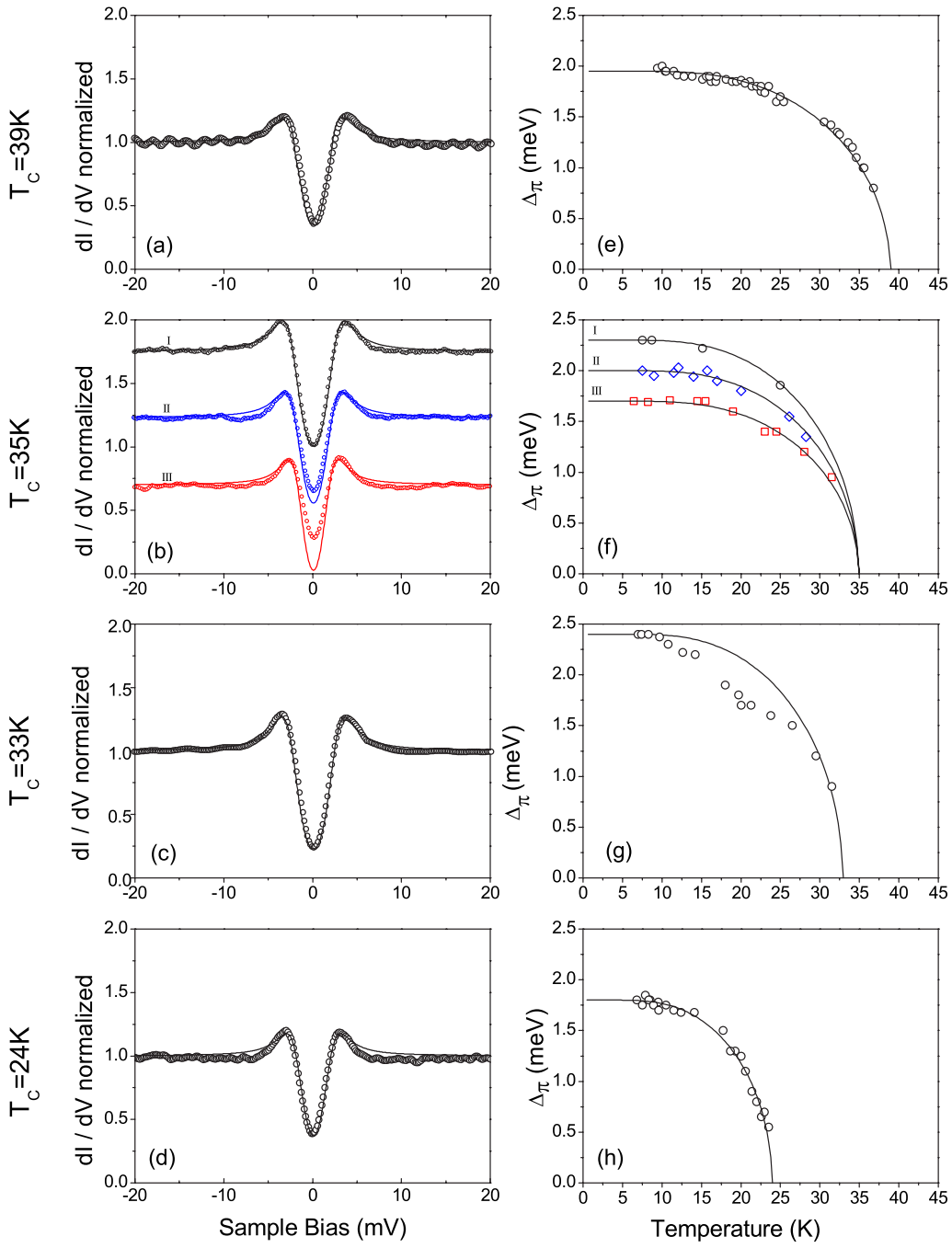

FIG. 1. (Color online) Left-hand plots: Low temperature spectra measured in $Mg_{1-x}Al_xB_2$ for samples having (a) T_C=39 K, (b) T_C =35 K, (c) T_C=33 K, and (d) T_C=24 K. Solid lines represent the theoretical fits calculated by considering a single gap isotropic BCS density of states with a smearing Γ parameter. Right-hand plots: Corresponding temperature dependence of the superconducting energy gap Δ_π as extracted from the theoretical fits. Experimental data are compared to the theoretical BCS behavior (solid lines).

the field perpendicular to the sample surface, for different doping levels. Moreover, the high spatial resolution of the STS technique allowed us to evidence possible nonhomogeneities of the superconducting properties on the sample surface with variation of Δ_π in the same sample depending on different local levels of doping.

Single crystals of $Mg_{1-x}Al_xB_2$ were grown by a high pressure method in a cubic-anvil press in the same way as the pure crystals.[34] The STS experiments were carried out on crystals with nominal Al doping up to 20%, and T_C ranging from 39 K to 24 K, by means of a UHV variable temperature STM. Recently, we have used the same system to study the vortex profile in undoped, *c* axis oriented MgB_2 single crystal.[36] The tunneling junctions were achieved by approaching a mechanically etched Pt/Ir tip to the *c*-axis oriented surface 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

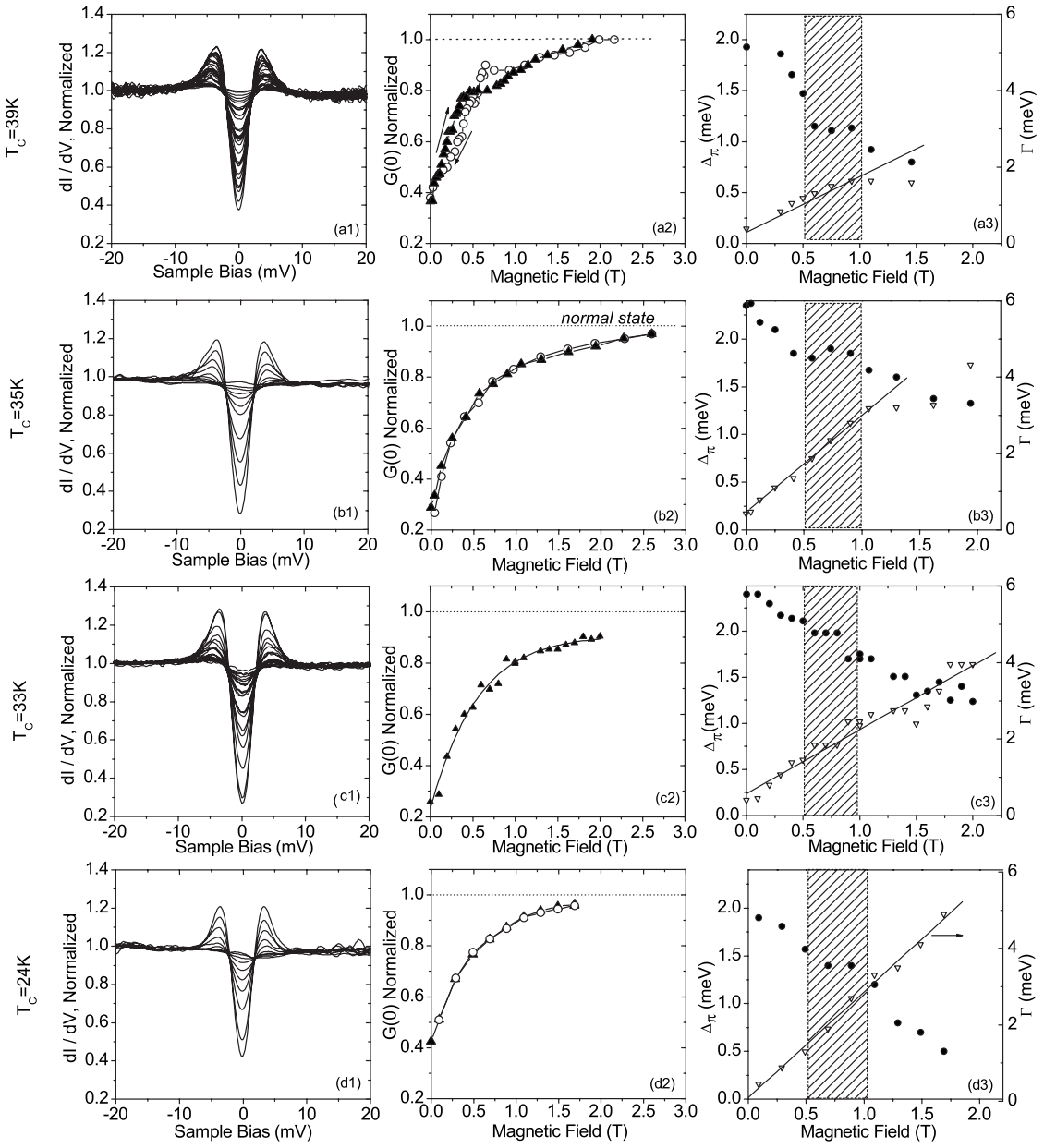

FIG. 2. Magnetic field dependence of the conductance spectra measured at $T \simeq 6.5$ K. Data referring to different samples (with different T_C) are reported on different rows. In the first column the tunneling conductance spectra measured for rising fields are reported. In the central column the field evolution of the ZBC, for increasing (solid triangles) and decreasing (empty circles) fields, are shown. In the third column the magnetic field dependence of the 3D Δ_π as obtained by theoretical fitting is presented. Solid symbols refer to the energy gap amplitude, while open symbols refer to the Γ values.

the Fermi surface which has no states with wave vector parallel to the c axis.

We have measured five samples with different doping levels and in the left-hand panels of Fig. 1 we show the dI/dV characteristics measured at $T=6.5$ K, respectively, on pure MgB_2 (a), on the crystal with the highest level of doping $x=0.2$ (d), and on two samples close to the critical doping level $x \simeq 0.1$ (Ref. 30) (b,c), samples with nominal T_C of 35 K ($x=0.1$), 33 K, 24 K ($x=0.2$). It can be observed that all the tunneling spectra are well reproduced by an isotropic BCS state density with a single gap value Δ_π, corresponding to the 3D π band, and a phenomenological smearing factor Γ, corresponding to finite lifetime of the quasiparticles, as introduced by Dynes.[35] 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 energy gap $\Delta_\pi = 2.00 \pm 0.05$ meV, i.e., with less than 3% spread of the values measured in different locations.

On the other hand, the behavior of the doped crystals appeared to be quite different. In particular, for the sample reported in Fig. 1(b) with nominal doping $x \simeq 0.1$, the 3D Δ_π resulted to be nonhomogeneous in its spatial distribution on nanometer scale, with values varying between 1.5 meV $< \Delta_\pi <$ 2.3 meV, in different locations of the same sample.

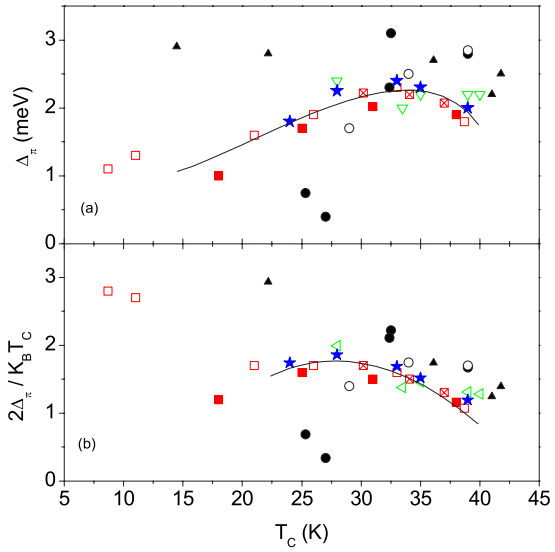

FIG. 3. (Color online) (a) $\Delta_\pi(0)$ and (b) $2\Delta_\pi(0)/K_BT_C$ as functions of T_C measured in this work (★) are compared with data already reported in the literature, evaluated by specific heat measurements in Ref. 23 (■), in Ref. 26 (□), and in Ref. 25 (⊠), by point contact spectroscopy in Ref. 24 (○), and in Refs. 29 and 30 (●), by STM in Ref. 28 (▽), and in Ref. 27 (▲). The same symbols have been used in both plots and the full lines are guides for the eyes.

However, it is worth to notice that the spectrum signed (I) for which we found $\Delta_\pi=2.3$ meV, was statistically most present while in different locations we have measured gap amplitudes as observed in curve (II) corresponding to $\Delta_\pi=2.0$ meV and in curve (III) with $\Delta_\pi=1.7$ meV, that we report here for the sake of completeness. It is our opinion that the energy gap variations in this sample, are due to different local Al concentrations arising during the crystal growth process. Indeed, as reported in the literature, this level of doping appears to be quite critical for inducing structural changes, segregation of a nonsuperconducting, Al-rich phase, and the formation of superstructures along the c axis.[30] We also notice that in Fig. 1(b) the most satisfactory agreement between theory and experiments was obtained for the spectra statistically more present, characterized by the largest value of the gap, $\Delta_\pi=2.3$ meV, corresponding to a 15% increase of the superconducting energy gap compared to the case of pure MgB_2.

By performing quite large statistics in different locations of the other substituted crystals, we have verified that the only relevant spread of the Δ_π values regards the sample of Fig. 1(b), while variations of less than 5% were registered in the other cases. We have found $\Delta_\pi=2.4$ meV ($\Gamma=0.27$) for the sample in Fig. 1(c), $\Delta_\pi=1.8$ meV ($\Gamma=0.2$) for the sample in Fig. 1(d), respectively. We notice that this last value results higher than the estimations previously reported for similar doping levels.[29]

For all samples, we have performed complete measurements of the temperature dependence of the tunneling spectra in the range between 5 K and 40 K. On the right-hand panels of Fig. 1(e)–1(h) the gap amplitudes as inferred from the theoretical fittings are plotted as a function of the temperature. In the case of pure MgB_2, Fig. 1(e), the BCS dependence (solid line) of the data (scattered symbols) indicates a local $T_C=39$ K, while for the highest level of doping ($x=0.2$), Fig. 1(h), $T_C=24$ K is inferred. The temperature dependence of the energy gap in samples close to the critical doping level, $x\simeq0.1$, again shows some criticality. Indeed, for the crystal reported in Fig. 1(f), gaps of different amplitudes seem to vanish at the same critical temperature $T_C\simeq35$ K (within the experimental error) indicating that the variation of the gap amplitude can be a surface effect due to the presence of thin metallic or dead layer and/or a result of a local structural inhomogeneity of the crystal not affecting the critical temperature. Moreover, we have found that for the sample in the Fig. 1(g), with $T_C\simeq33$ K, the gap amplitude shows a quite linear dependence in temperature, with reduced values respecting the BCS prediction.

TABLE I. Summary of the STM results.

T_C (K)	Δ_π (meV)	H_{c2} (T)	$2\Delta_\pi/K_BT_C$
39	2.0	2.2	1.19
35	2.3	≈3.0	1.52
33	2.4	≳3.0	1.69
28	2.2		1.86
24	1.8	1.8	1.74

We also performed a complete analysis of the local response to external magnetic fields up to 3 T, with the tunneling current and the applied field parallel to the c axis 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 reported spectra were averaged over many vortices passing under the tip,[36–38] the main effect of the magnetic field was, as expected, the progressive filling of states inside the energy gap.

In Fig. 2 we show a complete set of data recorded in the magnetic field for the same samples as in Fig. 1. In the first column we show the evolution of the normalized tunneling conductance spectra as measured at $T\simeq6.5$ 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. 2(a), 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 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 could be associated to the rotation of the vortex lattice in pure MgB_2,[39] 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 rearrangements.

In the case of the sample with $T_C=35$ K, Fig. 2(b), the data refer to locations with $\Delta_\pi=2.3$ meV. The field dynamics of the DOS at the Fermi level again show a rapid rising of

the ZBC for low magnetic fields. However, for increasing fields, the filling of states tends to saturate and, at 2.5 T, 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. Similarly, for the sample with $T_C = 33$ K, Fig. 2(c), from the evolution of the ZBC we infer a H_{c2} value higher than 3 T, while for the sample with $T_C = 24$ K, Fig. 2(d), the magnetic field behavior indicates a reduced value $H_{c2} \simeq 1.8$ T. We notice that, for all substituted samples, a clear separation of different dynamic regimes, as well as the hysteretic behavior, are not observed. Finally, in the third column of Fig. 2 we report the magnetic field effect on the energy gap Δ_π, accounting, as first approximation, for the field-induced pair breaking through the Γ term in the Dynes formula for the DOS. Although not rigorous, this approach can be useful for a first insight on the magnetic field effect on the evolution of the energy gap using only one fitting parameter. Indeed, by this oversimplified formula, we have obtained a satisfactory fitting of experimental data even at rather high fields, so, giving an indication about how fast the gap evolution is. We observe a severe 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. This observation suggests that around 0.5 T the contribution to the superconductivity due to the phonon mediated electron-electron interactions in the π band itself is not efficient anymore, while for higher fields the energy gap survives due to both the phonon exchange with the σ band[40] and/or to the quasiparticle interband scattering.

Finally, in Table I we summarize our results including the other measured sample with $T_C = 28$ K. In Fig. 3 a comparison with the literature is reported. The significant spread of the data initially reported by different groups is at the origin of the recent debate,[31–33] nevertheless a quite general trend (full lines) for both the 3D energy gap $\Delta_\pi(0)$ and the $2\Delta_\pi(0)/K_B T_C$ ratio as a function of T_C are inferred regardless to the nature of the measured samples: doped/irradiated/disordered—single crystals/polycrystals/thin films. Indeed, the extended two-band model predicts an increase of the Δ_π amplitude due to an increasing of the interband scattering.[19,41,42] Our STS data, obtained by means of a local probe on high quality single crystals, appear as a strong confirmation of this hypothesis with a maximum $\Delta_\pi(0)$ value measured in samples with $T_C \simeq 33$ K.

In conclusion, we have performed a systematic study of the local temperature and magnetic field dependence of the 3D energy gap Δ_π in $Mg_{1-x}Al_xB_2$ single crystals by means of scanning tunneling spectroscopy. We have succeeded in selectively measuring the behavior of the only Δ_π energy gap, and due to the high spatial resolution of the STS technique, we have been able to relate the local values of T_C, Δ_π, and H_{c2}. We have found a reduction of T_C for increasing doping with a nonmonotonous dependence of the amplitude of the energy gap and of the BCS ratio with T_C. In agreement with recent theoretical models, we have measured the largest gap value ($\Delta_\pi = 2.4$ meV, 20% larger than in pure MgB_2) in samples with $T_C = 33$ K.

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