Evidence for Two Superconducting Energy Gaps in MgB2 by Point-Contact Spectroscopy

P. Szabo, P. Samuely, J. Kacmarcík, Thierry Klein, J. Marcus, D. Fruchart, S. Miraglia, C. Marcenat, A. G. M. Jansen

Evidence for Two Superconducting Energy Gaps in MgB_2 by Point-Contact Spectroscopy

P. Szabó,[1,2] P. Samuely,[1] J. Kačmarčík,[1] T. Klein,[2] J. Marcus,[2] D. Fruchart,[3] S. Miraglia,[3]
C. Marcenat,[4] and A. G. M. Jansen[5]

[1]*Institute of Experimental Physics, Slovak Academy of Sciences, SK-04353 Košice, Slovakia*
[2]*Laboratoire d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, B.P. 166, F-38042 Grenoble Cedex 9, France*
[3]*Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, BP 166, 38042 Grenoble Cedex 9, France*
[4]*CEA-Grenoble, Département de Recherche Fondamental sur la Matiére Condensée, F-38054 Grenoble Cedex 9, France*
[5]*Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung and Centre National de la Recherche Scientifique, B.P. 166, F-38042 Grenoble Cedex 9, France*

(Received 18 June 2001; published 11 September 2001)

Experimental support is found for the multiband model of the superconductivity in the recently discovered system MgB_2 with the transition temperature $T_c = 39$ K. By means of Andreev reflection, evidence is obtained for two distinct superconducting energy gaps. The sizes of the two gaps ($\Delta_S = 2.8$ meV and $\Delta_L = 7$ meV) are, respectively, smaller and larger than the expected weak coupling value. Because of the temperature smearing of the spectra the two gaps are hardly distinguishable at elevated temperatures, but when a magnetic field is applied the presence of two gaps can be demonstrated close to the bulk T_c in the raw data.

DOI: 10.1103/PhysRevLett.87.137005 PACS numbers: 74.50.+r, 74.60.Ec, 74.70.Ad

Two decades of the boom in the field of superconductivity have recently been boosted by the surprising discovery of superconductivity in MgB_2 [1]. In contrast to the cuprates, the first tunneling [2–4] and point-contact [5,6] spectroscopy measurements have unequivocally shown that this system is a *s*-wave superconductor, and isotope effects [7,8] have pointed towards a phonon mechanism. However, the size of the superconducting energy gap has remained unclear. We report here on experimental support for the multiband model of superconductivity recently proposed by Liu *et al.* [9], thus showing that MgB_2 belongs to an original class of superconductors in which two distinct 2D and 3D Fermi surfaces contribute to superconductivity. Indeed, our point-contact spectroscopy experiments clearly show the existence of two distinct superconducting gaps with $\Delta_S(0) = 2.8$ meV and $\Delta_L(0) = 7$ meV. Both gaps close near the bulk transition temperature $T_c = 39$ K. Our measurements in the magnetic field show directly in the raw data the presence of two superconducting gaps at all temperatures up to the same bulk transition T_c, indicating that the two gaps are inherent to the superconductivity in MgB_2.

Although quite scattered, the first spectroscopy measurements [2–6,10] yielded to superconducting gap values surprisingly smaller than the BCS weak coupling limit $2\Delta/kT_c = 3.52$. Moreover simultaneous topographic imaging and quasiparticle density of states mapping [11] revealed substantial inhomogeneities at the surface of the sample as well as a large scattering of the energy gap values measured at different parts of the polycrystalline sample (with Δ ranging from 3 to 7.5 meV). This energy gap distribution can be caused by sample inhomogeneities. However, Giubileo *et al.* [11] also observed a superposition of two gaps [$\Delta_S(0) = 3.9$ meV and $\Delta_L(0) = 7.5$ meV] in some of their local tunneling spectra. The same inhomogeneity argument could of course also explain such a superposition but a much more attractive scenario would be a two-gap model. Such a model was first developed by Suhl *et al.* [12] in the case of overlapping *s* an *d* bands in conventional superconductors (such as V, Nb, Ta). Experimental evidence for the existence of two-band superconductivity was obtained by tunneling spectroscopy in Nb-doped $SrTiO_3$ [13]. A similar model was recently proposed by Liu *et al.* for MgB_2. It is here based on the coexistence of a two-dimensional Fermi surface (p_{x-y} orbitals) perpendicular to the *z* direction and a three-dimensional (p_z bonding and antibonding bands) one. This model then predicts the existence of two different energy gaps being smaller (for the 3D gap) and slightly larger (for the 2D gap) than the expected weak coupling value.

Indications for the existence of two gaps in MgB_2 have also been found in specific heat measurements [14,15], and low-temperature Raman-scattering [16] experiments reveal two peaks for two different gaps. However, it is still necessary to show that these two gaps coexist up to T_c in order to validate this scenario. We show here direct and clear evidence for this coexistence using point-contact spectroscopy in a magnetic field.

Blonder, Tinkham, and Klapwijk (BTK) have developed a theory [17] describing the electrical transport in ballistic contacts between a normal (N) and a superconducting (S) electrode with different possible interfaces between them: from a pure conducting interface where the Andreev reflection dominates up to the well-known insulating barrier (i.e., the Giaever tunneling case). The most important consequence of this theory is that any point-contact geometry will be able to provide direct spectroscopic information about the superconducting energy gap. In the pure Andreev limit, if a quasiparticle is accelerated by an applied voltage V such that $|V| < \Delta/e$, a direct transfer to the superconducting electrode is forbidden and a hole is then retroreflected in the normal electrode in order to allow the formation of a Cooper pair in the superconductor. The overall current (and differential conductance $\sigma = dI/dV$) for $|V| < \Delta/e$ is then two times higher than the value for $|V| > \Delta/e$. In the intermediate case a dip appears for $V = 0$. Two peaks are then visible at $V \sim \pm\Delta/e$. The evolution of the dI/dV vs V curves for different interfaces characterized with the barrier strength Z is schematically presented in Fig. 1a. Because the point-contact geometry directly probes the coherence of the superconducting state, it is probably the most adapted technique to determine the superconducting energy gap. Another advantage of the point-contact spectroscopy is that the normal electrode is pushed into the sample in order to probe a clean surface.

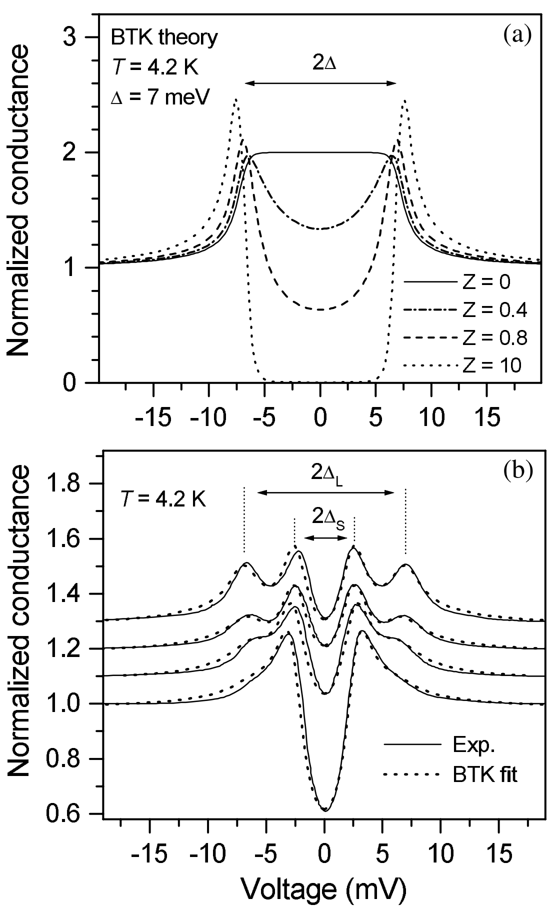

FIG. 1. (a) Numerical simulation of the BTK model at different values of the barrier strength Z, representing behavior of the point-contact spectra for $\Delta = 7$ meV between Giaever tunneling ($Z = 10$) and clean Andreev reflection ($Z = 0$) at $T = 4.2$ K. (b) Experimentally observed evolution of the Cu-MgB_2 point-contact spectra at $T = 4.2$ K (solid lines). The upper curves are vertically shifted for clarity. The dotted lines display fitting results for the thermally smeared BTK model with $\Delta_S = 2.8 \pm 0.1$ meV, $\Delta_L = 6.8 \pm 0.3$ meV for different barrier transparencies and weight factors.

Point-contact measurements have been performed on polycrystalline MgB_2 samples with $T_c = 39.3$ K and $\Delta T_c = 0.6$ K. A special point-contact approaching system with a negligible thermal expansion allows for the temperature and magnetic field measurements up to 100 K. The point contacts were stable enough to be measured in the magnetic field of a superconducting coil. A standard lock-in technique at 400 Hz was used to measure the differential resistance as a function of applied voltage on the point contacts. The microconstrictions were prepared by pressing a copper tip (formed by electrochemical etching) on the freshly polished surface of the superconductor. MgB_2 samples were prepared from boron powder (99.5% pure, Ventron) and magnesium powder (98% Mg + 2% KCl, MCP Techn.), in relative proportion 1.05:2. A 2 g mass of the mixed powders was introduced into a tantalum tube, then sealed by arc melting under argon atmosphere (purity 5N5). The tantalum ampoule was heated by high frequency induction at 950 °C for about three hours. After cooling down to room temperature, the sample was analyzed by x-ray diffraction and scanning electron microscope. Among the brittle dark grey MgB_2 powder (grain size <20 μm), a few hard but larger grains (0.1–1 mm) were found. Laue patterns show evidence for only a limited number of single crystals in each grain. Resistivity and ac susceptibility measurements of these larger grains reveal a particularly abrupt superconducting transition ($\Delta T_c \leq 0.6$ K), indicating their high quality in comparison with that of the fine powder.

Figure 1b shows typical examples of the conductance versus voltage spectra obtained for the various Cu-MgB_2 junctions with different barrier transparencies. All shown point-contact conductances were normalized to the value at the high-voltage bias. The spectrum had a more tunneling-like character when the tip first touched the surface (i.e., with a barrier resistance $R \sim 100\ \Omega$) and then continuously transformed into a form with a direct conductance as the tip was pushed into the sample (down to $R \sim 6\ \Omega$). Almost all curves reveal a two-gap structure, where the smaller-gap maxima are displayed at about 2.8 mV and the large gap maxima at about 7 mV, placed symmetrically around the zero bias. Even if, in some case, only the smaller gap is apparent (as shown in the lowest curve of Fig. 1b), its width hides the contribution of the second gap. Then, as we show below, a magnetic field can suppress the smaller gap and the large one will definitely emerge. All our curves could be fitted by the sum of the two BTK conductances $\alpha\sigma_S + (1 - \alpha)\sigma_L$ with the weight factor α varying from ~10% to ~90% depending on the position of the tip (this scattering of the α value is probably related to different crystallographic orientations at the different microconstrictions). We thus definitely observed two distributions with the smaller gap scattered at about 2.8 meV and the second one at about 7 meV.

As pointed out above, the smaller gap could be caused by a weakening of the superconducting state, possibly resulting from a proximity effect. That is why it is important to show that it still exists at high temperatures in order to validate the two-gap scenario with one single critical temperature. The temperature dependencies of the point-contact spectra have been examined on five different samples in about ten spectra with a clear two-gap structure. Because of thermal smearing, the two well-resolved peaks in the spectrum merge together as the temperature increases. Consequently, the presence of two gaps is not as evident in the raw data (see Fig. 2a). For instance, at 25 K the spectrum is reduced to one smeared maximum around the zero bias. Such a spectrum itself could be fitted by the BTK formula with only one gap, but the transparency coefficient Z would have to change significantly in comparison with the lower temperatures, and moreover a large smearing factor Γ would have been introduced. However, our data could be well fitted at all temperatures by the sum of two BTK contributions with the transparency coefficient Z and the weight factor α kept constant and without any parallel leakage conductance. The point-contact conductances of one spectrum at different temperatures are shown in Fig. 2a together with the corresponding BTK fits. The resulting energy gaps Δ_L and Δ_S, together with those obtained for two other point contacts with different weight values α, are shown in Fig. 2b. The error bars were obtained independently for each spectrum at a particular temperature.

Since it is evident from Fig. 2b that both gaps are closing near the same bulk transition temperature, our data give experimental support for the two-gap model. In the classical BCS theory, an energy gap with $\Delta_S = 2.8$ meV could not exist for a system with T_c above $2\Delta/3.5k \sim 19$ K. Moreover, we obtained a very weakly coupled gap with $2\Delta_S/kT_c \simeq 1.7$ and a strongly coupled gap with $2\Delta_L/kT_c \simeq 4.1$, in very good agreement with the predictions of Liu *et al.* (a 3D gap ratio $2\Delta_S/kT_c \simeq 1.3$ and a 2D gap ratio $2\Delta_L/kT_c \simeq 4.0$). The temperature dependencies are in good agreement with the prediction of the BCS theory. Small deviations from this theory were predicted by Liu *et al.* but these deviations are within our error bars for the large gap Δ_L, while in the case of the small gap Δ_S there is a tendency for more rapid closing at higher temperatures near T_c (see Fig. 2b), as expected theoretically.

Even much stronger evidence for the inherent presence of two gaps in the superconductivity of MgB_2 is obtained by our magnetic field measurements. Figure 3 displays the effect of the magnetic field up to 1 T on the two gaps measured at four different temperatures. At $T = 4.2$ K the two gaps are clearly visible for zero magnetic field $H = 0$ but the peaks corresponding to the small gap are rapidly affected by a magnetic field. The contribution of this small gap almost completely disappears at 1 T, whereas the large gap still remains clearly visible. The other sets of spectra were recorded at 10, 20, and 30 K. As already shown in Fig. 2a, the spectra are so smeared out above 20 K that the presence of the two gaps is not clearly visible and we have to rely on the fitting procedure. However, nothing like this holds when we apply the magnetic field. Indeed, the smaller-gap contribution to the overall point-contact conductance is rapidly suppressed by the field. As clearly visible at 4.2 and 10 K, this suppression leads to the formation of a deep broad minimum in the conductance at zero bias with increasing magnetic field with some traces of the smaller gap still surviving. Similarly, at 20 and 30 K the peaks corresponding to the large gap become much better resolved in a magnetic field. This could not happen if there was not a contribution of the small gap in the zero-field point-contact conductance at these elevated temperatures. Indeed, a one-gap spectrum would only smear out with increasing magnetic field due to the pair-breaking effect. This effect thus unambiguously shows that the two

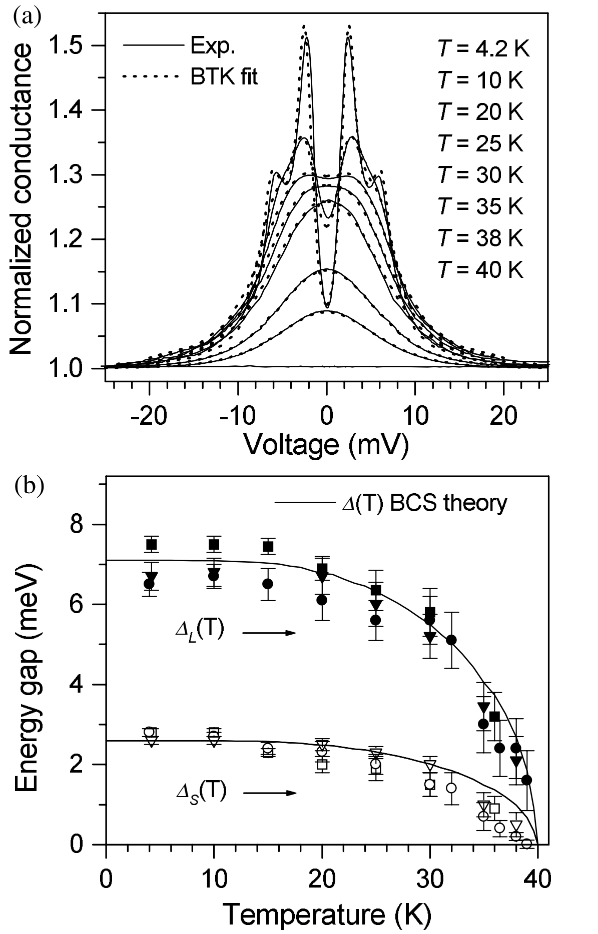

FIG. 2. (a) Differential conductances of Cu-MgB_2 point-contact measured (solid lines) and fitted (dotted lines) for the thermally smeared BTK model at indicated temperatures. The fitting parameters $\alpha = 0.71$, $Z = 0.52 \pm 0.02$ had the same values at all temperatures. (b) Temperature dependencies of both energy gaps ($\Delta_S(T)$, solid symbols; $\Delta_L(T)$, open symbols) determined from the fitting on three different point contacts are displayed with three corresponding different symbols. $\Delta_S(T)$ and $\Delta_L(T)$ points determined from the same contact are plotted with the same (open and solid) symbols. The solid lines represent BCS predictions.

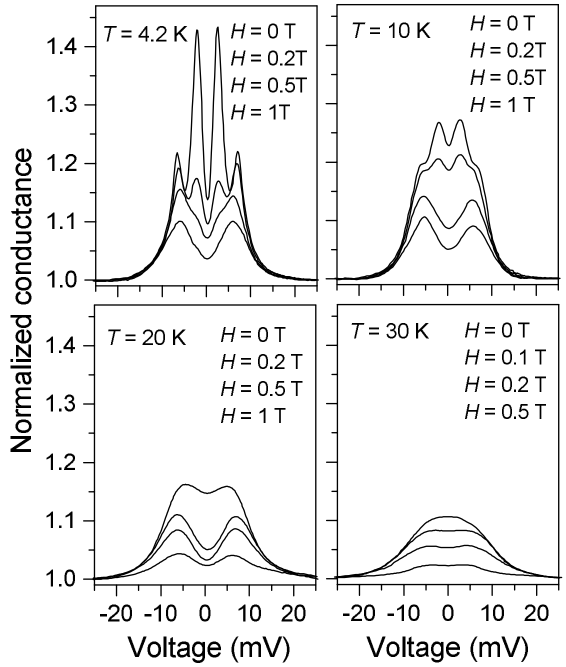

FIG. 3. Experimentally observed influence of the applied magnetic field on the two-gap structure of the normalized point-contact spectra at indicated temperatures. These spectra clearly reveal that both gaps exist in zero field up to T_c as shown by the rapid suppression of the small-gap structure ($\Delta_S = 2.8$ meV) with magnetic field which leads to a broad deep minimum at zero bias.

gaps coexist near T_c, thus supporting the two-band model of superconductivity in MgB_2.

A quantitative analysis of the magnetic field effect on the two gaps is a problem *sui generis* and will be a subject of further study. We suppose that due to the interaction between the 3D and 2D bands in MgB_2 there will be not only one common T_c but also one H_{c2} for a particular field orientation. Then, the rapid suppression of the smaller-gap contribution at low fields should be followed by its weak presence up to a common H_{c2}. On the spectra obtained thus far we never observed a full suppression of the gap structure below 10 T at 4.2 K.

The specific heat measurements performed by Bouquet *et al.* [14] revealed a strong reduction of the electronic density of states at low temperatures, suggesting the presence of a second small energy gap which, in striking similarity with our direct observations, could be suppressed by ~1 T magnetic field. Specific heat is a bulk thermodynamic quantity and the excellent consistency of these measurements with our spectroscopic results further demonstrates that the existence of these two gaps is an intrinsic property of MgB_2. The presence of two gaps has been recently detected in the specific heat data for three differently prepared samples [18]. Also, recently a body of optical and microwave measurements appeared (e.g., Tu *et al.* [19]) on MgB_2 samples of different forms, showing that the smaller gap is a bulk property. Indirect observations of two gaps were also obtained from the temperature dependence of the specific heat in the conventional superconductors Nb, Ta, and V [20] but, to the best of our knowledge, clear and direct observation for the presence of two gaps existing up to the same T_c was never observed before by spectroscopic measurements. The possibility that these two gaps have different dimensionalities makes this system particularly attractive for further studies.

In conclusion, we obtained strong experimental evidence for the existence of two gaps closing at the same bulk T_c of the MgB_2 superconductor. The regular observation of this effect in our spectra and the support for it by other techniques probing the the sample on a different scale indicate that this is an inherent property of the material.

This work was supported by the Slovak VEGA Grant No. 1148.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] G. Rubio-Bollinger, H. Suderow, and S. Vieira, cond-mat/0102242.
[3] G. Karapetrov, M. Iavarone, W. K. Kwok, G. W. Crabtree, and D. G. Hinks, Phys. Rev. Lett. **86**, 4374 (2001).
[4] H. Schmidt, J. F. Zasadzinski, K. E. Gray, and D. G. Hinks, cond-mat/0102389.
[5] A. Kohen and G. Deutscher, cond-mat/0103512.
[6] A. Plecenik, Š. Beňačka, P. Kúš, and M. Grajcar, cond-mat/0104038.
[7] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. **86**, 1877 (2001).
[8] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature (London) **411**, 457 (2001).
[9] Amy Y. Liu, I. I. Mazin, and J. Kortus, cond-mat/0103570; J. Kortus, I. I. Mazin, K. D. Belashenko, V. P. Antropov, and L. L. Boyer, cond-mat/0101446.
[10] T. Takahashi, T. Sato, S. Souma, T. Muranaka, and J. Akimitsu, cond-mat/0103079.
[11] F. Giubileo, D. Roditchev, W. Sacks, R. Lamy, and J. Klein, cond-mat/0105146.
[12] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. **3**, 552 (1959).
[13] G. Binning, A. Baratoff, H. E. Hoenig, and J. C. Bednorz, Phys. Rev. Lett. **45**, 1352 (1980).
[14] F. Bouquet, R. A. Fisher, N. E. Phillips, and D. G. Hinks, cond-mat/0104206.
[15] Y. Wang, T. Plackowski, and A. Junod, Physica (Amsterdam) **355C**, 179 (2001).
[16] X. K. Chen, M. J. Konstantinovic, J. C. Irwin, D. D. Lawrie, and J. P. Franck, cond-mat/0104005.
[17] G. E. Blonder, M. Tinkham, and T. M. Klapwijk, Phys. Rev. B **25**, 4515 (1982).
[18] F. Bouquet *et al.*, cond-mat/0107196.
[19] J. J. Tu *et al.*, cond-mat/0107349.
[20] L. Y. L. Shen, N. M. Senozan, and N. E. Philips, Phys. Rev. Lett. **14**, 1025 (1965).