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Energy gap from tunneling and metallic contacts onto MgB_2: Possible evidence for a weakened surface layer

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Point-contact tunnel junctions using a Au tip on sintered MgB_2 pellets reveal a sharp superconducting energy gap that is confirmed by subsequent metallic contacts made on the same sample. The peak in the tunneling conductance and the metallic contact conductance follow the BCS form, but the gap values of $4.3-4.6$ meV are less than the weak-coupling BCS value of 5.9 meV for the bulk T_c of 39 K. The low value of Δ compared to the BCS value for the bulk T_c is possibly due to chemical reactions at the surface.

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The surprising discovery[1] of superconductivity in a known, simple binary compound, MgB_2, with a high T_c of 39 K has initiated a flurry of activity to understand its properties. A significant isotope effect[2] strongly implies that phonon coupling is important for the mechanism. To complete this picture, one should observe strong-coupling effects in the electron tunneling density of states and connect them via the Eliashberg theory to the recently measured[3] phonon density of states.

We report here on point-contact tunnel junctions using a Au tip on sintered MgB_2 pellets that reveal a sharp energy gap, Δ, of $4.3-4.6$ meV, a value that is confirmed by subsequent metallic contacts[4] made on the same sample. The peak in the tunneling conductance follows a *thermally* smeared BCS density of states for $T\sim4.2$ K. The contact resistances varied from ~10 to 1200 Ω with the higher values showing tunneling characteristics that exhibit a superconducting gap at low voltages and at high voltages relatively low noise and only a small parabolic conductance correction that implies a high-quality tunneling barrier with a height significantly above 100 meV. Thus these junctions are attractive candidates to explore strong-coupling effects. Initial scanning-tunneling microscopy (STM) reports exhibit significantly smaller gaps[5] or larger in-gap currents and much greater smearing.[6]

An additional advantage of point-contact tunneling is in its ability to form metallic contacts, made *in situ* using the same sample and Au tip. The increased conductance below Δ in metallic contacts is due to Andreev reflections,[7] that are an unmistakable feature of superconductivity, whereas well-developed gap structures in point-contact tunneling and STM could be due to other effects, such as charge-density waves[8] or small-particle charging.[9] In one case we see the factor of 2 conductance increase that is predicted for a metallic contact in the limit of vanishing barrier height,[7] and results in $\Delta=4.3$ meV. However, in both cases, Δ is less than the weak-coupling BCS value of 5.9 meV for the bulk T_c of 39 K, and possible explanations are discussed below.

The MgB_2 sample was synthesized from high purity 3 mm diameter Mg rod and isotopic ^{11}B (Eagle Picher, 98.46 at. % ^{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 UHP Argon at 850 °C. At this temperature the gas-solid reaction was complete in about 1 h. The sample was contained in a machined BN crucible (Advanced Ceramics Corp. grade HBC) with a close-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 powder. The pellets were made by compacting the synthesized powder in a steel die at ~3 kbar and refiring under the same conditions used for the synthesis.

Figure 1 shows the current, *I*, and the differential conductance, dI/dV, plotted against voltage V at a temperature, $T\sim4.2$ K. Included is a fit to the thermally smeared BCS density of states for $T=4.2$ K, $\Delta=4.3$ meV and without a smearing parameter, Γ. Although the agreement in the peak region is acceptable, it is possible that slight sample inhomogeneities affect the width and height of the conductance peaks. An excess current is seen at zero bias and that can also affect the agreement below the peak voltage.

Figure 2 shows a few more of the large number of tun-

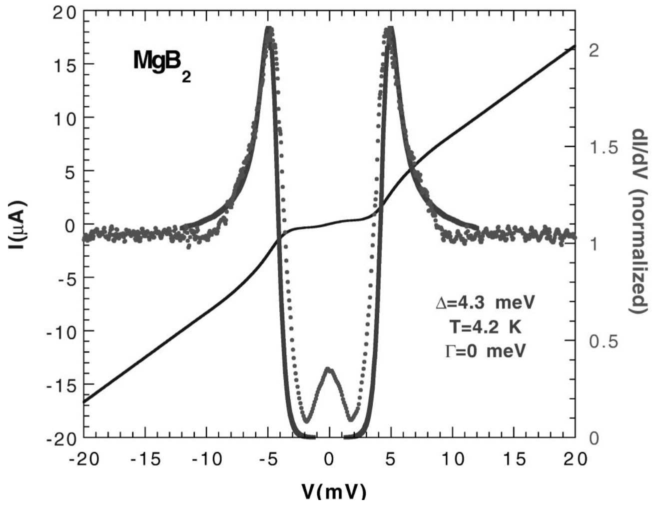

FIG. 1. For a particular point-contact tunnel junction between a Au tip and a sintered sample of MgB_2, the current (thin line) and the differential conductance (small dots) are plotted against voltage V at a temperature, $T\sim4.2$ K. Included is a fit (thick line) to the thermally smeared BCS density of states for $T=4.2$ K.

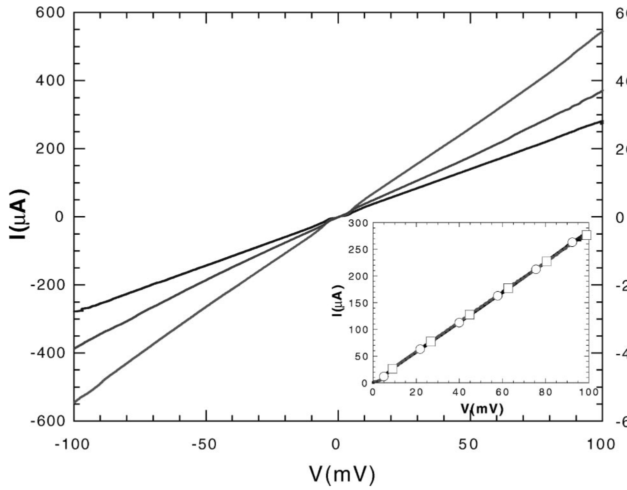

FIG. 2. The main panel shows a few more of the large number of tunneling junctions made. The data exhibit only a small parabolic term in the high-voltage conductance that implies high-quality tunneling with a barrier height significantly above 100 meV. Inset: symmetry of the data with respect to the voltage-bias polarity is shown by a plot of $|I|$ against $|V|$ for both polarities.

neling junctions made. Out to voltages of 100 meV, these low-resistance point-contact tunnel junctions appear electrically stable and show no evidence of heating effects or dielectric breakdown: thus the native barrier is suitable for sensitive spectroscopy measurements. The data exhibit only a small parabolic term in the high-voltage conductance (~20% increase at 100 meV) that implies a high-quality tunneling barrier with a height significantly above 100 meV. It is of interest to compare this to artificial MgO tunneling barriers that have shown[10] excellent tunneling spectra and conductance increases of ~10−15% at 65 meV. Thus it is possible that the native barrier on our MgB_2 pellets is MgO. Strong-coupling effects due to VN phonons (~1% conductance changes) were readily observed in these large area (VN-MgO-Pb) junctions.[10] Thus these point-contact junctions on MgB_2 are attractive candidates to explore strong-coupling effects *over the entire phonon spectrum* that may extend up to ~100 meV. The data are highly symmetric with respect to the voltage-bias polarity, as seen in the inset to Fig. 2 that plots $|I|$ against $|V|$ for both polarities. This result does not particularly support the theory of hole superconductivity.[11]

The observation of a conductance peak at zero bias deserves further discussion, especially in light of the fact that such peaks are used[12] as evidence for a *d*-wave gap symmetry in the high-T_c cuprates (HTS). The peaks in HTS junctions arise from Andreev bound states that develop when quasiparticles scatter off a vacuum interface and change the sign of the order parameter as might occur for *d*-wave symmetry.[13] However, this effect *can be ruled out* as an explanation of our data because of the very sharp coherence peaks found at the gap voltage and the junction to junction variation that is seen in Fig. 3. The Andreev bound state peak removes spectral weight from the coherence peaks and thus they should appear considerably broadened as is found experimentally[12] in HTS junctions and is predicted theoretically.[13] However, as we have shown, our conductance peaks are fit very well by an *s*-wave, BCS density of states, broadened by little more than would be expected from thermal smearing alone. Examination of the *I*-*V* characteristics in Fig. 1 suggests the appearance of a Josephson-like origin for the zero-bias conductance peak. Thus a more likely explanation is a parallel conductance channel, perhaps from a filamentary piece of the MgB_2 that has a low-resistance Ohmic contact to the Au tip and contacts the bulk MgB_2 with a higher-resistance Josephson junction. When the critical current of this contact is exceeded, its large normal-state resistance is shunted by the superconductor-insulator-normal metal junction.

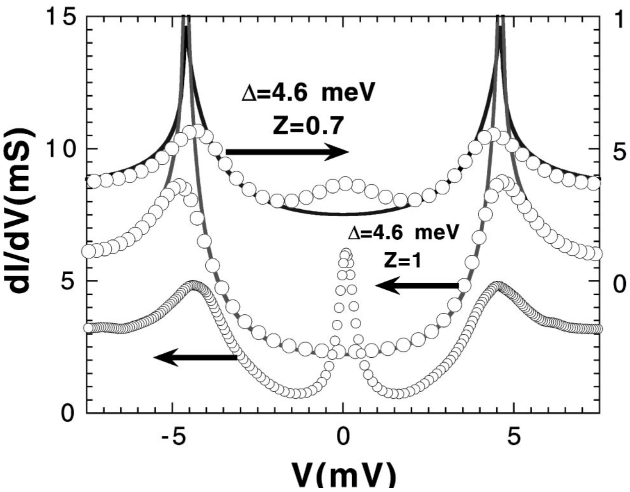

FIG. 3. The low-voltage conductance peaks, shown for the same junctions as in Fig. 2, indicate reasonably sharp coherence peaks, but variable subgap conductivities and zero-bias peaks. One shows the complete absence of the zero-bias peak and two of these are fit to the BTK model using intermediate *Z* values of 0.7 and 1 and $\Delta = 4.6$ meV.

In addition to the tunneling junctions, manipulation of the Au tip could produce the characteristics shown in Fig. 4 of a metallic contact.[4,7] Whereas gaps in point-contact tunneling and STM could be due to other effects such as charge-density waves[8] or small-particle charging,[9] the increased conductance below Δ in metallic contacts is an unmistakable feature of superconductivity, due to Andreev reflections.[7] We find an equally sharp gap feature (also at $\Delta = 4.3$ meV) in the metallic contact of Fig. 4, and a conductance curve that is quite close to the Blonder-Tinkham-Klapwijk (BTK) model[7] that predicts a factor of 2 conductance change (dashed line). The dips seen at zero bias and at larger voltages are not understood but are systematically seen here and in metallic contacts made on $YBa_2Cu_3O_7$ single crystals.[14] Multiple Andreev reflections seem unlikely as the counterelectrode is a normal metal, Au.

In fact, all our data can be fit to the BTK model using its one parameter, the dimensionless barrier strength, *Z*. The *I*-*V* for high-barrier tunneling junctions (e.g., Fig. 1) is found in the limit of $Z \gg 1$, and the pure metallic contact (e.g., Fig. 4) is found for $Z \ll 1$. The conductance data in Fig. 3 are fit with intermediate values of *Z*, in the $T = 0$ limit of the BTK model, and slightly larger gaps, $\Delta = 4.6$ meV. The absence

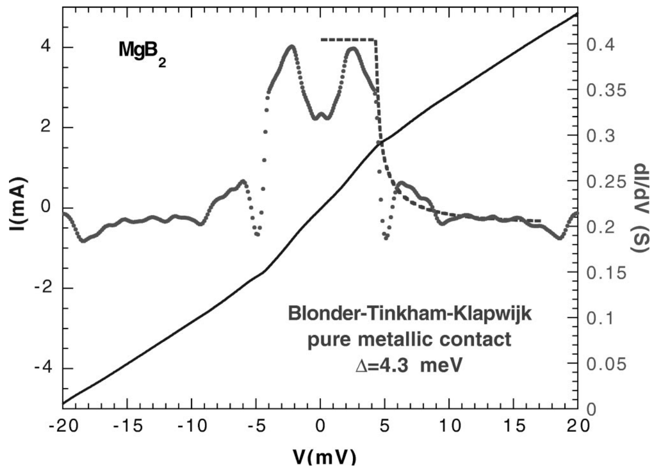

FIG. 4. An equally sharp gap feature (also at $\Delta = 4.3$ meV) is seen in the metallic Sharvin contacts, that exhibit an *I-V* curve (solid line) and conductance curve (small dots) that is quite close to the theoretical prediction (Ref. 7) (dashed line). The dip at zero bias is similar to that seen (Ref. 14) in metallic Sharvin contacts made on $YBa_2Cu_3O_7$ single crystals.

of sharp discontinuities in the data of Fig. 3 reflect the finite temperature, but possibly also sample inhomogeneity.

Since the energy gap values ($4.3-4.6$ meV) are quite robust in a number of junctions and by two techniques, the fact that Δ is consistently smaller than the BCS weak-coupling limit must be taken seriously. In addition, recent NMR results[15] imply the bulk gap is $\sim$40% *higher* than the weak-coupling BCS value. A possible cause of the small Δ is a lower T_c on the surface. Weak-coupling BCS theory would require $T_c \sim 30$ K in our case and about 14 K for Ref. 5. One possibility is a proximity effect with a thin layer that is metallic but with a much lower T_c. However, this would be expected to give additional structure[16] in the conductance curve at the bulk gap and our data show no consistent evidence for this. Chemical modifications of the surface (e.g., MgB_2 reacts with water) can potentially produce a layer with a lower T_c and a BCS-like density of states. If the layer is thick enough the proximity effect becomes secondary. A possible scenario is linked to the high tunneling barrier that is reminiscent of materials such as MgO. Since Mg dopes the B layers, any loss of Mg in the near-surface regions, to form a MgO cap layer, could lead to lower T_c and thus Δ. Hydrogen, or OH^-, must be implicated at least as a catalyst, e.g., H^+ could enter the compound interstitially or as a replacement for missing Mg^{2+} in the MgB_2 structure. It should be pointed out that this would be strictly a surface effect, since Mg vacancies are not stable defects in the bulk.[17] Chemically modified surfaces could also explain the sample-dependent variations of Δ ($4.3-4.6$ meV here and 2.0 meV in Ref. 5). Another possibility is related to pressure effects caused by the point-contact tip, since a decrease of T_c with pressure of 2 K/GPa has been found[18] in MgB_2. The upper limit for the pressure is dictated by the yield stress of the Au tip and handbook values[19] indicate that at low temperatures it is only $\sim$2% of the 5 GPa needed to explain the discrepancy with the BCS energy gap (i.e., a pressure-reduced T_c of ~ 30 K). In addition, the metallic contacts likely result from significantly higher forces on the tip, yet the gap values for a number of junctions with vastly different resistances seem insensitive to this.

In summary, a well-defined relatively sharp energy gap feature at $4.3-4.6$ meV is seen consistently in metallic contacts and high-quality (high-barrier) tunnel junctions. Each are consistent with a BCS density of states that is at most only very slightly smeared. The low value of Δ compared to the bulk T_c is possibly due to a chemically modified surface layer that could also weaken the intergrain coupling of sintered samples.[20] In order to investigate the intrinsic phonon coupling in bulk MgB_2 by tunneling, this weakened surface layer must be eliminated. Our observation of a robust native barrier on MgB_2 could have positive implications for devices, especially if thin films become available.

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