Tunneling Spectroscopy in Small Grains of Superconducting MgB_2

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We report on tunneling spectroscopy experiments in small grains of the new binary intermetallic superconductor MgB_2. Experiments have been performed at 2.5 K using a low temperature scanning tunneling microscope. Good fit to the BCS model is obtained, with a gap value of 2 meV. In the framework of this model, this value should correspond to a surface critical temperature of 13.2 K. No evidence of gap anisotropy has been found.

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The recent discovery of superconductivity at 39 K in magnesium diboride by Nagamatsu *et al.* [1] has produced a notable excitement in the people investigating in the field. This novel achievement is extremely exciting as it opens a new route towards the search of high temperature superconductors. Indeed, the composition and the hexagonal structure of this compound is simpler than those of the other known systems that are superconducting at these or higher temperatures, as, e.g., the copper-oxide high T_c materials or as the C_{60} based compounds. First measurements of the thermodynamic properties [2] (magnetization and specific heat) and of the isotope effect on the B atoms are already available [3]. These data demonstrate that this system is a type II superconductor (with Ginzburg-Landau parameter $\kappa \simeq 26$) and that replacement of ^{10}B by ^{11}B leads to a decrease of the critical temperature, in agreement with phonon mediated BCS superconductivity.

As recently reported [4], band structure calculations show a highly isotropic character for the electronic properties of this compound, favoring the phonon mediated superconductivity. Other very recent theoretical proposals by Hirsch [5] have pointed towards hole superconductivity, based on the negative values for the Hall coefficient in other metal diborides with the same crystal structure. This author proposes several experimental tests of his theory, one of them being the tunneling characteristic which is predicted to be asymmetric having always a larger current for a negatively biased sample. Tunnel spectroscopy experiments are of keen interest to shed light on the mechanism of superconductivity in this material.

We present in this Letter tunneling characteristic curves of MgB_2, obtained at liquid helium temperatures, using a homemade low temperature scanning tunneling microscope (LT-STM) with a gold tip as counterelectrode. We have used commercially available magnesium diboride powder (Alfa-Aesar 98% pure).

We have done magnetization measurements of the powder and find the same behavior as reported in Ref. [3], with $T_c = 37.5$ K and the transition broader than in samples prepared by solid state reaction of pure elements [3]. X-ray characterization of our powder shows an extra peak at $2\theta = 36.6°$ due to a small magnesium content. These inclusions correspond to 0.2% of the sample volume, as obtained from a more detailed analysis of the peak intensity.

We measure the tunneling *I-V* characteristics on individual magnesium diboride grains whose preparation involved several steps. The MgB_2 powder was first dispersed in high purity acetone in an ultrasound bath and a drop of this dispersion was deposited on the surface of a high purity gold sample. Acetone was then evaporated putting the sample in an oven at 80 °C. Then the dry disperse powder was gently pressed into the gold surface with a flat synthetic ruby, forcing the hard magnesium diboride grains to penetrate into the softer gold substrate. The sample was then immersed in an acetone ultrasound bath in order to remove grains that were not tightly fixed to the gold substrate. Inspection of the resulting sample with an optical microscope showed a distribution of single MgB_2 grains separated by clean gold regions several microns wide. This preparation method overcomes difficulties arising from the preparation of pellets that often result in artifacts in the *I-V* curves possibly due to bad intergrain connection [6]. In addition, the grains of MgB_2 result embedded in the gold matrix and are expected to have a good electrical connection to the substrate, and therefore to the electrodes. In Fig. 1 we present two scanning electron microscopy (SEM) images of grains embedded in the gold substrate.

In order to be able to find on the gold substrate different individual grains we use a homebuilt STM operating at low temperature supplemented with a coarse *X-Y* positioning stage [7]. This stage allows for precise positioning of the tip over the entire sample surface (2×2 mm^2) in steps as small as 20 nm, without impairing its mechanical stability. Characteristic *I-V* curves in the tunneling regime were recorded with the STM in a four terminal configuration. The voltage and the current are measured using two low-noise differential preamplifiers, and all lines connecting the tip and the sample to the room temperature electronics are carefully filtered by feedthrough capacitors

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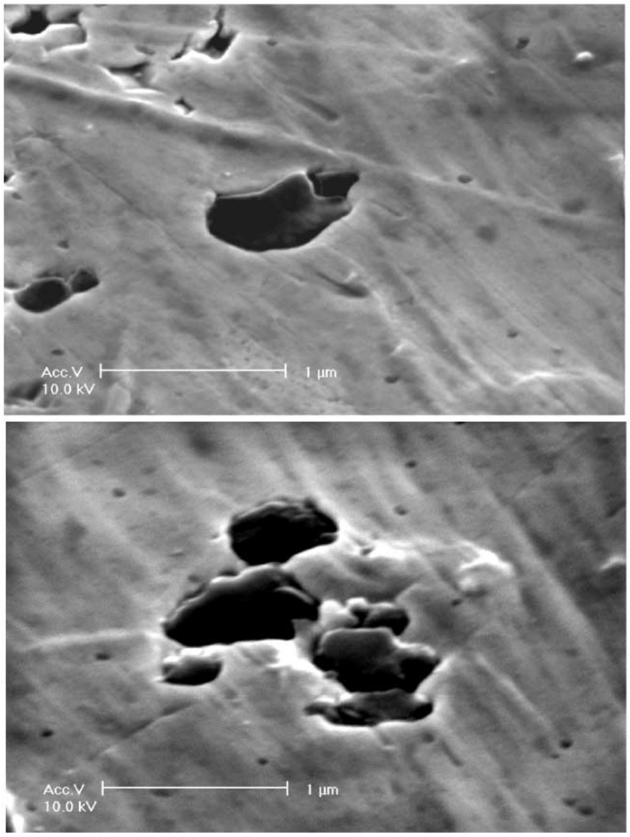

FIG. 1. SEM micrographs of the magnesium diboride grains (dark) embedded in the gold substrate. Typical grain sizes are between 0.5 and 1 μm, thus much larger than the superconducting coherence length.

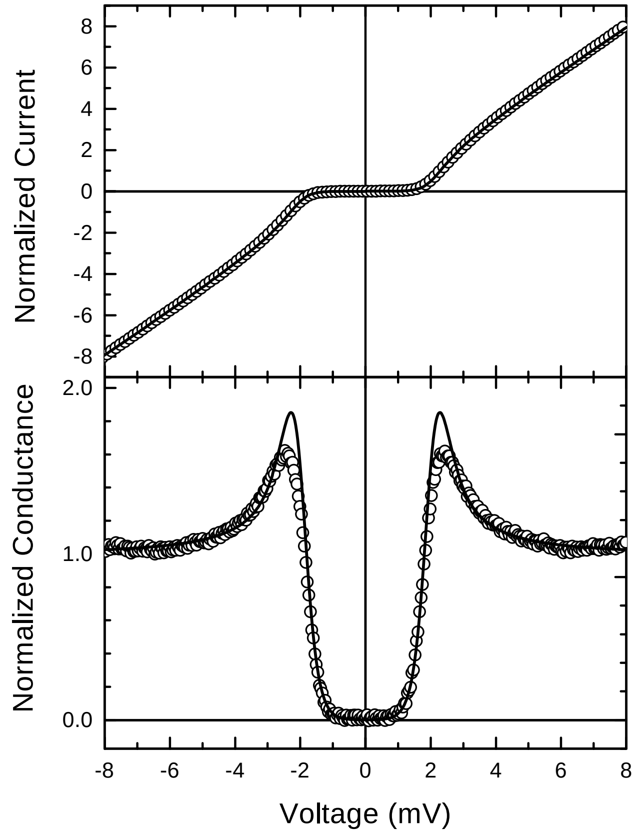

FIG. 2. Experimental (open circles) tunneling *I-V* characteristic curve and its differential conductance, normalized to $R_N = 2.5\ \mathrm{M}\Omega$. The solid line corresponds to a BCS normal-superconductor tunnel curve with a gap of $\Delta = 2.0$ meV and $T = 2.5$ K.

and a combination of lossy coaxial and twisted pair cables. This electronic setup has been previously shown to be necessary to avoid external electromagnetic noise to smear out superconducting features in tunneling spectroscopy measurements with local probe techniques [8,9].

The measured tunneling *I-V* curves obtained at the clean gold surface are Ohmic. However, using the STM coarse *X-Y* positioning stage we can find locations at which the *I-V* curves show superconducting features, indicating that the tip is on top of a MgB_2 grain. In addition, the topographic STM images at these locations look very flat, probably due to the appearance of crystalline faces. We scanned along many different, well-separated (10 μm) positions on the surface and therefore studied several grains. Current vs distance curves obtained at the MgB_2 grains show exponential behavior characteristic of tunneling with a work function of about 0.5 eV.

In Fig. 2 we show a representative tunnel *I-V* curve that is obtained at the MgB_2 grains. Both the *I-V* curve and its differential conductance show the expected behavior for a tunnel junction between a normal metal and a superconductor with BCS density of states, using a gap $\Delta = 2.0$ meV and $T = 2.5$ K. This was the temperature at which the experiment was performed. We also show in Fig. 3 a sample of several reproducible curves taken at different grains. All of them can be fitted, as the data of Fig. 2, with $\Delta = 2.0 \pm 0.1$ meV and $T = 2.5$ K.

The data show clearly that the density of states (DOS) inside the gap is very close to zero since the curve can be fitted to a BCS expression without any extra parameters, with thermal quasiparticle excitations (at $T = 2.5$ K) the only source of nonzero differential conductance inside the gap. We note that such resolution in energy, as mentioned before, is achievable only after proper filtering of the electric wiring of the setup.

The gap value ($\Delta = 2.0 \pm 0.1$ meV) for all the curves shown in Figs. 2 and 3 is significantly lower than what would be expected from the conventional BCS expression $\Delta = 1.76 k_B T_c$ (5.9 meV) taking the critical temperature that we have measured for our powder ($T_c = 37.5$ K). This discrepancy could be due to a deviation of the DOS at the surface of this material with respect to the bulk. Also note that in tunneling spectroscopy measurements it is the surface DOS that is probed, which could be significantly influenced by the presence of impurities, strong defects, or stoichiometry variations close to the surface, at distances in the range of the superconducting coherence length $\xi_0 = 5.2$ nm [2].

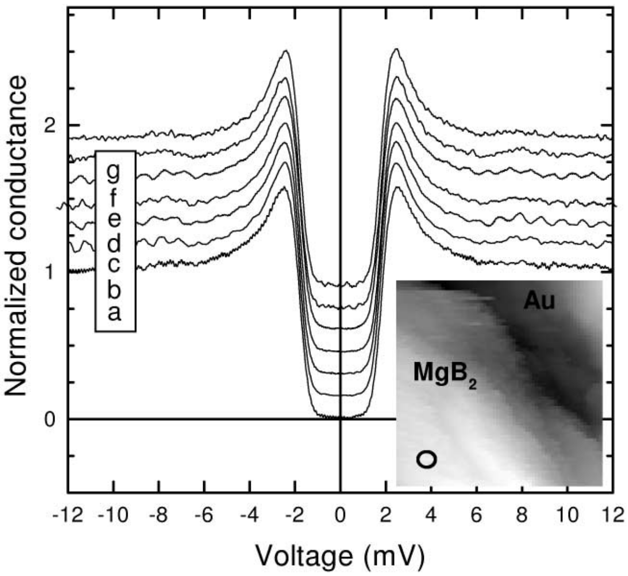

FIG. 3. Representative sample of several differential conductance curves obtained at different grains. Curves (a), (b), (c), and (f) are normalized to $R_N = 2.5\ \mathrm{M}\Omega$ and curves (d), (e), and (g) to $R_N = 10\ \mathrm{M}\Omega$. Curves (b)–(g) are shifted for clarity by increments of $+0.15$. Inset: Topography STM image ($90 \times 90\ \mathrm{nm}^2$) of the sample surface. Part of a MgB_2 grain can be seen bottom-left while the top-right region is the gold surface. Corrugation of the magnesium diboride surface is 2 nm. The black circle on the image indicates where curve (a) was recorded.

Such defective surfaces have very often been taken into account in the calculation of tunneling characteristics via the introduction in the model of pair-breaking centers which result in a reduced life of Cooper pairs. Such kind of calculations, like the Dynes model with a finite broadening parameter [10], result in a finite DOS inside the gap. However, our observations do not show the presence of low-energy excitations within the gap.

Using the preparation method described above, where no preferential grain orientation was induced, we are probably testing different crystal directions, and no signal of gap anisotropy was found. At some locations on the sample, curves indicative of S-I-S intergrain tunneling were found, being consistent with the gap value measured on the free surface.

In conclusion, we have presented tunneling spectroscopy experiments in the recently discovered superconducting compound MgB_2. To do that we have developed a sample preparation method that combined with the versatile positioning device of our low temperature STM allows for studying many individual small particles. In the framework of the BCS model, a critical temperature at the surface ($T_c = 13.2$ K) is found for the measured gap value ($\Delta = 2.0$ meV). We note again that we have used commercial powder without any special cleaning or regenerating process. That is in our opinion a good test of the stability and goodness of the superconductivity at the grain surface, a region of paramount importance to prepare this compound for its applications as a ceramic superconductor.

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