Point-contact spectroscopy of Al- and C-doped MgB2: Superconducting energy gaps and scattering studies

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The two-band and/or two-gap superconductivity in aluminum- and carbon-doped $MgB₂$ has been addressed by the point-contact spectroscopy. Two gaps are preserved in all samples with $T_c^t s$ down to 22 K. The evolution of two gaps as a function of the critical temperature in the doped systems suggests the dominance of the band-filling effects, but for the increased Al doping, the enhanced *interband* scattering must also be considered. The extraction of the zero-energy density of states for the π and σ bands using a simple physical model demonstrates that significant changes in the relative weighting of the *intraband* scattering are created in the case of the C doping with the scattering in the π band enhanced faster than in the σ one. The Al doping does not change the relative weight of the scatterings within the bands.

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I. INTRODUCTION

Magnesium diboride owes its high critical temperature of 40 K (Ref. [1](#page-5-0)) to the interplay between two distinct electronic bands crossing a Fermi level. About half of quasiparticles belong to a quasi-two-dimensional hole σ band, and Cooper pairs there are strongly coupled via the boron vibrational mode E_{2g} . The rest of the quasiparticles reside in the threedimensional π band with a rather moderate electron-phonon interaction. Without the effect from the σ band, the transition temperature T_c would be considerably smaller than the one found in real MgB_2 ^{[2,](#page-5-1)[3](#page-5-2)} The two-band superconductivity is the most spectacularly revealed by the presence of two very distinguished energy gaps, a large one in the σ band, Δ_{σ} , and a small one in the π band, Δ_{π} , respectively.^{4[–8](#page-5-4)} Superconducting properties of such system should be sensitive to scattering processes. Due to the coexistence of charge carriers from two almost completely separated bands, two intraband and one interband scattering channels have to be distinguished. It is the interband scattering which is supposed to have a particularly strong effect in a two-band superconductor. It blends the strongly and weakly coupled quasiparticles, merges two gaps, and consequently decreases T_c . In the case of MgB_2 , T_c can drop down to about 20 K (Ref. [3](#page-5-2)) due to this effect. Fortunately, a different symmetry of the bands ensures that the interband scattering remains small also in very dirty MgB_2 samples, which show about the same T_c as the purest material.⁹ A systematic decrease of T_c is achieved in substituted $MgB₂$ samples. The substitutions of carbon for boron and aluminum for magnesium are the only on-site substitutions by nonmagnetic elements known so far. The carbon and aluminum atoms in $MgB₂$ indeed take a role of scatterers, but they also dope the system with one extra electron which inevitably leads to the filling effect in the σ band with strongly coupled holes, decreasing their density of states (DOS). Recently, Kortus *et al.*^{[10](#page-5-6)} have introduced a model incorporating both mentioned effects taking place in a doped $MgB₂$, namely, the interband scattering and the band filling. The former effect leads to an increase of Δ_{π} and decrease of the Δ_{σ} , while the latter suppresses both Δ_{π} and Δ_{σ} . The model is general with no prediction on the strength of the band filling and the interband scattering effects in a particular doped material. The published experiments bring rather controversial picture as far as the strength of both effects and the development of two gaps in the Al- and C-doped $MgB₂$ are concerned[.11–](#page-6-0)[17](#page-6-1)

In contrast to the interband scattering, the increase of the scattering within the bands is not supposed to have any effect on the two gaps. The selective tuning of the intraband scattering can lead to an expressive variation of the values of the upper critical magnetic field $H_{c2}(0)$ and its anisotropy.^{18[,19](#page-6-3)} Indeed, upon the increased C doping, $H_{c2}(0)$ is enhanced significantly in both principal crystallographic directions parallel to the *ab* hexagonal boron layers and the *c*-axis direction). On the other hand, the Al substitution suppresses $H_{c2}(0)$ in the *ab*-plane direction and has almost no effect on H_{c2} along the *c* axis. This different behavior is apparently due to a different influence of C and Al dopings on intraband scatterings. The strong increase of $H_{c2}(0)$ with the C doping indicates a graduation of the dirty limit conditions. On the other hand, the Al-doped samples still seem to stay in the clean limit and the decreased H_{c2} is just a consequence of the lower T_c ^{[18](#page-6-2)} A weight of scatterings in the separated bands is still unclear.

In this paper, we present a systematic study and comparison of the scattering processes in the Al- and C-doped magnesium diboride samples. The effect of both dopings on the interband scattering is deduced from the evolution of the energy gaps as a function of T_c 's of the doped samples. The values of the two gaps Δ_{π} and Δ_{σ} have been obtained from point-contact (PC) spectroscopy measurements on numerous $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ samples with T_c 's from 39 down to 22 K. It is shown that the band-filling effect is prevailing over the interband scattering in the investigated doping range, particularly in the C-doped $MgB₂$ samples, while in the case of the Al doping, the interband scattering plays

more considerable role. The Effect of applied magnetic field on the PC spectra is used to study the scattering processes within the two bands. A relative weight of the intraband scattering is estimated from the fitting of the field dependence of the PC spectra to a simple empirical model. Significant changes in the relative weighting of the scattering are found in the case of C doping because of the increased scattering particularly in the π band. The Al doping does not change the relative weight of the scatterings within the bands, and the samples seem to stay in the clean limit.

II. EXPERIMENT

Polycrystalline samples $Mg_0A1_0B_2$ and $Mg_0A1_0B_2$ with T_c =30.5 and 23.5 K, respectively, have been prepared by a two-step synthesis at high temperatures.¹⁸ The carbon substituted samples $Mg(B_{(1-y)}C_y)_2$, with *y*=0.055, 0.065, and 0.1 and with corresponding transition temperatures $T_c = 33$, 28, and 22 K, were synthesized in the form of pellets following the procedure described in Ref. [18](#page-6-2) from magnesium lumps and B_4C powder. In the case of $y=0.021$ and 0.038, we have worked with the wire segments exhibiting T_c =37.5, and 36.2 K, respectively.²⁰ For the undoped MgB₂, two kinds of samples have been used: very clean $MgB₂$ wires (the residual resistivity of 0.5 $\mu\Omega$ cm) with T_c =39 K and the small upper critical magnetic fields $H_{c2\parallel c} \approx 3 \text{ T},^{20}$ compatible with the clean limit theoretical calculations, $2¹$ and the polycrystalline pellets prepared from boron and magnesium powder⁴ also with T_c =39 K but with a higher upper critical field $H_{c2||c} \approx 5$ T in a dirty limit.

The point-contact measurements have been performed in the way described previously.¹² The applied magnetic field was always oriented perpendicular to the sample surface and parallel with the tip having the point-contact area in the vortex state. The point-contact spectrum (the differential conductance as a function of applied voltage) has been theoretically described by the Blonder-Tinkham-Klapwijk (BTK) theory²² using as input parameters the energy gap Δ , the parameter ζ (measure for the strength of the interface barrier), and the parameter Γ for the spectral broadening.²³ In the case of two-gap superconductor, the voltage-dependent normalized point-contact conductance can be expressed as a weighted sum of two partial conductances $g_{\sigma(\pi)}$, those from the quasi-two-dimensional σ band (with a large gap Δ_{σ}) and those from the three-dimensional π band (with a small gap Δ_{π}), as follows:

$$
G/G_n(V) = \alpha g_\pi + (1 - \alpha) g_\sigma. \tag{1}
$$

The weight factor α for the π -band contribution can vary from 0.6 for the point-contact current strictly in the MgB_2 *ab* plane to 0.99 in the *c*-axis direction.²⁴ The two-band BTK model does not include the effect of interband scattering and is thus limited to a weak scattering between the bands. Recently, Dolgov *et al.*[25](#page-6-10) have shown that an increased interband scattering mixing the pairs in the two bands (the states appear in the σ band at the energy range of the π -band gap) will broaden the resulting total density of states. In this case also, the point-contact spectrum will get broadened. Nevertheless, fitting to the simple two-band BTK model can still

FIG. 1. Influence of the applied magnetic field on the representative point-contact spectra of Mg1−*x*Al*x*B2 samples measured at indicated temperatures (solid lines). Open circles show the fitting curves for the two-gap BTK model in zero and finite magnetic fields.

provide a good estimate of the size of the gaps if they are resolved in the measured spectrum.

III. RESULTS AND DISCUSSION

A large number of the point-contact measurements have been performed on the investigated samples of pure MgB_2 and both substituted series. Since the C doping leads the $MgB₂$ samples deeply into the dirty limit (with an increase of H_{c2} despite a decreased T_c), we have chosen the undoped $MgB₂$ sample being already in a dirty limit for a comparison with the C-doped samples in the discussion about the effect of magnetic field. On the other hand, the Al doping seems to keep the clean limit conditions. Thus, we have chosen the pure $MgB₂$ wire as a reference in the studies of the magneticfield effects. By trial and error, we looked for the spectra showing both gaps in polycrystalline specimens. For more detailed studies, we chose the junctions revealing the spectra with a low spectral broadening Γ , i.e., with an intensive signal in the normalized PC conductance. As a result, we succeeded in obtaining many point-contact spectra with well resolved two superconducting gaps directly visible in the raw data for all of the studied substitutions except for the highest dopings, namely, $Mg_{0.8}Al_{0.2}B_2$ and $Mg(B_{0.9}C_{0.1})_2$. As shown in the following, the application of magnetic field can help resolve the two gaps directly also in these cases. Figure [1](#page-1-0) displays the representative spectra of the Al-doped series. The upper curves in the panels are the spectra in zero magnetic field, and the others display an effect of the field. Figure [2](#page-2-0) shows in the same way the results for the C-doped

FIG. 2. Influence of the applied magnetic field on the representative point-contact spectra of $Mg(B_{(1-y)}C_y)_2$ samples measured at indicated temperatures (solid lines). Open circles show the fitting curves for the two-gap BTK model in zero and finite magnetic fields.

 $MgB₂$. The experimental data are presented by the full lines, while the fits to the two-gap formula are indicated by the open circles. The fitting formula for the spectra in magnetic field is explained below. All shown PC spectra have been normalized to the spectra measured in the normal state at a temperature above T_c .

The retention of two gaps for all dopings apart from the highest substitution is evident already at zero magnetic field. For the highest dopings (always with a larger spectral broadening, $\Gamma \approx 0.2\Delta$), the spectra reveal only one pair of peaks without an apparent shoulder at the expected position of the second gap. The size of the apparent gap is well indicated by the peak position, which is about 2 meV for $Mg_0.8Al_0.2B_2$ and 1.6 meV for $Mg(B_{0.9}C_{0.1})_2$. However, this size is too small to explain the superconductivity with the respective T_c 's equal to 23.5 and 22 K within the single-gap BCS scenario. The presented data document a strong effect of magnetic field on the π -band contribution to the spectrum. The zero-field spectrum of the clean undoped $MgB₂$ measured on the wire sample (bottom panel in Fig. [1](#page-1-0)) reveals a clear twogap structure. At small fields, the peak corresponding to the small gap Δ_{π} is very rapidly suppressed and only the peak related to the large gap Δ_{σ} is apparently visible above 1 T. At 10% of Al doping, the zero-field spectra also show both gaps, but the large one is now revealed more as a pronounced shoulder. Again at a small magnetic field, the π -band-gap peak is rapidly suppressed but its signature is still distinguishable at 0.5 T. At higher fields, the signatures of both gaps are not resolvable due to an interference of the related peaks placed at closed positions. The resulting maximum is located in the intermediate position between them. At the

FIG. 3. Distribution of the superconducting energy gaps of $Mg(B_{(1-y)}C_y)_2$ (gray columns) and $Mg_{1-x}Al_xB_2$ (open columns). The dashed and dotted lines are guides for the eyes.

highest doping (20% Al), such an interference of even closer gaps is graduated; so, already at zero magnetic field one can see only one pair of peaks at the position of the small gap (it always has much higher weight at zero field) and a minor shoulder at the voltage of the large one. In the increasing field, the peak position, which is about 2 mV in zero field, is shifted toward 3 mV at 1 T. In the case of a single-gap superconductor, the application of magnetic field can only lead to a shrinkage of the distance between the peak positions in the PC spectrum. This is a simple consequence of the introduction of the vortices and magnetic pair breaking.²⁶ The shift of the peak of the PC spectra to higher voltages is then due to an interplay between the two gaps. The dominance of the Δ_{π} peak at zero field is suppressed in increasing magnetic field and Δ_{σ} contributes more.

In Fig. [2,](#page-2-0) the existence of both gaps is evidenced in a similar way for the 6.5% and 10% carbon dopings. For example, in the upper panel, the spectrum at μ_0H =0.5 T shows that the π -band-gap peak at 1.6 mV is already partially suppressed and the large-gap shoulder clearly appears near 3 mV. We remark that for the 10% C-doped MgB₂, the existence of the large gap has also been shown in our previous paper by PC spectroscopy¹² and also by the specific-heat measurements on the samples from the same batch as used here.²⁷

The overall statistics of the energy gaps obtained from fitting of the zero-field PC spectra to the two-band BTK formula is shown in Fig. [3](#page-2-1) for each C and Al concentration. The left coordinate indicates the transition temperature of the junctions, while the right one counts the number of junctions with the same size of the gaps. The energy width of a particular count indicates the fitting uncertainty. All the samples, the undoped MgB_2 as well as the Al- and C-doped materials,

FIG. 4. Averaged values of the superconducting energy gaps as a function of the critical temperatures of $Mg(B_{(1-y)}C_y)_2$ (solid circles) and $Mg_{1-x}Al_xB_2$ samples (open squares). The error bars represent the standard deviations in the distribution shown in Fig. [3.](#page-2-1) For the lines, see text.

reveal a certain distribution of the small and large gaps, but the two gaps are well distinguishable in the histogram and no overlap of Δ_{σ} and Δ_{π} is observed. Already from this figure, a general tendency is evident, namely, that the reduction of the large gap is proportional to the decreasing transition temperature. On the other hand, the changes in the small gap are proportionally smaller.

Figure [4](#page-3-0) summarizes the energy gaps as a function of T_c 's. The points (open squares for Al dopings and solid circles for C ones) are positioned at the averaged energies of the gap distributions in Fig. [3,](#page-2-1) and the error bars represent the standard deviations. The large gap Δ_{σ} is essentially decreased linearly with the corresponding T_c 's. The behavior of Δ_{π} 's is more complicated. For both kinds of substitution, the gap is almost unchanged at smaller dopings. In the case of C-doped MgB₂, it clearly holds down to $T_c = 33$ K. In the case of $(Mg, Al)B_2$, Δ_{π} of the 10% Al-doped sample seems to even slightly increase, but for the highest dopings, Δ_{π} decreases in both doping cases. The solid lines in Fig. [4](#page-3-0) are calculations of Kortus *et al.*[10](#page-5-6) for the case of a pure bandfilling effect and no interband scattering. Although the constant Δ_{π} is not reproduced, the T_c dependence of Δ 's for carbon doping can be broadly described indicating smaller interband scattering. The dashed lines show the calculations of Kortus *et al.* including the interband scattering with the rate $\gamma_{IB} = 1000x$ cm⁻¹ (or 2000y cm⁻¹). As can be seen, the evolution of the gaps in the Al-doped samples cannot be accounted for without an interband scattering, although its rate is certainly smaller than in the presented calculations. A proper weighting of both effects will naturally explain the constant value of the π -band gap and the expected position of gaps merging in both doping cases.

Recently, similar results on the superconducting energy gaps have been obtained with the Al-doped single crystals by Klein *et al.*[28](#page-6-13) exploring the specific heat as well as the PC spectroscopy measurements. Those data also show a tendency of approaching of the two gaps with their possible merging in the Al-doped samples with T_c below 10–15 K. It is worth noticing that our previous results²⁸ and those presented here show neither a decrease of the large gap below the canonical BCS value¹⁶ nor a drop of Δ_{π} below 1 meV (Ref. [17](#page-6-1)) for the Al-doped MgB_2 with T_c 's below 30 K found earlier.

In contrast with the data obtained on C-doped single crystals by Gonnelli *et al.*, [15](#page-6-15) we have not found any stronger tendency to blend both gaps down to $T_c = 22$ K. On the other hand, our data are very compatible with the recent ARPES measurements of Tsuda *et al.*, [14](#page-6-16) where both gaps have been directly seen in the raw data down to T_c of 23 K. A presence of the two gaps is also evidenced by the PC measurements of Schmidt *et al.*^{[13](#page-5-7)} on the heavily carbon-doped MgB₂. We remark that the data showing no merging of the gaps on the heavily doped MgB_2 with T_c 's down to 22 K have been collected from the measurements on the samples of different forms (wires, sintered pellets, and polycrystals) prepared by different methods. It is also important that the two gaps have been directly experimentally evidenced in the raw data without any dependence on the model or fit.

Theoretical calculations of Erwin and Mazin²⁹ on merging of the gaps due to a substitution support the picture presented here. According to this work, the carbon substitution on the boron site should have zero effect on the merging of the gaps. This is due to the fact that replacing boron by carbon does not change the local point symmetry in the π and σ orbitals which are both centered at the boron sites. Consequently, the interband scattering will only increase if extra defects are incorporated as a result of doping that produces a change of the symmetry of the orbitals. On the other hand, much bigger effect is expected for the out-of-plane substitutions (Al instead of Mg) or defects which would indeed change the local point symmetry. The substitution of Al instead of Mg leads also to a significant decrease of the c -lattice parameter¹⁶ (it is basically useless in the case of carbon doping), which helps the interlayer hopping from a p_z orbital (π band) in one atomic layer to a σ bond orbital in the next one. Of course, a particular strength of the interband scattering can vary among samples due to a lack of control over defect type and their density. Thus, the merging of the two gaps can indeed be strongly sample dependent.

In the following paragraph, we will focus on more quantitative analysis of the magnetic-field effect on the pointcontact spectra of the Al- and C-doped $MgB₂$, which can yield information on the intraband scattering processes in the samples. In both sets of the Al- and C-doped samples shown in Figs. [1](#page-1-0) and [2](#page-2-0) strong effect of an applied magnetic field on the π -band-gap peak has been observed. It is a consequence of a rapid filling of the π -band-gap states up to a crossover π -band "upper critical field" $H_{c2,\pi}$. At higher fields, the superconducting properties are determined mainly by the σ band, and the real upper critical field can be identified with $H_{c2} = H_{c2,\sigma}$ ^{[30](#page-6-18)} If the samples are in the clean superconducting limit, a magnitude of the upper critical fields of the two bands can be estimated³¹ as $H_{c2,\pi} \approx \Delta_{\pi}^2/v_{F,\pi}^2$ and $H_{c2,\sigma} \approx \Delta_{\sigma}^2/v_{F,\sigma}^2$, with $v_{F,\pi}$ or $v_{F,\sigma}$ the Fermi velocity of the respective band (since here only $H_{c2\parallel c}$ is considered, the anisotropy due to an effective mass tensor is neglected). A similar estimate can be done in the dirty limit by taking into account the

respective diffusion coefficients $D_{\pi(\sigma)}$. Then, $H_{c2,\pi(\sigma)}$ is proportional to $\Delta_{\pi(\sigma)}/D_{\pi(\sigma)}$. Koshelev and Golubov have shown in their model 32 that in a two-band superconductor in the dirty limit, the gap filling in the presence of magnetic field is a function of the intraband diffusivities. They have calculated maximum pair potentials Δ_{max} and averaged zero-energy densities of states $N_{\pi(\sigma)}$ in both bands as a function of magnetic field normalized to the upper critical one $H_{c2\parallel c}$ and found that the field slope of $N_{\pi}(0, H)$ is very sensitive to the ratio of the diffusion coefficients D_{σ}/D_{π} .

Recently, Bugoslavsky *et al.* proposed an empirical model which enables to infer the zero-energy averaged density of states as a function of magnetic field from the PC conductance data measured in the mixed state. 33 In this model, vortex cores represent a normal-state region *n*, where $n = N^A/A$ is a factor characterizing the normal-state region N^A of the PC junction area *A*. This normal-state region and/or vortex density increases linearly up to the upper critical magnetic field. In order to take into account the normal cores of vortices, the point-contact conductance will be a sum $G/G_N(V) = n + (1-n)g$, where *n* represents the normal-state channel and $(1-n)g$ the superconducting channel contribution normalized to the normal-state PC conductance $G_N(V)$. In the case of a two-gap superconductor, the normalized PC conductance will be represented as a weighted sum of both band contributions as follows:

$$
G/G_n(V) \approx \alpha [n_\pi + (1 - n_\pi)g_\pi] + (1 - \alpha)[n_\sigma + (1 - n_\sigma)g_\sigma].
$$
\n(2)

Considering that n_{π} and n_{σ} represent the number of normalstate vortex-core excitations, these parameters can be identified with the zero-energy density of states $N_{\pi}(0, H)$ and $N_{\sigma}(0, H)$ averaged over the vortex lattice.³⁴ In this way, the field dependent energy gaps and zero-energy DOS $N(0, H)$ can be determined.

Unfortunately, the fitting of the PC conductance of $MgB₂$ in the mixed state is not trivial because of the number of variables as many as 9. Moreover, two pairs of the parameters N_{π} vs Γ_{π} and N_{σ} vs Γ_{σ} manifest themselves very similarly in the fit. Hence, before fitting the spectra the formula ([2](#page-4-0)), we estimate $N_{\pi}(0, H)$ values from the excess currents *Iexc*, calculated from the PC spectra integrating the superconducting area. Here, the following simplifications are made. For the case of a two-gap superconductor, I_{exc} is represented similarly, like in formula ([2](#page-4-0)), as a weighted sum of the both band contributions,³⁵ $I_{exc} \approx \alpha(1-n_{\pi})\Delta_{\pi} + (1-\alpha)(1-n_{\sigma})\Delta_{\sigma}$. If the real upper critical field H_{c2} is large compared to $H_{c2,\pi}$, in the region $0 \leq H \leq H_{c2,\pi}$, the suppression of the σ -band contribution by the field can be neglected $[N_{\sigma}(0, H)=0]$. If we also neglect a small reduction of the energy gaps at these fields,^{33[,36](#page-6-23)} then $I_{exc}(H)$ can be represented by a single parameter formula expressed as $I_{exc} \propto \alpha [1 - N_{\pi}(0, H)] \Delta_{\pi}(0) + (1$ $-\alpha)\Delta_{\sigma}(0)$, since all other parameters $[\Delta_{\pi}(0), \Delta_{\sigma}(0),$ and $\alpha]$ have already been determined from the BTK fit at *H*=0. The resulting $N_{\pi}(0, H)$ is later used as a first approximation in the fit of the PC conductance spectrum. There, also the values of z_{π} , z_{σ} , Γ_{π} , and Γ_{σ} determined from BTK fits at *H*=0 are kept

unchanged. In the second step, all parameters except for z_{π} , z_{σ} , and α are adjusted for the best fit. The fitting curves are shown in Figs. [1](#page-1-0) and [2](#page-2-0) by open circles. The resulting values of $N_{\pi}(0, H)$ are decreased by 5%–20% in comparison with the first estimate from $I_{\text{exc}}(H)$.^{[37](#page-6-24)} Also, the values of the smearing parameters Γ_{π} and Γ_{σ} reveal about 10%–20% of increase in the interval $0 < H < 1$ T accounting for the magnetic pair breaking of the superconducting DOS. In the same field interval, a small ($\approx 5\% - 10\%$) suppression of the values of the energy gaps has been obtained.

The zero-energy DOS $N_{\pi}(0, H)$ has been calculated for several point contacts on every particular doped sample. In none of the cases a linear increase of $N_{\pi}(0, H)$ has been observed. On the contrary, a strong nonlinearity observed in all curves points to two gaps in the quasiparticle spectrum of the material. We ascribe a rapid increase of $N_{\pi}(0, H)$ at low magnetic fields to a strong filling of the π -band-gap states up to the π -band crossover upper critical field $H_{c2,\pi}$. Then, at higher fields, the low-temperature superconductivity is maintained mainly by the σ band,³⁰ with the σ gap getting filled smoothly up to the real upper critical field of the material $H_{c2} = H_{c2,\sigma}$. Due to a small but finite coupling of the two bands, the superconductivity is maintained also in the π band above $H_{c2,\pi}$, but as shown in the tunneling data of Eskildsen *et al.*,^{[38](#page-6-25)} the π -gap states are filled much more slowly here than in the low-field region. Due to the measurements on the polycrystalline specimens, an orientation of applied magnetic field with respect to the particular crystallite under the point contact is not controlled, but independent of the random-field orientation, the resulting $N_{\pi}(0, H)$ dependencies for a particular aluminum- or carbon-doped sample are practically identical in the range of smaller fields up to $1-1.5$ T. This fact underlines an isotropic character of the π band in our samples. Moreover, no change was observed in the field dependencies of $N_{\pi}(0, H)$ measured on the samples with different Al concentrations. It suggests the unchanged upper critical field of the π -band $H_{c2,\pi}$ here. Then, the doping independent $H_{c2,\pi} \approx \Delta_{\pi}^2/v_{F,\pi}^2$ (the clean limit) and almost constant Δ_{π} for $x=0-0.2$ indicate that $v_{F,\pi}$ remains also unchanged at this doping range. In the aluminum-doped $MgB₂$, also the real upper critical field $H_{c2|c}$ remains unchanged and is equal approximately to 3 T for all three dopings.¹⁸ From this follows the constant ratio between Δ_{σ} and $v_{F,\sigma}$, so the electron filling of the hole σ band decreases both parameters proportionally. In Fig. $5(a)$ $5(a)$, the zero-energy DOSs $N_{\pi}(0, H)$ are shown as a function of applied field normalized to $H_{c2\parallel c}$.

The situation is different for the carbon-doped samples. There, the slope of the zero-energy DOS $N_{\pi}(0, H)$ decreases significantly with increased carbon doping, indicating an increase of the π -band upper critical field at higher carbon concentrations. From the transport and magnetization measurements on the samples from the same batch, it is known that the upper critical fields for both principal crystallographic orientations are significantly enhanced³⁹ with respect to pure $MgB₂$, i.e., the samples are driven deeper to the dirty limit by carbon doping. Then, the change of the slope of $N_{\pi}(0, H)$ can be just a simple consequence of the enhanced H_{c2} , but when the isotropic $N_{\pi}(0, H)$ dependencies are displayed as a function of the applied field *H* divided by the

FIG. 5. (a) Zero-energy DOS $N_{\pi}(0,h)$ of $Mg_{1-x}Al_xB_2$ determined from the fitting to the two-band mixed-state BTK formula. The applied field has been rescaled to the value of $H_{c2||c} \approx 3$ T (Ref. [18](#page-6-2)). (b) $N_{\pi}(0, h)$ of Mg(B_(1-y)C_y)₂. The applied field has been rescaled to $H_{c2\parallel c} \approx 5$, 8, and 8 T. (Refs. [4](#page-5-3) and [39](#page-6-26)) The dashed and dotted lines represent the theoretical predictions of $N_{\pi}(0,h)$ (Ref. 32) for the dirty MgB₂ samples with the ratios of in-plane diffusivities D_{σ}/D_{π} =0.2 and 1, respectively. The solid lines are guides for the eyes.

respective $H_{c2\parallel c}$ (in Fig. [5](#page-5-8) denoted as *h*), it can be seen that the π -band crossover upper critical field $H_{c2,\pi}$ is enhanced stronger than $H_{c2\parallel c,\sigma}$. In the previous paragraphs, we have shown that the ratio between the σ and π gaps is approximately constant at different carbon concentrations. Then, the change of the position of $H_{c2,\pi}$ with respect to $H_{c2|c}$ will be given by an increase of the ratio of the diffusion coefficients D_{σ}/D_{π} . Figure [5](#page-5-8)(b) shows by the dashed line the calcula-

tions of the model of Koshelev and Golubov³² for D_{σ}/D_{π} =0.2, corresponding well with the data from the undoped dirty MgB_2 . It means that the σ band in this case is dirtier than the π band. The subsequent decrease of the low-field slope of $N_{\pi}(0,h)$ upon the C doping can be explained by an increase of the D_{σ}/D_{π} ratio, i.e., by a more rapid enhancement of the π -band intraband scattering as compared with the scattering in the σ band. Indeed, the dotted line plotting the theoretical $N_{\pi}(0, h)$ dependence at $D_{\sigma}/D_{\pi} = 1$ indicates this tendency.

IV. CONCLUSIONS

The comparative study between the Al- and C-doped $MgB₂$ on the inter- and intraband scatterings has been performed by means of the point-contact spectroscopy in magnetic field. It has been shown that the decreased transition temperatures and the evolution of two superconducting energy gaps upon both substitutions are mainly consequence of the band-filling effect. However, especially in the case of Al doping, also an increase of the interband scattering has to be taken into account to explain the behavior of both gaps as a function of T_c . By the analysis of the field effect on the point-contact spectra, it has been shown that the C doping increases the scattering in the π band more rapidly than in the σ band. On the other hand, the Al doping does not introduce significant scatterings within the two bands and the samples remain in the clean limit.

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