Scanning Tunneling Spectroscopy in MgB$_2$

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We present tunneling microscopy measurements of the surface of superconducting MgB$_2$ with a critical temperature of 39K. In zero magnetic field the conductance spectra can be analyzed in terms of the standard BCS theory with a smearing parameter $\Gamma$. The value of the superconducting gap is 5.2 meV at 4.2 K, with no experimentally significant variation across the surface of the sample. The temperature dependence of the gap follows the BCS form, fully consistent with phonon-mediated superconductivity in this novel superconductor. The application of a magnetic field induces strong pair-breaking as seen in the conductance spectra in fields up to 6 T.

One route for finding new superconducting compounds with a high critical temperature combines light elements with high ionicity, a large density of electronic states at the Fermi level, and stiff elastic response due to high frequency phonon modes. Many carbides and nitrides fall into this category, and some of them show superconducting transition temperatures as high as 10-20 K. The recent discovery of superconductivity at 40 K in MgB$_2$ [1] reinvigorates strong interest in this approach.

MgB$_2$ has a remarkably high $T_c$ for a simple binary compound. The chemical structure is quite simple as well, consisting of alternating hexagonal layers of Mg atoms and boron honeycomb layers. Band structure calculations [2,3] show that this compound is ionic, has a high density of states at the Fermi level, high phonon frequencies, and strong electron-phonon interactions. These features favor a high superconducting transition temperature arising from phonon mediated electron pairing. The presence of the isotope effect [4] confirms the important role of phonons in the superconductivity of this compound. Transport and magnetic measurements [5–9] are beginning to probe the macroscopic response of the superconducting and normal states, and the superconducting performance for applications is being evaluated [10,11].

Here we report the superconducting energy gap of polycrystalline MgB$_2$ pellets as seen in scanning tunneling spectroscopy. These measurements directly probe the quasiparticle excitations near the Fermi energy and provide key information on the nature of the superconducting energy gap and its temperature and field dependence. We achieve clean vacuum tunneling with conductance spectra that are identical within experimental error across the sample scan area. The tunneling spectroscopy at 4.2 K is consistent with the modified BCS density of states [12] (DOS) with a superconducting gap value of 5.2 meV and pair-breaking strength $\Gamma$ of 3 meV. From STM measurements we show that the temperature dependence of the gap follows a BCS behavior. In addition, we present the magnetic field dependence of the tunneling spectra at 4.2 K showing the pair-breaking effect of the magnetic field in this material.

The MgB$_2$ sample was synthesized from a high purity, 3 mm diameter Mg rod and isotopic $^{11}$B (Eagle Picher, 98.46 atomic % $^{11}$B). The Mg rod was cut into pieces about 4 mm long and mixed with the 200 mesh $^{11}$B powder. The reaction was done under moderate pressure (50 bars) of ultra-high purity argon at 850°C. At this temperature the gas-solid reaction was complete in about one hour. The sample was contained in a machined BN crucible (Advanced Ceramics Corp. HBC grade BN) with a closely fitting cover. There was no reaction between the BN crucible and the reactants at the synthesis temperature. X-ray diffraction showed no impurity peaks in the resultant powder. The powder was compacted in a steel die at about 3 Kb and refired using the same conditions to form the compacted pellet. The transition temperature of the material was 39 K measured by DC field cooled magnetization in an applied field of 2 Oe. Part of this pellet was used for our STM measurements without additional treatment of the as-grown surface. The samples were exposed briefly to air before being inserted in an inert helium atmosphere in the STM. The tunneling measurements were performed with a home-built STM operating in helium exchange gas with an electrochemically etched tip of Pt-Ir wire. The nature of the last atom on the tip was unknown.

Topographic images over a scale of 300 × 300 nm$^2$ showed a flat zone with surface roughness less than 1 nm. To confirm the vacuum nature of the tunneling we measured the relationship between the value of the tunneling current and the tip displacement from the surface. The exponential behavior of this dependence was verified and indicated a clean vacuum tunneling. The extracted value of the apparent work function [13] is a few hundred meV. The low value of the tunneling barrier is familiar in the boride family of compounds although the possibility of modified layer on the surface of the MgB$_2$ grain cannot be ruled out.

Current-voltage $I(V)$ and differential conductance
$dI/dV(V)$ curves were recorded using standard lock-in techniques with a small modulation voltage superimposed on the slowly varying DC bias voltage while the distance between the tip and sample was kept constant. The amplitude of the modulation was kept at 0.4 mV, i.e. three times smaller than the intrinsic thermal broadening (=3.5$k_B T$) at 4.2 K. Figure 2 shows a series of $dI/dV(V)$ curves normalized at $V=-20$ mV for tunneling resistance ranging between 125 MΩ and 2 GΩ in zero magnetic field. The tunneling spectra are independent of the junction resistance, an additional verification of a clean vacuum tunnel junction. The remarkable reproducibility of the coherence peak and the value of the zero-bias conductance across the sample surface is in sharp contrast to STM measurements in cuprate superconductors. Thermal cycling to 50 K did not change the junction characteristics.

Unlike the cuprate superconductors, the conductance spectra in MgB$_2$ are very symmetric implying a BCS-like energy gap. It is important to note a relatively high zero-bias conductance which is approximately 50% of the normal background, and the broad coherence peak at $V=\pm 8$ mV. The zero-bias value and the intensity of the peaks are absolutely reproducible at different tunneling junction resistances and different locations (Fig. 2) on the sample surface within the scanning area 300 x 300 nm$^2$. We exclude RF noise as the cause of such broadening since measurements performed with the same set-up on Pb and Nb superconducting samples show much lower zero bias values and much less broadening even though the reduced temperature $T/T_c$ is much higher. The sizable zero-bias conductance is accompanied by quite linear conductance dependence inside the gap region that might suggest the possibility of coverage of the MgB$_2$ superconductor with a thin layer of normal material. This case is very similar to the one observed in YNi$_2$B$_2$C and LuNi$_2$B$_2$C in which the large zero-bias conductance was attributed to tunneling through an overlayer of normal material.

The value of the gap was estimated using the standard expression for tunneling conductance[7] with the modified BCS expression for the superconducting density of states from the phenomenological model by Dynes et al.[13]:

$$N(E) = \text{Re} \left[ \frac{|E-i\Gamma|}{\sqrt{(E-i\Gamma)^2-\Delta^2}} \right] \quad (1)$$

where $\Delta$ is the superconducting energy gap and $\Gamma$ is the pair-breaking strength. In Figure 3, we show an example of the experimental tunneling conductance spectrum and calculated conductance using the above approximation. The best fit at 4.2K produces $\Delta=5.2$ meV and $\Gamma=3$ meV. The ratio $2\Delta/k_B T_c = 3$ for the bulk value of $T_c = 39$ K, indicating a weakly coupled superconductor. Our fits described below suggest that the transition temperature and the gap in the top layer of the crystalline surface of the grain are slightly suppressed, bringing the bulk value of $2\Delta/k_B T_c$ nearly in line with the BCS value of 3.5. The value of $\Gamma=3$ meV is consistent with the electron scattering rate expected for a normal state resistivity of the order of 1 $\mu\Omega$cm and the band structure value of the plasma frequency $\Omega_p=7$ meV [14]. If so, then the pronounced V-shaped gap we observe cannot be attributed to $d$-wave pairing symmetry, because the large ratio of $\Gamma/\Delta$ would strongly suppress $T_c$ for non-s-wave pairing.

Our results show a superconducting gap significantly larger than the one obtained by Rubio-Bollinger et al. on isolated grains of commercially prepared material. In addition to a larger gap, our tunneling spectra show a pronounced V-shape with many more subgap states than the relatively flat bottomed form of Rubio-Bollinger et al. These differences cannot be easily explained by simple surface layer effects. Rather, the qualitatively different spectra seem to reflect intrinsic differences in the superconducting nature of the sample surface, perhaps due to the different preparation histories of the two samples.

The temperature dependence of the superconducting gap was extracted from tunneling spectra at a series of temperatures, as shown in the inset of Fig. 3. The fitting curve and the experimental points have been normalized to the gap value at 4.2 K ($\Delta=5.2$ meV) and a $T_c=35$ K. This confirms our original idea that the origin of the broadening is rather due to a depressed superconducting layer on the surface. The data are fit remarkably well with a standard BCS form, further supporting the importance of phonons for the pairing interaction.

It has been shown[15] that MgB$_2$ is a type II superconductor and therefore the magnetic flux penetrates the material in the form of vortices. The superconducting order parameter inside the vortex core is suppressed, providing additional quasiparticle states below the zero-field superconducting gap energy. These states inside the core in-crease the zero-bias conductance and smear the coherence peaks in the conductance spectra. The spectral differences inside the vortex core enable real space imaging of the vortex configurations in type II superconductors with STM[16,20]. We have examined tunneling spectra as a function of location on the surface in applied magnetic fields and found remarkably reproducible spectra that gave no indication of an order parameter variation induced by vortices. This could indicate that natural pinning in the material is low and the vortices tend to be pinned in the grain boundaries. Alternatively, if the pinning is weak, the tunneling current near the tip could disturb the static position of vortices when scanning, masking their presence. Although individual vortices were not resolved, the tunneling conductance spectra taken at different magnetic fields and different locations show the spatially averaged pair-breaking effect of the magnetic field (Fig. 4). The magnetic field dramatically increases the number of quasiparticle states in the gap and smears...
the superconducting peaks. No additional features in the gap were observed in applied field.

In conclusion, we performed extensive scanning tunneling microscopy and spectroscopy measurements on the surface of superconducting MgB$_2$. Remarkably consistent conductance spectra were observed across the surface of the sample from which a superconducting gap of 5.2 meV at 4.2 K was extracted. The temperature dependence of the gap follows the BCS expression strongly indicating the importance of phonon-mediated superconductivity in this material. Applied magnetic fields produce a strong pair-breaking effect on the conductance spectra increasing the number of quasiparticle states in the gap.

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[1] J. Akimitsu, Symposium on Transition Metal Oxides, January 10, 2001, Sendai, Japan; J. Nagamatsu, N. Nakagaw, T. Muranaka, Y. Zenitani, and J. Akimitsu, to be published.
[2] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, cond-mat/0101446.
[3] K. D. Balashchenko, M. van Schilfgaarde, and V. P. Antropov, to be published.
[4] S. L. Budko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. (in press), cond-mat/0101463.
[5] D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, and P. C. Canfield, condmat/0102114.
[6] Y. Takano, H. Takeya, H. Fujii, H. Kumakura, T. Hatano and K. Togano, cond-mat/0102167.
[7] G. Rubio-Bollinger, H. Suderow, and S. Vieira, cond-mat/0102242.
[8] B. Lorenz, R. L. Meng, C. W. Chu, cond-mat/0102264.
[9] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. Loureiro, M. K. Haas, H. W. Zandbergen, R. J. Cava, cond-mat/0102262.
[10] C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seg Kim, S. Y. Lee, Sung-Il Lee, cond-mat/0102213.
[11] D. C. Larbalestier, M. O. Rikel, L. D. Cooley, A. A. Polyanskii, J. Y. Jiang, S. Patnaik, X. Y. Cai, D. M. Feldmann, A. Gutervich, A. A. Squitieri, M. T. Naus, C. B. Eom, E. E. Hellstrom, R. J. Cava, K. A. Regan, N. Rogado, M. A. Hayward, T. He, J. S. Slusky, P. Khalifah, K. Inumaru, M. Haas, cond-mat/0102216.
[12] P. C. Canfield, D. K. Finnemore, S. L. Bud’ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, C. Petrovic, cond-mat/0102283.
[13] R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. 41, 1509 (1978).
[14] J. H. Coombs and J. B. Pethica, IBM J. Res. Dev. 30, 455 (1986).
[15] H. Suderow, P. Martinez-Samper, S. Vieira, N. Luchier, J. P. Brison, and P. Canfield, cond-mat/0102152.
[16] G. T. Jeong, J. I. Kye, S. H. Chun, Z. G. Khim, W. C. Lee, P. C. Canfield, B. K. Cho, D. C. Johnston, Physica C 253, 48 (1995).
[17] E. L. Wolf, Principles of Electron Tunneling Spectroscopy, (Oxford University Press, New York, 1985).
[18] H. F. Hess, R. B. Robinson, R. C. Dynes, J. M. Valles, Jr., and J. V. Waszczak, Phys. Rev. Lett. 62, 214 (1989).
[19] I. Maggio-Aprile, Ch. Renner, A. Erb, E. Walker, and O. Fisher, Phys. Rev. Lett. 75, 2754 (1995).
[20] Y. DeWilde, M. Iavarone, U. Welp, V. Metlushko, A. E. Koshelev, I. Aranson, G. W. Crabtree, and P. C. Canfield, Phys. Rev. Lett. 78, 4273 (1997).
FIG. 2. Tunneling conductance spectra measured on the scanning area of 300 x 300 nm$^2$ show excellent reproducibility (for clarity the spectra are equidistantly shifted vertically and normalized to the conductance value at -20 mV). Junction resistance is 250 MΩ.

FIG. 3. Scanning tunneling characteristics on the MgB$_2$ surface at 4.2 K: (a) experimental tunneling conductance (circles) and calculated conductance curves using a smeared BCS density of states (solid line) give an estimate of $\Delta = 5.2$ meV and $\Gamma = 3$ meV; (b) experimental current-voltage characteristic of the same tunneling junction (circles) and its fit to the same model with identical parameters (solid line). Insert shows the temperature dependence of the superconducting energy gap extracted from tunneling conductance curves at different temperatures (points) following the conventional BCS behavior (line).

FIG. 4. Magnetic field dependence of the normalized tunneling conductance at 4.2 K. The zero bias conductance sequentially increases with the magnetic field for fields H=0 T, 0.5 T, 0.75 T, 1 T, 2T, 3T, 4T, 5T and 6T.