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.

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 in 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 home-made low temperature scanning tunneling microscope (LT-STM) with a gold tip as counter-electrode. 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. [1], being $T_c=37.5$ 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 $2\theta = 36.6^\circ$ due to a small magnesium content. This inclusions correspond to a 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 rubi, 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 home-build 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 (2x2 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 feed-through ca-
Fig. 1. SEM micrographs of the magnesium diboride grains (dark) embedded in the gold substrate. Typical grain sizes are between 0.5 µm and 1 µm, thus much larger than the superconducting coherence length.

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 behaviour 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, being thermal quasiparticle excitations (at $T = 2.5$ K) the only source of non-zero differential conductance inside the gap. We remark that such resolution in energy, as mentioned before, is only achievable 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.
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 remark 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, region of paramount importance to prepare this compound for its applications as a ceramic superconductor.

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