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Direct observation of the superconducting gap of Sr_2RuO_4

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We report the direct observation of the superconducting gap of Sr_2RuO_4, by means of tunnelling spectroscopy. The tunneling conductance parallel to the *c* axis was measured using a scanning tunneling microscope operating in a dilution refrigerator. Our results show a suppression in the density of states of Sr_2RuO_4, which disappears at temperatures higher than T_c or in the presence of a magnetic field larger than the critical field. This demonstrates that superconductivity persists up to the crystal surface and allows us to infer a lower limit of 8.0 for $2\Delta_{max}/kT_c$ in the bulk. We attribute this large value to a strong in-plane anisotropy of the gap.

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Sr_2RuO_4 is a layered compound that exhibits spin-triplet superconductivity below 1.5 K.[1] Although a lot is known about the electronic structure and the superconducting properties of this material,[2] no investigation of the low-energy density of states in the superconducting regime has been performed so far. For this reason, also, no direct observation of the superconducting energy gap has been reported. The knowledge of the low-energy density of states and of the superconducting gap are of interest, since they can assist in the determination of the vector order parameter describing the superconducting state of Sr_2RuO_4, which is currently unknown.

At present, the only attempt to perform energy-resolved spectroscopy on Sr_2RuO_4 in the superconducting state is due to Laube *et al.*,[3] who recently performed point-contact spectroscopy experiments below T_c. In order to extract a value for Δ from the experiments, these authors assumed a vector order parameter $\mathbf{d}(\mathbf{k})=(k_x \pm ik_y)\mathbf{z}$ to interpret the measured differential resistance in terms of Andreev bound states. It was concluded that Δ in Sr_2RuO_4 is isotropic (in two dimensions) and equal to 1.1 meV, for crystals whose T_c was lower than the optimal value (1.5 K). This corresponds to a surprisingly large value for $2\Delta/kT_c \simeq 20$. Since the value of Laube and co-workers is an indirect estimate of Δ based on the assumption of a specific order parameter, it is important to measure the superconducting gap of Sr_2RuO_4 directly to assess the validity of this result. This also because recent experiments indicate that $\mathbf{d}(\mathbf{k})=(k_x \pm ik_y)\mathbf{z}$ may not be the correct order parameter for Sr_2RuO_4.[2]

In this paper we report the direct observation of the superconducting gap in single crystals of Sr_2RuO_4 by means of scanning tunneling spectroscopy. At $T=80$ mK the density of states (DOS) exhibits a low-energy suppression and BCS-like peaks occurring at a bias between 380 and 500 μeV. This effect disappears when the temperature is increased above the superconducting critical temperature $T_c \simeq 1.5$ K and when a magnetic field larger than $\simeq 700$ G is applied perpendicular to the RuO_2 planes. We conclude that what we observe is a manifestation of superconductivity, which persists up to the crystal surface. We identify the position of the BCS-like peaks with the maximum (in *k* space) value of the energy gap (Δ_{max}) at the surface, from which we obtain a lower bound for $2\Delta_{max}(0)/kT_c=8.0$ in the bulk. This is substantially larger than what is expected for a isotropic gap in the weak-coupling regime. We attribute such a large value for $2\Delta_{max}(0)/kT_c=8.0$ to the gap anisotropy in the RuO_2 plane.

The measurements reported in this paper have been performed using a home-built scanning tunneling microscope (STM) mounted in the inner vacuum can of a Kelvinox 100 dilution refrigerator. The base temperature of the mixing chamber during STM measurements is $\simeq 80$ mK, much lower than the T_c of Sr_2RuO_4. The basic configuration of the STM and of the cryogenic system has been described in detail elsewhere.[4] High-frequency filtering of the sample and tip wires has been incorporated, by letting these wires pass through a 10-cm-long hollow copper cylinder thermally anchored to the mixing chamber and filled with fine copper powder.

Sr_2RuO_4 crystals were grown by a floating-zone method in an infrared image furnace[5] and had a T_c of 1.42 K, as determined by ac susceptibility measurements. At the beginning of every measurement run a crystal was glued to the STM sample holder using conducting silver epoxy, cleaved and mounted on the STM head inside the dilution refrigerator. The system was then evacuated and cooled to 4.2 K.

Images of the crystal surface taken at 4.2 K are shown in Fig. 1. Different set-point voltages (between 40 mV and 1 V) and tunneling currents (between 50 and 200 pA) were used, with no substantial difference in the image quality. The surface (normal to the *c* axis) exhibits large flat terraces, sometimes as large as our scanning field ($\simeq 0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ at 4.2 K), but no clear atomic resolution was achieved. In order to better characterize the conditions of the surface, photoemission spectroscopy measurements were performed on samples prepared in the same way as those used for the tunneling experiments. The photoemission data show a Fermi

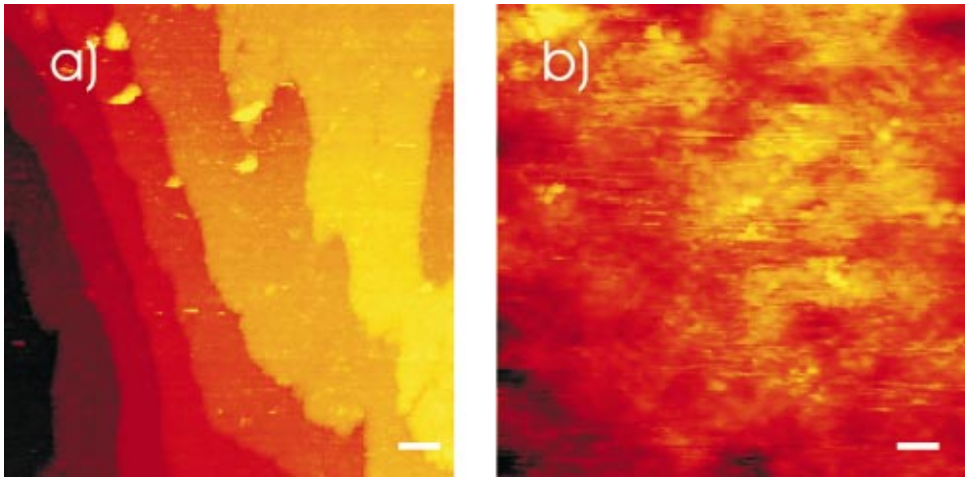

FIG. 1. (Color) Unfiltered images of an in-air cleaved Sr_2RuO_4 crystal, taken at 4.2 K. (a) On a larger scale (the white bar is 50 nm long) flat terraces are visible. The terrace height corresponds to the thickness of a unit cell (1.28 nm), within the accuracy of the STM calibration. (b) Although a rather regular structure is visible on a smaller scale (the white bar is 2 nm), no clear atomic resolution has been achieved.

edge and energy-resolved features originating from the valence bands of Sr_2RuO_4.[6] These observations (along with the flat terrace structure observed by STM) indicate that the surface is metallic and no major chemical degradation has taken place, in spite of some disorder introduced by the in-air cleaving procedure.

Tunneling spectroscopy at base temperature was performed on three crystals, repeatedly cleaved and used in different measurement runs. The STM tip (Pt/Ir) was stabilized at the desired set-point voltage (normally 5 mV) and tunneling current (between 100 and 600 pA), after which the STM feedback was disengaged. The differential conductance was measured using a lock-in amplifier in a standard configuration where a dc bias was applied to the STM tip, together with a small, low-frequency ac modulation. The modulation amplitude was varied between 10 and 50 μV without observing any difference in the experimental results. This is consistent with an effective electron temperature of the tunneling electrons of $T_{eff}=500$ mK (larger than the crystal temperature, 80 mK), as deduced in separate experiments using the same setup, by measuring and fitting with the BCS theory tunneling curves from an Al tip into a Au substrate (Fig. 2, inset).

Typical dI/dV vs V spectra measured on the surface of Sr_2RuO_4 are shown in Fig. 2. The data exhibit a suppression of the tunneling conductance that is reproducibly observed in all samples. The magnitude of the suppression is $\simeq 15\%$ in all crystals; the energy at which the suppression sets in ranges from 380 to 500 μeV. To demonstrate that this suppression is due to superconductivity in Sr_2RuO_4, we have investigated its temperature and magnetic-field dependence.

The low-energy suppression in the DOS should disappear when $T>T_c$ if its origin is related to superconductivity. Since our dilution refrigerator cannot be operated under stationary conditions above 1 K, we measured in this temperature range by stopping the circulation of ^{3}He and letting the mixing chamber warm up slowly, over the course of several hours. The data [see Fig. 3(a)] show that the low-bias suppression in the differential conductance decreases as the temperature is increased, and that it eventually disappears between 1.6 and 1.7 K. The difference between this value and the value of T_c measured by ac susceptibility originates from a small temperature gradient that develops between the sample and the thermometer, as the dilution refrigerator is warmed above 1 K.

A magnetic field applied perpendicular to the RuO_2 planes also suppresses the dip in the density of states [Figs. 3(b) and 4]. The dip disappears completely at a field between 600 and 800 G,[7] which compares well to the expected critical field ($H_{c2}=750$ G). This indicates that the low-energy suppression in the DOS disappears when the crystal is driven into the normal state by a magnetic field.

We conclude that the dip in the density of states is due to superconductivity, which persists up to the surface of Sr_2RuO_4. The persistence of superconductivity at the crystal surface is of particular interest in view of the recent proposal

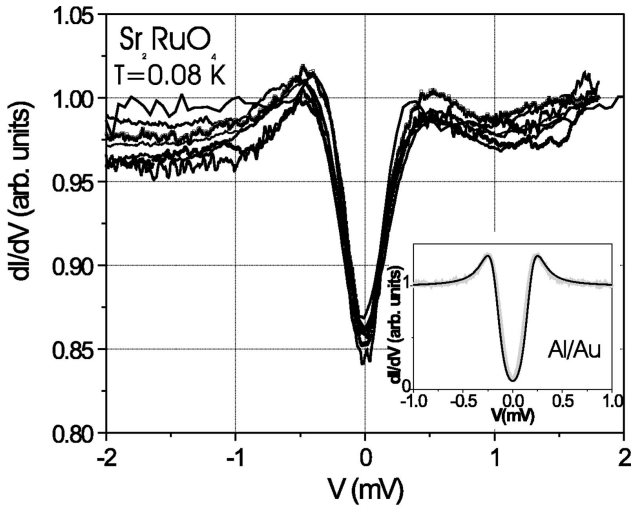

FIG. 2. Tunneling spectra measured at 80 mK on different crystals or at different locations of a same crystal (dI/dV is normalized to the value at $V=2$ mV, for ease of comparison). A $\simeq 15\%$ suppression of the conductance at low bias is observed in all curves, demonstrating the reproducibility of our results. The position of the side lobes varies from 380 to 500 μV. The inset shows the tunneling conductance of an Al tip on Au substrate (thick gray line) and its fit according to BCS theory (black line), from which we infer an effective electron temperature of 500 mK (larger than the crystal temperature) which sets the energy resolution of our measurements.

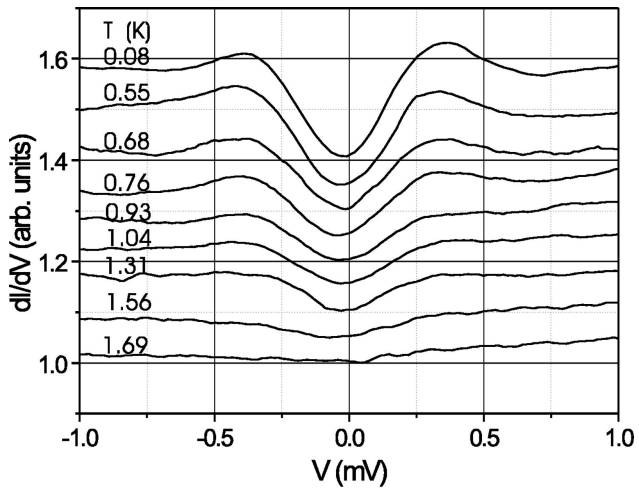

FIG. 3. Tunneling conductance as a function of bias, measured at different temperatures showing that the low-bias suppression of the conductance disappears above T_c (curves are offset for clarity).

of surface ferromagnetism in Sr_2RuO_4,[8] since it allows the possibility that superconductivity may coexist with ferromagnetism at the surface of this material (note, however, that surface ferromagnetism in Sr_2RuO_4 has been questioned by very recent angle-resolved photoemission spectroscopy experiments[9]).

The side lobes observed in the tunneling spectra at $\pm 380-500\ \mu$V are a direct manifestation of the singularity in the DOS expected at Δ_{max}, the maximum value of the energy gap in k space. Within the BCS theory, a peak in the DOS located at Δ_{max} is predicted to exist for essentially all superconducting states.[10] The shape (but not the location) of this peak depends on the specific state and, for unconventional superconductors, it is smoothed by the presence of disorder. Therefore, at sufficiently low temperature,[11] the value of bias voltage corresponding to the maximum of tunneling conductance is a good measure of Δ_{max}. This means that we do not have to assume any specific order parameter to infer the value of Δ_{max} from our data.

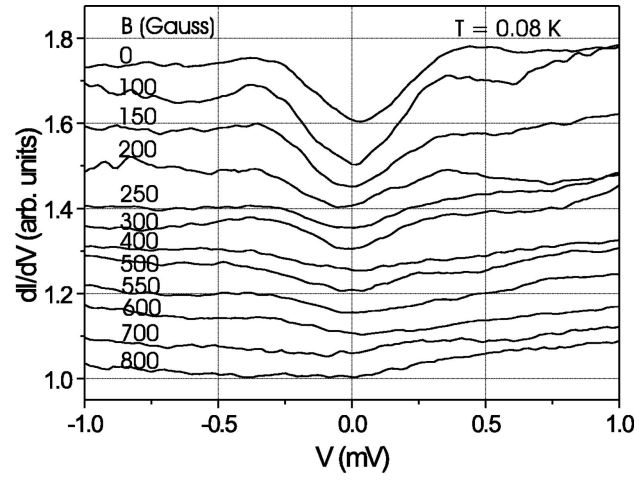

FIG. 4. Tunneling conductance as a function of bias, measured for different values of the applied magnetic field (the magnetic field is applied perpendicular to the RuO_2 planes; curves are offset for clarity). The data show that the low-bias suppression of the conductance disappears above the critical field.

From the experimental data we obtain a $2\Delta_{max}/kT_c$ ratio that lies between 6.2 and 8.0 in different crystals and different locations of the same crystal. Such a spread in values for Δ_{max} can be accounted for by the surface disorder. Our results therefore set a lower limit of 8.0 for $2\Delta_{max}/kT_c$ in the bulk of Sr_2RuO_4, much larger than the usual BCS value $2\Delta/kT_c=3.52$.

Within the BCS theory, deviations from the value of $2\Delta/kT_c=3.52$ can originate from either strong-coupling effects or from a large anisotropy of the gap at the Fermi surface.[12] It is unlikely that strong-coupling effects are responsible for our observation, since a value of $2\Delta/kT_c=8$ would imply the presence of very large strong-coupling effects, whereas no experimental evidence for these effects has been reported so far in Sr_2RuO_4. On the contrary, experimental evidence exists for the presence of a sizable anisotropy in the a-b plane, at least in the normal state of this material.[13]

Among the main theoretical models currently considered for the description of superconductivity in Sr_2RuO_4, those based on a f-wave order parameter[14] exhibit a strong in-plane anisotropy of the superconducting gap (and so they are, in principle, compatible with our observations). Within the multiband model of Zhitomirsky and Rice,[15] the large measured value of $2\Delta_{max}/kT_c$ could only originate a strong anisotropy of the magnitude of the gap in the active γ band. This anisotropy may be due, for instance, to an angular dependence of the pairing interaction. Since the order parameter in the active band is also essentially two dimensional (the dispersion in the z direction is important for the passive bands only), even in the multiband model the large value of $2\Delta_{max}/kT_c$ indicates the presence of in-plane anisotropy.

The anisotropy associated with the limit found for $2\Delta_{max}/kT_c$ is *compatible* with the presence of a vertical line of nodes in the superconducting gap of Sr_2RuO_4 (such as those occurring in an f-wave state). To show this, we consider the example of a gap with a vertical line of nodes described in two dimensions by $\Delta=\Delta_0\cos(\phi)$. This gap function has been used by Ishida *et al.*[16] to fit quantitatively the power-law temperature dependence of the nuclear spin-lattice relaxation rate in Sr_2RuO_4. With this angular dependence $\Delta_{max}=\Delta_0$ and $\Delta_{av}=2\Delta_0/\pi$. If Δ_{av}, the average of the gap around the Fermi surface, is related to kT_c by the standard BCS weak-coupling relation ($2\Delta_{av}/kT_c=3.52$), we find that $2\Delta_0/kT_c=5.5$, which is smaller than the lower limit established by our tunneling experiments. Note however that our data do not *require* the presence of vertical lines of nodes, since they can also be accounted for by a very strong in-plane anisotropy of Δ without any node. This is important, since the occurrence of vertical lines of nodes in Sr_2RuO_4 has been claimed to be inconsistent with the results of recent experiments probing the angular dependence of the superconducting gap.[17] In any case, irrespective of whether or not vertical lines of nodes are present, the large value of $2\Delta_{max}/kT_c$ indicates that the angular dependence of Δ in Sr_2RuO_4 is nontrivial.

Since tunneling spectroscopy experiments directly probe

the density of states at the crystal surface, a comparison with theoretical predictions is, in principle, possible. We have estimated the suppression of low-energy DOS within the model of Zhitomirsky and Rice[15] and for a gap with a vertical line of nodes [$\Delta=\Delta_0\cos(\phi)$], and in both cases we have found that the expected suppression is more than four times larger than the one measured. This is because disorder at the surface introduces states at subgap energies that dominate the measured subgap DOS.[10] Since existing models for Sr_2RuO_4 do not consider the effect of impurity scattering, theoretical calculations largely overestimate the suppression in the subgap DOS observed in our experiments. Note that, although vacuum cleaving would reduce the amount of disorder, it is not clear whether this would help the study of superconductivity. This is because the surface of Sr_2RuO_4 crystals cleaved in vacuum undergoes a reconstruction[8] that modifies its electronic properties[9] and that would most likely affect the superconducting properties as well.

The limit on $2\Delta_{max}/kT_c$ that we have found in our experiments is compatible with the results of Laube and co-workers[3] mentioned in the beginning. However, on the basis of the considerations made above, we believe that the interpretation of those point-contact experiments is questionable. This is because the superconducting gap corresponding to the order parameter $\mathbf{d}(\mathbf{k})=(k_x\pm ik_y)\mathbf{z}$ used to interpret the data is isotropic in two dimensions. For an isotropic gap, the expected value for $2\Delta/kT_c$ is 3.52, which is more than five times smaller than the value inferred ($2\Delta/kT_c\simeq 20$) in Ref. 3. In view of this large discrepancy, a quantitative interpretation of the point-contact spectroscopy data in terms of $\mathbf{d}(\mathbf{k})=(k_x\pm ik_y)\mathbf{z}$ seems not to be self-consistent and the value of $\Delta=1.1$ meV inferred in Ref. 3 too large.

In conclusion, we have performed scanning tunneling spectroscopy experiments on high quality Sr_2RuO_4 crystals in the superconducting state, which have allowed the direct observation of the superconducting gap in this material. We have shown that superconductivity persists up to the surface of Sr_2RuO_4 and have found a lower limit of 8.0 for $2\Delta_{max}/kT_c$ in the bulk. This value is considerably larger than the value expected for a weakly coupled superconductor with a uniform gap and it originates from a strong (in-plane) anisotropy of the superconducting gap.

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[7] Note that Sr_2RuO_4 is a type-II superconductor [T.M. Riseman *et al.*, Nature (London) **396**, 242 (1998)] and in the presence of a magnetic field vortices are present. We have not been able to image the vortex lattice with our STM and therefore at intermediate field we cannot tell where the DOS is measured, relative to the position of the vortices. The apparent closing of the gap as the magnetic field is increased is probably related to this, i.e., the tunneling spectra can have been taken within a few coherence lengths from the center of vortex. This is likely because the coherence length in Sr_2RuO_4 is rather large (66 nm) and the scanning field of our microscope at low temperature is 500×500 nm^2.

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[11] In general, the statement that within the BCS theory the position of the peak in the DOS corresponds to Δ_{max} is strictly correct only at $T=0$ K. At finite temperature the position of the peaks in the DOS is shifted to higher energy. This shift is due to the convolution of the Fermi distribution with an asymmetric DOS. For instance, in *s*-wave superconductors the DOS vanishes at energy smaller than Δ and is very large just above Δ (for aluminum this shift is visible in the inset of Fig. 3). In the present case of Sr_2RuO_4 the asymmetry of the DOS around Δ_{max} is small (the low-energy suppression in the DOS is only 15%) and the effective temperature ($T_{eff}=500$ mK$\simeq 40$ μeV) is much lower than Δ_{max} (>500 μeV). Therefore at the lowest temperature of our measurements the shift in the position of the peak in the DOS with respect to Δ_{max} is negligible (less than 10%). As a confirmation we note that in Al (see inset of Fig. 2) this shift is only 50 μeV (at the same T_{eff} used in the Sr_2RuO_4 experiments), in spite of large asymmetry in the DOS present around Δ.

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