Observation of the Crossover from Two-Gap to Single-Gap Superconductivity through Specific Heat Measurements in Neutron-Irradiated MgB_2

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We report specific heat measurements on neutron-irradiated MgB_2 samples, for which the critical temperature is lowered to 8.7 K, but the superconducting transition remains extremely sharp, indicative of a defect structure extremely homogeneous. Our results evidence the presence of two superconducting gaps in the temperature range above 21 K, while single-gap superconductivity is well established as a bulk property, not associated with local disorder fluctuations, when T_c decreases to 11 K.

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The two-gap nature of superconductivity is a unique feature of MgB_2 that stimulates many theoretical and experimental investigations. From the beginning this peculiar feature was emphasized by different experimental investigations [1–3]. *Ab initio* calculations [4,5] showed that MgB_2 has two weakly coupled gaps, $\Delta_\sigma(0) \approx 7$ meV and $\Delta_\pi(0) \approx 2$ meV, residing on disconnected sheets of the Fermi surface formed by in-plane p_{xy} boron orbitals (the σ bands) and out-of-plane p_z boron orbitals (the π bands). The two-gap Eliashberg theory accounts for many anomalies in superconducting and normal properties of pure MgB_2, but some aspects still need to be clarified. Golubov and Mazin [6] pointed out that the two-gap superconductivity must be strongly affected by disorder. In particular, interband scattering by nonmagnetic impurities is expected to induce pair breaking, which suppresses the critical temperature T_c down to 20 K, where an equivalent one-gap BCS system with isotropic coupling stabilizes. The pair breaking mechanism is expected to induce the increase of the small gap and the decrease of the large one, so that these have to merge to the BCS value once a complete isotropization has taken place. While the suppression of superconductivity may be driven by different effects, for instance, the filling of electronic σ bands [7], the merging of the two gaps is a peculiar result of the interband scattering. So, a direct observation of the crossover from two- to single-gap superconductivity will provide the final direct evidence for the two-band model [8].

Several efforts have been made to evaluate the energy gaps in samples where the defects were introduced by substitution (Al in sites of Mg [9–12], C in sites of B [13–18]), by neutron irradiation [19], and in disordered thin films [20]. Despite the variety of procedures used to induce disorder and the different experimental techniques employed to estimate the gaps (tunneling, point contact spectroscopy, specific heat, photoemission spectroscopy), it turns out that the two gaps, Δ_π and Δ_σ, scale in a quite general way with the critical temperature of the sample. The gap associated with the π band is only weakly sensitive to the critical temperature, while Δ_σ decreases almost linearly, so that the two gaps tend to join at low temperature. This behavior is rather well established for T_c values ranging from 39 to 25 K, while, when T_c approaches 20 K, the results are less clear. In Al-doped samples there is no evidence of single-gap superconductivity [9–12]. In C-doped samples several experiments [13–17] suggest that the extrapolated energy gaps do not merge, except for a C-doped single crystal with $T_c = 19$ K for which single-gap superconductivity was claimed [18]. Gap values of undoped MgB_2 with T_c values below 20 K are not available. The lack of unambiguous evidences of the merging of the gaps is disappointing, but some explanations can be considered. In Al- and C-doped samples the suppression of T_c is due to at least two concomitant mechanisms, i.e., σ band filling and interband scattering; when T_c is decreased to 20 K, the interband scattering might be not strong enough to induce the merging of the gaps [7]. Moreover, heavily doped compounds become structurally unstable and present inhomogeneous properties, inadequate to check such a critical point. To overcome these problems, we studied samples in which disorder has been introduced by neutron irradiation, which does not induce remarkable changes in the band structure.

In this Letter we report experimental evidences for the crossover from two- to single-gap superconductivity in neutron-irradiated MgB_2 samples in which the critical temperature was suppressed down to 8.7 K. The irradiation procedure we used produces samples with defect structure extremely homogeneous so that the superconduncting transition remains extremely sharp even in the heavily irradiated samples. Our results demonstrate that the two-gap feature is evident in the temperature range above 21 K, while the single-gap superconductivity is well established as a bulk property, not associated with local disorder fluctuations, when T_c is lowered to 11 and 8.7 K.

Polycrystalline MgB_2 samples, prepared by direct synthesis from Mg and isotopically enriched ^{11}B, were irradiated at the spallation neutron source SINQ (thermal

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TABLE I. Thermal neutron fluence, Φ, resistivity value at 40 K, $\rho(40)$, the critical temperature, T_c, and width of superconducting transition, ΔT_c, of measured samples. T_c was determined by susceptibility measurements, and ΔT_c was estimated as the difference between T_c estimated at 10% and 90% of the transition.

Samples	Φ (cm^{-2})	$\rho(40)$ ($\mu\Omega$ cm)	T_c (ΔT_c) (K)
P0	0	1.6	38.8 (0.3)
P3.5	2.0×10^{18}	26	32.6 (0.5)
P3.7	5.5×10^{18}	41	25.8 (0.6)
P4	1.0×10^{19}	64	20.7 (0.9)
P5	3.9×10^{19}	124	11.0 (0.4)
P6	1.4×10^{20}	130	8.7 (0.5)

neutron flux density up to 1.6×10^{13} cm^{-2} s^{-1}) at the Paul Scherrer Institut. The thermal neutron fluence was varied from 10^{17} to 1.4×10^{20} cm^{-2}; the largest fluence corresponds with four months of irradiation. We demonstrated [21] that the most important damage mechanism in our samples consists in neutron capture reactions by the residual ^{10}B present (less than 0.5%). Because of the large cross section of this reaction, the neutron penetration in bulk samples rich in ^{10}B is partially shielded (natural boron consists of 80% of ^{11}B and 20% of ^{10}B). Thus, to avoid self-shielding effects, we irradiated $Mg^{11}B_2$ samples for which the penetration depth of thermal neutrons is much deeper than the sample thickness, so that nuclear reactions take place homogeneously inside the sample. The defects in the form of atom displacements are created by the nuclear reaction products, ^4He and ^7Li, emitted in isotropic directions. This makes the defect distribution very homogeneous.

Resistivity value at 40 K, $\rho(40)$, T_c, and superconducting transition width, ΔT_c, of samples are reported in Table I. As the fluence increases, $\rho(40)$ increases by 2 orders of magnitude, and T_c decreases to 8.7 K. On the other hand, ΔT_c remains very narrow in all the irradiated samples.

Figure 1 shows the critical temperature as a function of $\rho(40)$. T_c decreases linearly with $\rho(40)$ in the whole range, in agreement with that observed in ^4He irradiated MgB_2 thin films [22]. It is clear that our data, as well as those of Ref. [22], do not show any T_c saturation. This suggests that pair breaking due to interband scattering is not the only mechanism which suppresses superconductivity in irradiated MgB_2 samples. On the other hand, the roughly linear scaling of T_c with $\rho(40)$ indicates that a strong correlation exists between the mechanism increasing $\rho(40)$ (scattering with atomic scale defects) and that suppressing superconductivity. This behavior is common to other superconductors. In amorphous transition metals and damaged A15 superconductors, for instance, a smearing of the peak in the electron density of states (DOS) at the Fermi level was suggested [23]; yet this mechanism does not simply apply to MgB_2, whose density of states is rather flat around the Fermi level, so other mechanisms that suppress the electron-phonon coupling should be invoked.

The energy gaps have been estimated by analyzing specific heat c data. Such measurements probe the bulk properties of materials and are not affected by local fluctuations of disorder.

Specific heat measurements were performed on the six samples listed in Table II by a Quantum Design PPMS-7T, which makes use of the relaxation method. For each sample we performed a set of measurements between 2 and 40 K and in magnetic field of 0 and 7 T. Addenda with the exact amount of Apiezon N grease used for thermal contact were carefully measured before each run.

The T_c values estimated from specific heat are reported in Table II; they are close to the values estimated from susceptibility (see Table I). In Fig. 2 we plot the zero field data as c/T vs T^2 for P0, P3.5, P3.7, and P6 samples. Note that the superconducting transition is remarkably sharp in all the irradiated samples. It is worth comparing the curves in Fig. 2 with the analogous ones obtained in Al-doped MgB_2 [9,12]. In Al-doped samples the superconducting transition becomes broader and broader as the doping increases, while for the irradiated samples the transitions remain sharp, whatever the level of disorder introduced.

In order to extract information on the superconducting energy gaps, the reduced electronic specific heat, $c_{sc}/\gamma T$, has been estimated (here γ is the Sommerfeld constant) by following the usual procedure described in Ref. [9]. Briefly, data obtained in magnetic field were fitted in order to evaluate the lattice and the normal state electronic contributions. The superconducting contribution is evaluated by subtracting the lattice contribution to zero field data. The entropy balance was checked after this step. The results for P0, P4, P5, and P6 are reported in Fig. 3 as a function of the reduced temperature $t = T/T_c$.

The superconducting specific heat is analyzed within the two-band α model [24]. Within this model the σ and π bands contribute to the specific heat proportionally to the γ_σ/γ and γ_π/γ fractions, respectively, γ_σ and γ_π being

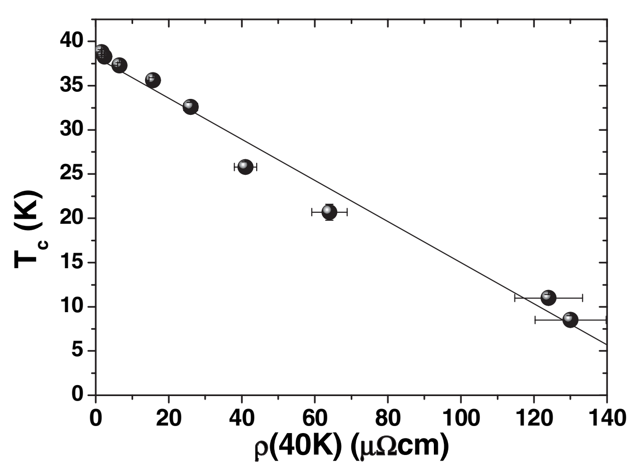

FIG. 1. T_c versus $\rho(40)$ for the samples listed in Table I and Ref. [21]. The continuous line is a guide for the eye.

TABLE II. T_c estimated as midpoint of the specific heat anomaly; ΔT_c estimated as the difference between the onset of c_{sc} and the temperature at which c_{sc} is maximum; the Sommerfeld coefficient γ, estimated by fitting the normal state experimental data measured at 7 T; the best fit parameters $2\alpha_\sigma = 2\Delta_\sigma(0)/k_BT_c$, $2\alpha_\pi = 2\Delta_\pi(0)/k_BT_c$, and $x = \gamma_\sigma/\gamma$, and the gap values $\Delta_\sigma(0)$ and $\Delta_\pi(0)$ evaluated for P0, P3.5, P3.7, P4; the best fit parameter $2\alpha = 2\Delta(0)/k_BT_c$ and the gap value $\Delta(0)$ evaluated for P5, P6.

Samples	T_c (K)	ΔT_c (K)	γ (mJ/mol K^2)	γ_σ/γ	$2\Delta_\sigma(0)/k_BT_c$	$2\Delta_\pi(0)/k_BT_c$	$\Delta_\sigma(0)$ (meV)	$\Delta_\pi(0)$ (meV)
P0	38.7	1.5	3.0 ± 0.1	0.54 ± 0.05	3.8 ± 0.1	1.07 ± 0.06	6.3 ± 0.4	1.8 ± 0.2
P3.5	33.0	1.6	3.0 ± 0.1	0.47 ± 0.03	3.7 ± 0.5	1.6 ± 0.2	5.3 ± 0.3	2.3 ± 0.2
P3.7	26.0	1.8	3.0 ± 0.1	0.56 ± 0.05	3.5 ± 0.3	1.70 ± 0.1	3.9 ± 0.5	1.9 ± 0.3
P4	21.0	2.3	2.4 ± 0.2	0.58 ± 0.8	3.5 ± 0.2	1.7 ± 0.1	3.1 ± 0.5	1.6 ± 0.3
P5	11.0	1	2.5 ± 0.2		2.7 ± 0.1		1.3 ± 0.2	
P6	8.7	0.8	2.4 ± 0.2		2.8 ± 0.1		1.1 ± 0.1	

the Sommerfeld coefficient of the σ and π bands; a BCS temperature dependence of the superconducting gaps is assumed, and the amplitude of the reduced gaps at $T = 0$, $\alpha_\sigma = \Delta_\sigma(0)/k_BT_c$, $\alpha_\pi = \Delta_\pi(0)/k_BT_c$, are introduced as adjustable parameters. In clean MgB_2 the evidence of the π gap comes from the excess of $c_{sc}/\gamma T$ at $t \sim 0.2$, which cannot be accounted for by the σ band contribution alone that, in this t range, falls down exponentially. Such excess is well evident in the pristine sample (P0) and progressively disappears in irradiated samples. Recently, Dolgov *et al.* [25] showed that, in spite of the strong modifications of the density of states by interband scattering, the α model is sufficiently accurate to extract gap values from the specific heat of disordered samples. Therefore, we systematically performed two fitting procedures: within a two-gap framework, three free parameters, α_σ, α_π, and $x = \gamma_\sigma/\gamma$, were introduced while within a single-gap framework, only one free parameter, $\alpha = \Delta(0)/k_BT_c$, was used. For P0, P3.5, P3.7, and P4, the experimental data can be reproduced only by considering two gaps, while the curves of P5 and P6 can be fitted with the same accuracy (nearly equal values of χ^2 despite the larger number of free parameters in the two-gap case) by using single-gap and two-gap analyses. This is shown in Fig. 3 where we report $c_{sc}/\gamma T$ vs t for P0, P4, P5, and P6 and the best fitting curves as continuous lines. For the sake of clarity, only for P4 and P5 are the single- and the two-gap best fit curves plotted. For sample P4, it is clear that the single-gap curve cannot reproduce the feature of the experimental data, and we conclude that for this sample the merging of the gaps has not occurred yet. For P5 the single- and two-gap best fit curves perfectly overlap. In fact, the two-gap curve comes out to be the sum of nearly equal σ and π contributions; the so-obtained $\Delta_\sigma(0)$ and $\Delta_\pi(0)$ are very close and coincide, within the errors, with $\Delta(0)$ obtained by the single-gap analysis. The same occurs for P6. For these samples there is no evidence of two separated gaps, and we conclude that the merging of the gap has occurred.

The best fit parameters for all the samples are reported in Table II. In Fig. 4, $\Delta_\sigma(0)$, $\Delta_\pi(0)$, and $\Delta(0)$ are plotted as a function of T_c. We may easily distinguish two regions: for $T_c \geq 21$ K, the two-gap feature is observed, while for samples with $T_c < 20$ K, superconductivity is characterized by a single gap. In the two-gap region we find that $\Delta_\sigma(0)$ decreases almost linearly with T_c, while $\Delta_\pi(0)$ remains nearly constant. A close inspection shows that, out of the error bars, as T_c decreases, $\Delta_\pi(0)$ slightly rises,

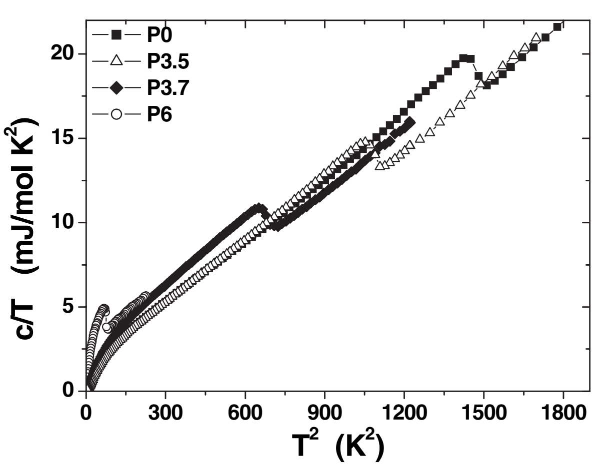

FIG. 2. c/T as a function of T^2 for the samples P0, P3.5, P3.7, and P6.

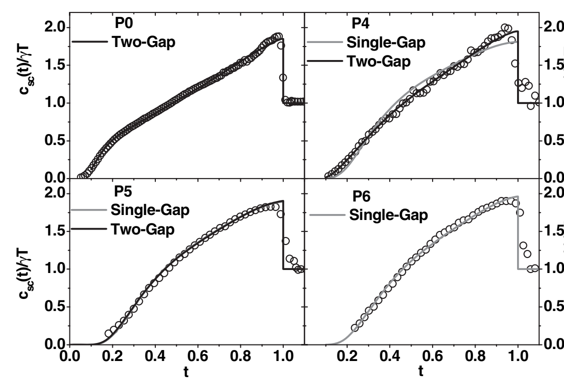

FIG. 3. $c_{sc}/\gamma T$ as a function of t for the samples P0, P4, P5, and P6. The best fit curves are plotted as continuous lines. For the samples P4 and P5 the best fit curves obtained within the single-gap (gray line) and two-gap (black line) analyses are presented for comparison.

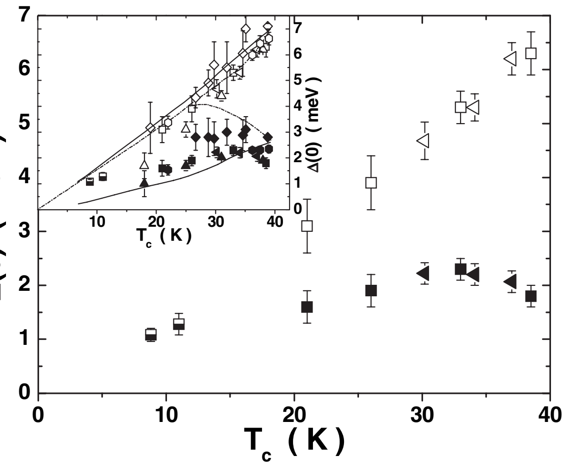

FIG. 4. $\Delta_\sigma(0)$ (empty symbols), $\Delta_\pi(0)$ (filled symbols), and $\Delta(0)$ (half-filled symbols) as a function of T_c. In the main figure data from this work (■) and Ref. [19] (◀). In the inset, data from this work (■), Ref. [19] (◀), Ref. [9] (▲), Ref. [16] (▶), Ref. [18] (◆), and the theoretical curves calculated in Ref. [7] in the case of only interband scattering (dotted line) and only reduced DOS (continuous line).

showing a flat maximum around 30 K, and then decreases; this trend is confirmed by $\Delta_\pi(0)$ values obtained on neutron-irradiated MgB_2 by Wang *et al.* [19], shown in the same figure for comparison. As discussed in Ref. [7], this behavior can be associated with the compensation of the interband scattering, which increases $\Delta_\pi(0)$, and with the diminution of electron-phonon coupling driven by the disorder.

In the single-gap region, not investigated before, $\Delta(0)$ decreases with T_c reaching a value of 1 meV at $T_c = 8.7$ K. Since the gaps are still separated at 21 K, the merging has to take place at a temperature lower than the 20 K predicted for isotropic MgB_2. Recently Wilke *et al.* [26], analyzing the upper critical field of neutron-irradiated samples, suggested that the bands become fully mixed only when T_c is near 10 K. As discussed before, the lack of T_c saturation at 20 K suggests that disorder not only increases the interband scattering, but also affects the electron-phonon coupling. On the other hand, the observation of single-gap superconductivity unambiguously indicates that interband scattering has effectively led to the merging of the gaps.

Interestingly, in the single-gap regime, the reduced gap values, $2\Delta(0)/k_B T_c$, are 2.8–2.7, lower than the BCS value 3.52. Reduced gap values lower than the BCS one were observed also in a conventional disordered superconductor [27]. This is an intriguing point, which will require further investigation.

Finally, in the inset of Fig. 4 the energy gap values of irradiated and doped samples are plotted as a function of T_c. Although different mechanisms (σ-band filling, interband scattering, intraband scattering, etc.) should suppress the superconductivity in these samples, the behaviors of the two gaps look similar. On the other hand, experimental results are not well reproduced by the theoretical curves calculated in Ref. [7] in the case of only interband scattering (dotted line) and only reduced DOS (continuous line) indicating that in irradiated and doped samples more mechanisms cooperate to suppress superconductivity.

In conclusion, we succeeded in introducing defects in pure $Mg^{11}B_2$ by thermal neutron irradiation. The critical temperature has been suppressed down to 8.7 K, but the superconducting transitions remain sharp. The electronic specific heat of these samples has been analyzed within the α model in order to study the crossover from two-gap to single-gap superconductivity. For T_c values above 21 K the two-gap feature remains evident, while below 21 K there is no more evidence of the presence of two gaps. So we fix between 11 and 21 K the T_c value at which the merging of the gaps occurs, in agreement with the prediction of the two-band theory. The next step will be to understand what mechanism, together with interband scattering, suppresses the superconductivity in heavily disordered MgB_2.

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