Two-Gap State Density in MgB_2: A True Bulk Property Or A Proximity Effect?

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We report on the temperature dependence of the quasiparticle density of states in the simple binary compound MgB_2 directly measured using scanning tunneling microscope (STM). To achieve high quality tunneling conditions, a small crystal of MgB_2 is used as a tip in the STM experiment. The "sample" is chosen to be a 2H-$NbSe_2$ single crystal presenting an atomically flat surface. At low temperature the tunneling conductance spectra show a gap at the Fermi energy followed by two well-pronounced conductance peaks on each side. They appear at voltages $V_S \simeq \pm 3.8$ mV and $V_L \simeq \pm 7.8$ mV. With rising temperature both peaks disappear at the T_C of the bulk MgB_2, a behavior consistent with the model of two-gap superconductivity. The possibility of a particular proximity effect is also discussed.

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Since January of this year the scientific community has expended considerable effort in order to understand the origin of superconductivity in the simple binary compound MgB_2 [1]. Its high critical temperature $T_C = 39$ K is close to or even above the upper theoretical value predicted by the BCS theory [2]. This was a strong argument to consider MgB_2 as a nonconventional superconductor. However, soon after the discovery of superconductivity in MgB_2, a significant boron isotope effect has been observed [3]. Subsequently, a large body of experimental work has been reported (nuclear spin-lattice relaxation rate measurements [4], inelastic neutron scattering measurements [5], specific heat measurements [6,7]), all supporting an *s*-wave symmetry of the order parameter. On the other hand, measurements of the temperature dependence of the penetration depth [8,9] and of the microwave surface resistance [10] imply the possibility of an unconventional superconductivity. Many attempts to determine the superconducting gap have also been reported, using different techniques: tunneling spectroscopy [11–14], photoemission spectroscopy [15,16], Raman measurements [17], etc. Although the results seem to indicate an isotropic order parameter, they are controversial on the gap width.

Adding to this controversy, the existence of two superconducting gaps in MgB_2 was predicted theoretically by Liu *et al.* [18]. The electronic structure of MgB_2 is quite complex; in particular, the Fermi surface presents both quasi-2D cylindrical sheets and a 3D-tubular network, which raises the possibility of having, in the clean limit, two distinct gaps, both closing at the same critical temperature.

In this Letter we give a direct experimental evidence of the existence of two distinct gaps on the surface of superconducting MgB_2. Using our homebuilt low temperature STM we study the tunneling junction obtained between one small crystal of MgB_2 mounted as the STM tip, and an atomically flat 2H-$NbSe_2$ single crystal. At low temperature the tunneling conductance spectra clearly show a gap followed by a two-peak structure. The temperature dependence of the tunneling spectra, measured with such a superconducting MgB_2 tip, clearly demonstrates that two different gap features coexist up to the critical temperature of the bulk MgB_2.

Up to now, there has been no clear experimental evidence for the existence of two gaps in MgB_2. Characterization of its normal and superconducting states has been done by thermodynamic measurements [19,20]. As a result, the existence of a multiple-valued gap was suggested. Photoemission spectroscopy has also been performed on MgB_2 [15], revealing a spectral shape that cannot be explained by the existence of a simple isotropic gap. However, the low energy resolution, together with the observation that both gaps were smaller than the BCS value (5.9 mV), did not allow any firm conclusion about the superconducting density of states (DOS) of bulk MgB_2.

On the other hand, vacuum tunneling spectroscopy is a technique allowing a direct measure of the quasiparticle DOS with high energy resolution. Moreover, most of the studies having been done on naturally inhomogeneous granular samples, scanning tunneling spectroscopy (STS) appears as the major tool with its high spatial and energy resolution. Double-gap structures in the differential conductance spectra have been indeed observed by STS [21] but only locally in some selected regions of a granular sample of MgB_2. This observation alone does not allow one to elucidate the nature of such a feature in the conductance spectra. While it is consistent with two-gap superconductivity in MgB_2, it could in principle have different origins. For example, two tunneling terms may exist, one small, indeed reflecting the DOS of the bulk material, and another dominant state density of the weakened superconductivity of the surface. The existence of such a weakened layer on the very surface was already suggested in previous studies [11,14]. It is not excluded that the double-gap DOS originates from the superconductivity induced by the proximity effect in a thin metallic surface layer [22].

The study of the temperature dependence of the tunneling spectra is therefore necessary to clarify the origin of these particular features. This requires an STM experiment in which the tunneling junction remains stable, unaffected by the thermal drift due to the temperature variations, which is almost impossible to achieve with powder-based inhomogeneous samples. As a result of such an inhomogeneity, small lateral movements of the tip due to the thermal expansion of the STM unit cause dramatic changes in the junction characteristics. The most straightforward solution to avoid the effect of lateral drift would be the use of high quality thin films or single crystals of MgB_2; the sample surface being in such a case flat and the DOS spatially homogeneous. These samples are still, unfortunately, unavailable.

As a simple measure, we inverted the tunneling junction in our experimental setup. A small (about 50 μm size) crystal of MgB_2 is glued with silver paint on the flat top of a mechanically etched Pt/Ir wire, and a 2H-$NbSe_2$ single crystal is taken as the sample [Fig. 1(a)]. $NbSe_2$ is a layered material presenting, after cleavage, an atomically flat and highly inert surface. It is a conventional superconductor with $T_C = 7.2$ K, and thus, for higher temperatures the experimental configuration corresponds to a *S-I-N* junction. At lower temperatures it is a *S-I-S* one, but this fact does not affect the spectroscopy for the temperature range studied, since $NbSe_2$ is characterized by a small gap, practically smoothed out at $T = 4.2$ K.

Geometrically such a junction is stable with respect to thermal drift, due to a fixed tip-surface orientation. Moreover, 2H-$NbSe_2$ being a well-known and widely studied material, the quality of the MgB_2 tip is easily tested by direct STM imaging. Such an image is presented in Fig. 1(b). Both atomic and charge density wave (CDW) patterns, characteristic of 2H-$NbSe_2$, are evident there, and even a point defect locally perturbing the translational order of the CDW is resolved. Such a situation clearly corresponds to vacuum tunneling. The high quality of the junction is independently confirmed by the flat spectral background observed in the $dI(V)/dV$ curves at $T = 4.3$ K, as in Fig. 1(c) [23]. These two results unambiguously show that the STM tip apex is not contaminated

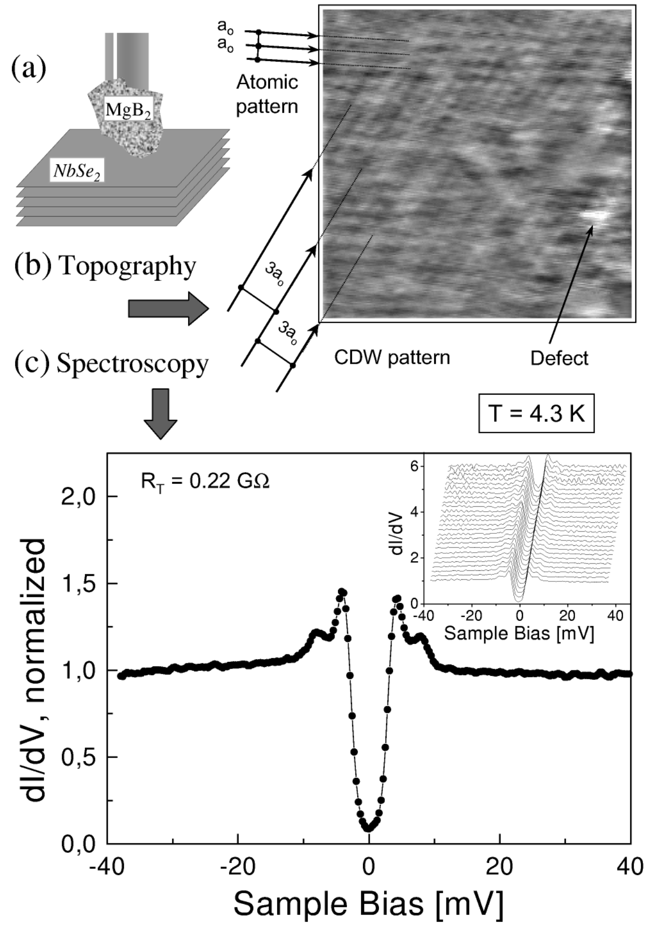

FIG. 1. (a) Experimental setup. (b) An 8 nm × 8 nm topographic image of sample surface ($T = 4.3$ K, $I_T = 150$ pA at $V_{bias} = -18$ mV). The atomic lattice and a CDW pattern are resolved. (c) Typical $dI(V)/dV$ spectrum. Inset: series of spectra taken along a 10 nm line.

and manifests a metallic behavior. In the spectrum of Fig. 1(c), the double-gap features are clearly observed: well defined coherence peaks appear at $V_S \simeq 3.8$ mV, followed by bumps at higher energy $V_L \simeq 7.8$ mV. The spectra show very few states inside the gap; they are independent of tunneling resistance R_T and of lateral position of the tip [see inset of Fig. 1(c)]. The curves are almost identical to those previously observed in standard *S-I-N* geometry on a granular sample of MgB_2 using Pt/Ir tip [21].

Using such a high quality tunnel junction, we performed the tunneling spectroscopy in the temperature range between 4.3 and 45 K. The results of this experiment are reported in Fig. 2. The overall trend is a smoothing of the gap features, and an increase of the number of states inside the gap, with rising temperature. The curves up to 10 K have a clear double-peak shape, confirming that it is an intrinsic behavior of the superconducting MgB_2 electrode. For higher temperature values, the filling of the gap continues, however. Enlarging the scale of the curves measured

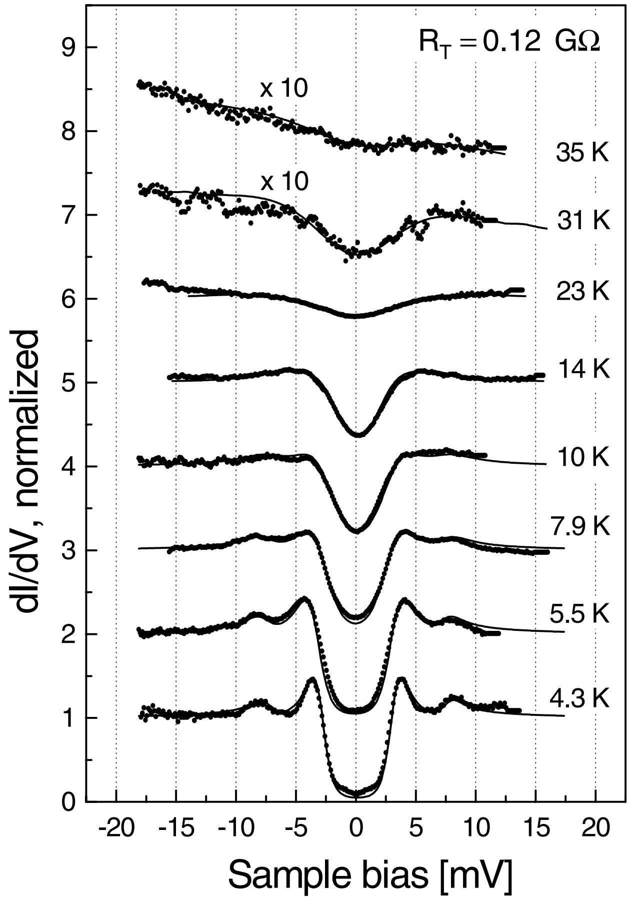

FIG. 2. Temperature dependence of tunneling conductance spectra in the range between 4.3 and 35 K. All experimental curves (black dots) are fitted by a sum of two weighted BCS-shape DOS (solid lines). The spectra are shifted by unity for clarity. The curves at $T = 31$ K and $T = 35$ K are reported magnified by a factor of 10.

for $T > 30$ K in Fig. 2, it is evident that the depletion at the Fermi level is still present.

Such a temperature dependence is nontrivial. To obtain a more precise description, a proper fit to the tunneling spectra is very useful. As a first step, we fit the experimental data in Fig. 2 by considering the weighted sum of two contributions ($\sigma^{(L)}, \sigma^{(S)}$) corresponding to two isotropic BCS-like DOS. The fitting formula is written

$$\sigma(V,T) = \sum_{x=L,S} C_x \cdot \sigma^{(x)}(V,T), \qquad (1)$$

where $\sigma^{(x)}$ is the tunneling conductance for the *S-I-N* geometry, considering also the effect of the thermal smearing, the damping parameter Γ, and the weight factors C_x of the two contributions ($C_L + C_S = 1$). The fit parameters at $T = 4.3$ K are $\Delta_L = 7.5$ mV, $\Delta_S = 3.5$ mV, $C_L = 0.9$ ($C_S = 0.1$), and $\Gamma = 0.15$ mV, where Γ is the same for both densities [24]. These values give a BCS ratio ($2\Delta/k_BT_C$) of 4.5 for the large gap and 1.9 for the small one, i.e., respectively, well above and well below the weak coupling limit, 3.52.

Once determined from the fits at $T = 4.3$ K, the weight factors (C_L and C_S) and Γ are kept fixed in all other fits for higher temperatures. Thus, Δ_L and Δ_S remain the only two free parameters. The success of this simple approach is evident in Fig. 2, all fits (solid lines) concur extremely well with the experimental data. The two curves for $T > 30$ K are enlarged by a factor of 10, being near the superconducting transition. In fact, in this temperature region, the contribution of the small gap is strongly smeared by the temperature, while the effect of the large gap remains small due to its low spectral weight $C_L = 0.1$. In spite of this, even at these temperatures it is still possible to determine a value for each gap although with larger uncertainty.

In comparison to the good match between the experimental data and the fit curves, one may suppose that the spectra measured for $T > 15$ K are not double gapped. To clarify this, we fitted the spectra of Fig. 2 by only one BCS-like DOS. In this case one obtains an extremely large smearing term ($\Gamma > \Delta$), in contradiction with the low temperature results. In any case, the latter fits are not as satisfactory as those using two BCS terms.

In Fig. 3, the gap widths derived from the fit values are plotted as a function of temperature. Here the uncertainty bars are determined independently for each data set. It is immediately evident that both gaps vanish at a temperature close to the T_C (~39 K) of bulk MgB_2. The BCS ratio $2\Delta(0)/k_BT_C$, extracted from the 4.3 K spectra, is 4.5 and 1.9, respectively, for Δ_L and Δ_S. The two gaps vary in a different way with temperature: the small gap reduces more rapidly than the large one. Thus, the ratio Δ_L/Δ_S between the two gaps increases with temperature.

Recently, it has been suggested [21] that, in principle, the particular tunneling conductance spectra showing two gap features may originate from different physical scenarios. One possibility is the presence at the MgB_2 surface of a contaminated layer responsible for a weak superconductivity. Of course, this could explain the observation of double-gap features as due to two tunneling channels (one in the weak layer and another one directly in the bulk

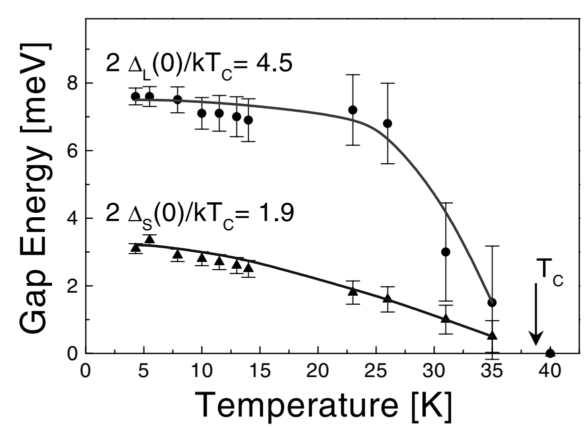

FIG. 3. Evolution of the gaps with the temperature. Both gaps close near the T_C of the bulk MgB_2.

material), but cannot account for the small gap survival right up to the bulk T_C.

On the other hand, these data seem to confirm the existence of a multiple-gap superconductivity, as theoretically predicted, originating from the complicated Fermi surface of MgB_2 together with an interband anisotropic coupling. In this scenario, the two gap features represent a bulk superconducting property, giving the first direct experimental proof that MgB_2 is the precursor of a new class of multiple-gap superconductors. Although the possibility that the presence of two overlapping bands can result in the observation of a two-gap spectrum for conventional superconductors was predicted many years ago [25], until now no experimental evidence has been found for conventional materials. This is probably because their usually large coherence length has made the appearance of two-gap spectra unrealistic, being difficult to realize the clean limit condition. Only the unconventional Nb-doped $SrTiO_3$ has revealed a two-gap spectrum [26].

These conclusions must still be taken with a grain of salt [27], and one must discuss a second possible interpretation of the spectra we described here. It is generally claimed that in the case of superconductivity induced by the proximity effect in a metallic surface layer, the large gap feature is connected to the bulk superconductivity, while the proximity induced small gap should be related to a lower critical temperature. This is correct only when the metallic layer is not "too thin." If the ratio of the mean free path to layer thickness becomes large, and the *N-S* interface presents a small transmittivity, it is possible that the smaller induced gap shows a critical temperature close to or even equal to the bulk transition temperature. This behavior has already been observed in tunneling experiments on tin-lead sandwiches [28]. However, the fact that the width of the induced gap depends on the metallic layer thickness suggests that this could not be the right scenario to explain our observations. Indeed, our data, in addition to those reported for low temperature [21], indicate statistically a value of 3.5 ± 0.5 mV for the small gap with no large variations, which would be expected in the case of random thickness values of the "normal layer."

Very recently it has also been suggested [29] that the double structure observed at low temperature in the tunneling spectra can be explained by the existence of a low-frequency phonon mode at 8 mV revealed in the inelastic neutron scattering experiment [30]. Although the calculation [29] is in good agreement with the low temperature spectra, the temperature dependence reported here and the data in Fig. 2 of [21] contradict this model.

In conclusion, we have reported the temperature dependence of the tunneling DOS on superconducting MgB_2. To avoid the problem of thermal drift and to obtain optimal tunneling conditions we have realized an STM experiment with a superconducting tip (small MgB_2 crystal) and a normal and atomically flat sample. Double-gap features are clearly observed in the conductance spectra, and their temperature dependence showed that both close at the bulk T_C, strongly suggesting the existence of two-gap superconductivity.

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