First direct observation of the Van Hove singularity in the tunnelling spectra of cuprates

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In two-dimensional (2D) lattices, the electronic levels are unevenly spaced, and the density of states (DOS) displays a logarithmic divergence known as the Van Hove singularity (VHS). This is the case in particular for the layered cuprate superconductors. The scanning tunnelling microscope (STM) probes the DOS, and is therefore the ideal tool to observe the VHS. No STM study of cuprate superconductors has reported such an observation so far giving rise to a debate about the possibility of observing directly the normal state DOS in the tunnelling spectra. In this study, we show for the first time that the VHS is unambiguously observed in STM measurements performed on the cuprate $Bi_2Sr_2CuO_{6+\delta}$ (Bi-2201). Beside closing the debate, our analysis proves the presence of the pseudogap in the overdoped side of the phase diagram of Bi-2201 and discredits the scenario of the pseudogap phase crossing the superconducting dome.

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The scanning tunnelling spectroscopy (STS) is known to probe the density of states (DOS)[1,2], and a logarithmic peak is therefore expected in the tunnelling spectrum of materials having a Van Hove singularity (VHS) near the Fermi level. However, there is a strong theoretical debate around the possibility to observe such features in tunnelling spectra. The compelling absence of such a peak in the tunnelling spectra of the cuprates has lead to claims that the normal state DOS would in fact be cancelled just like as in ideal planar tunnel junctions[3,4]. An alternative is that the VHS peak is suppressed because of the interaction of electrons with collective excitations[5–7].

Among the cuprates, $Bi_2Sr_2CuO_{6+\delta}$ (Bi-2201) has a combination of two properties required for an optimal STS investigation of the VHS: it is nearly 2D and has a low maximal T_c of around 12 K giving access to the normal state at low temperature. Producing large and pure non-cation-doped single crystals of Bi-2201 is difficult and consequently, this compound has attracted little attention. We succeeded in growing such crystals and tuning their macroscopic doping level[8], allowing doping-dependent STS studies.

In this study, we demonstrate that the VHS is directly seen in the tunnelling spectra of Bi-2201. We observe that all the spectra can be fitted by a model involving a VHS and a *d*-wave gap as described in the theory by Bardeen, Cooper, and Schrieffer (BCS). This suggests that the VHS shows up in the low T_c Bi-2201 because of a weak coupling to collective modes. Moreover, our measurement at a temperature above T_c of a heavily overdoped Bi-2201 sample clearly exhibits a gap feature that we interpret as the signature of the pseudogap phase.

Results

STM data for overdoped Bi-2201 samples. Low temperature spatially resolved STS of an as-grown sample (AG11K) with $T_c = 11$ K and a transition width $\Delta T_c = 4.5$ K is depicted in Figure 1. Most of the surface presents spectra with a clear superconducting gap in the 15–45 meV range. However, extended regions covering 11% of the sample exhibit qualitatively different spectra, without a gap but with a single sharp peak 10–40 meV below the Fermi energy. A broadly peaked background has been seen earlier in Bi-2201 but only at high temperature[9]. The observation of this new type of spectra at low temperature, which we attribute to the VHS, is our main finding. To each spectrum, we assign a characteristic energy E_p which is either the peak to peak gap value (if two peaks are detected) or the energy position of the single peak. The transition between the two characteristic kinds of spectra is remarkably gradual and reproducible, both spatially (Fig. 1d) and when the spectra are sorted according to the value of E_p (Fig. 1a). The general trend is that as the height of the peak decreases, a coherence peak emerges at positive energy signalling the opening of the gap, and the negative-bias peak shifts to larger negative energy. The nanometre-sized red to yellow areas corresponding in Figure 1b to single-peak spectra are all surrounded by green regions that have small gaps.

We have then acquired E_p maps and the corresponding histograms for two overdoped samples (OD10K and OD7K; Fig. 2). A comparison of the histograms reveals a steady increase in the number of single-peak spectra with doping from 11% at $T_c = 11$ K to 28% at $T_c = 10$ K and 48% at $T_c = 7$ K. The mean peak position also shifts towards the Fermi energy with values -28, -26 and -21 meV at $T_c = 11$, 10 and 7 K, respectively, as expected in a rigid-band picture. Along with the increased proportion of single-peak spectra with increasing overdoping, we also observe a decreased proportion of wide-gap spectra that are excluded from the histograms, as one or both coherence peaks are missing. These spectra (depicted as black pixels in the E_p maps) have a proportion of 28% in AG11K, 6% in OD10K and 5% in OD7K. Much of this decrease is an effect of the postannealing treatments, which favour a more homogeneous distribution of oxygen, as confirmed by the drop in the superconducting transition width ΔT_c.
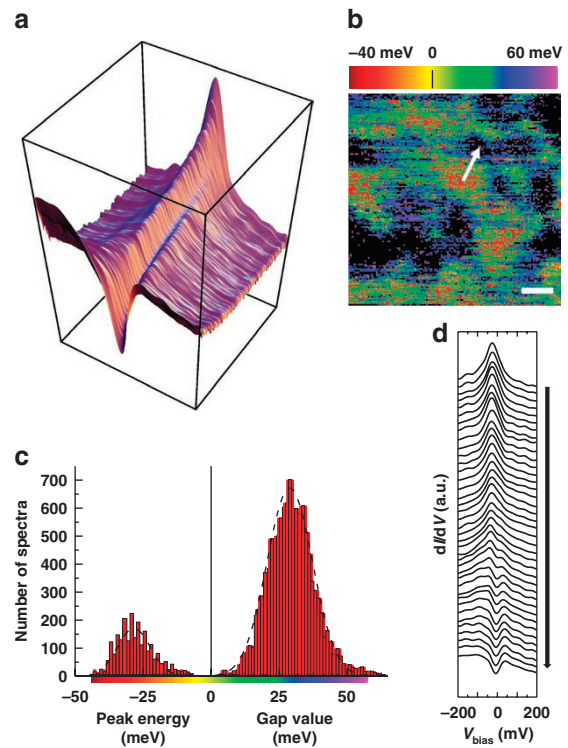
**Figure 1 | Low-temperature (5 K) STS spectroscopy of as-grown Bi-2201 (AG11 K).** (**a**) Three-dimensional overview of the data: each curve is the average of 60 spectra sharing the same E_p value (E_p is the peak position for single-peak spectra, and half the peak-to-peak distance for two-peak spectra); the curves are sorted by increasing E_p. Note the smooth transition between completely different curves at extremal values of E_p. (**b**) E_p map of a 14×14 nm^2 area. The white bar corresponds to 2 nm. The red and yellow regions correspond to negative E_p (single-peak spectra) while in green, blue and purple regions, the spectra exhibit a gap width of $\Delta_p = E_p$. Red-yellow spots are surrounded by green regions where the smallest gap is measured (~20 meV). Black patches are composed of spectra (~4,000 in total) in which no gap could be extracted due to a missing left peak (or sometimes no peak at all); these spectra are not included in the histogram of panel **c**. (**c**) Distribution of E_p values. The dashed lines are Gaussian fits. The average peak position and average gap values are -28 and $+29$ meV, respectively. (**d**) Spatial evolution of the spectra on the path depicted by the arrow in **b**. The path goes from a red region (top-most single-peak spectrum) to a black region where the left coherence peak is barely visible. Notice the strong similarity with the global evolution shown in **a**.

Finally, we have studied heavily overdoped sample in which T_c has been reduced to < 1.8 K. The proportion of single-peak spectra increases to ~65% and some of these spectra even exhibit a peak at energy above E_F (Fig. 3a). This suggests that a transition from a (π,π)-centered hole-like to a $(0,0)$-centered electron-like Fermi-surface takes place in the overdoped region near the border of the superconducting dome. Fits to angle resolved photoemission spectroscopy data in cation-doped Bi-2201 have led to the same conclusion[10]. As seen in Figure 3b, as the gap vanishes and the peak moves to positive energy, the spectra develop a remarkable electron-hole asymmetry with a drastic suppression of spectral weight for occupied states. This trend mirrors the common phenomenology observed in all cuprates with increasing gap, namely an excess of spectral weight at negative energy. The data of Figure 3 were collected well above the bulk T_c of the sample. It is therefore natural to interpret the series of spectra in Figure 3b as a transition from the
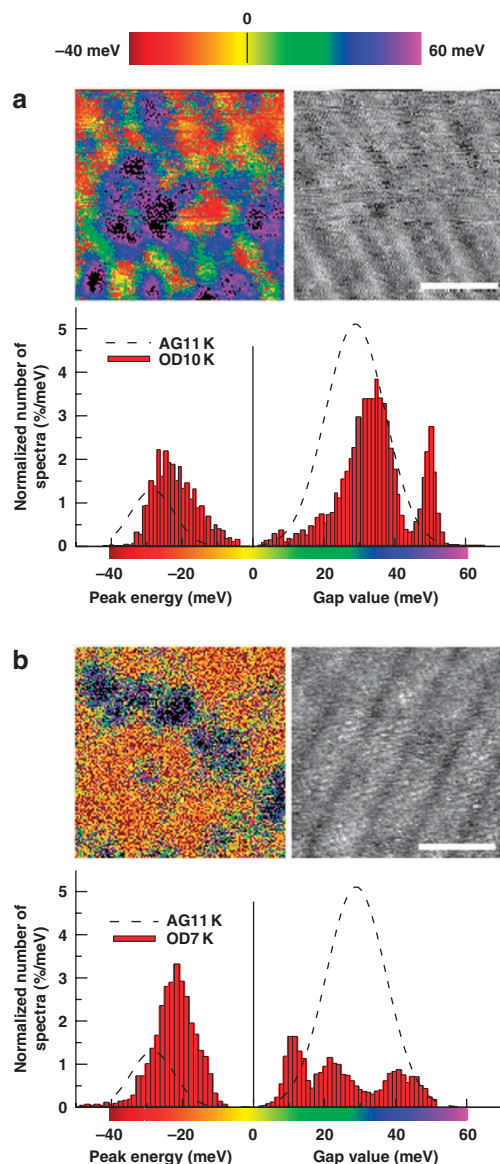
Figure 2 | Evolution of the Bi-2201 spectroscopic properties with overdoping. The top-left panels show the E_p maps (E_p is the peak position for single-peak spectra, and half the peak-to-peak distance for two-peak spectra) for **a**, an overdoped sample with $T_c = 10$ K and $\Delta T_c = 2.5$ K (OD10 K), and for **b**, an overdoped sample with $T_c = 7$ K and $\Delta T_c = 1.5$ K (OD7 K). The white bars correspond to 5 nm. The distributions of E_p values presented in the histograms were normalized and compared with the histograms obtained in the least overdoped AG11 K sample (dashed lines). The top-right panels are simultaneously acquired topographies: white regions are physically higher than black ones. They show the superstructure common to all Bi-based cuprates[23,24]. Especially in OD10 K, the smallest gaps (green) are preferentially located on the minima of the superstructure. A similar correlation between gap size and the superstructure has been reported in Bi-2212[25] and Bi-2223[16]. Our measurements further show that the preferred location of single-peak spectra (red-yellow) is also the minimum of the superstructure, suggesting that the local doping level itself is modulated.

non-superconducting pseudogapped state to the un-pseudogapped normal state at fixed temperature (Fig. 3c). As it is not possible to overdope Bi-2212 or Bi-2223 so as to reach a T_c as low as in pure Bi-2201 (refs 8,11), such a transition has not been observed before
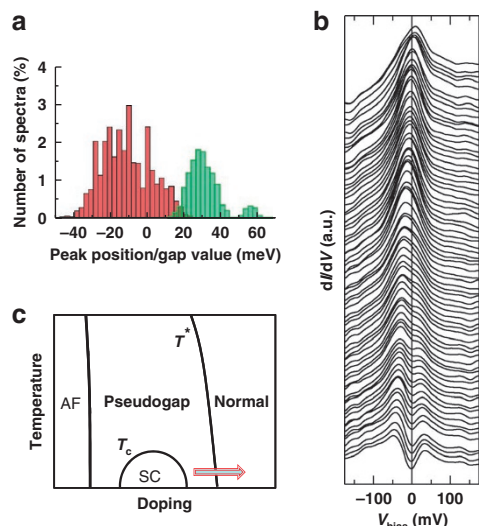
Figure 3 | Spectral properties of strongly overdoped Bi-2201 ($T_c < 1.8$ K) measured at 5 K. (**a**) Distribution of E_p values for single-peak spectra (red part of the histogram corresponds to the position of the single peak) and gapped spectra (green part of the histogram). (**b**) Representative spectra showing single peak at positive energy (top), single peak at negative energy and gapped structures. This series was obtained by ordering the spectra according to the position of their maximum. (**c**) Interpretation of **b** as a transition from the pseudogap to the normal state. T^*, the frontier between normal and pseudogap states.

by STM and can now be investigated because of the identification of the VHS.

Theoretical modelling of the tunnelling spectra. In the first STS study of Bi-2201, the shape of the normal state spectra was not addressed[9,12]. More recently, sharp features in the tunnelling characteristics have been reported in lead-doped Bi-2201 (ref. 13). The observed structure was a narrow peak very close to the Fermi level (± 2 meV) superimposed on the superconducting gap. Such spectra were found at isolated locations on the surface and, based on earlier works in Bi-2212 (refs 14,15), they were convincingly explained as native impurity resonances. The single-peak spectra in our measurements show no trace of a superimposed superconducting gap, cover extended regions of the surface and have their maxima at a doping-dependent energy up to 40 meV below the Fermi level. To support our interpretation that the single-peak spectra are direct manifestations of the VHS in the DOS, we have modelled the dI/dV curves obtained in our samples. Following previous analysis for Bi-2212 (ref. 6) and Bi-2223 (refs 7,16), we consider here the minimal tight-binding model featuring a VHS and a d-wave BCS gap. We then perform least-square fits to determine the band parameters, the gap size Δ_0 and a scattering rate Γ. Fits to some representative spectra obtained on the as-grown sample are shown in Figure 4. We observe that the model is able to follow the variety of measured spectral shapes with good accuracy. The amplitude of the BCS gap deduced from the fits is reported in Figure 4b. The fits correctly yield a vanishing gap for single-peak spectra. We thus find that the single-peak spectra exhibit the same shape as the VHS in a 2D tight-binding band. In general, the spectra measured in Bi-2201 are considerably broader than in Bi-2212 or Bi-2223. This hallmark can be captured by a phenomenological energy-independent scattering rate Γ. The typical values of Γ are indeed larger than that in other Bi-based cuprates in which $\Gamma \lesssim 10$ meV (refs 6,7,16), and we observe a tendency of Γ to follow the trend of the gap, as expected if both would result from the same pairing interaction.

a

AG11 K

b

Δ_0
Γ
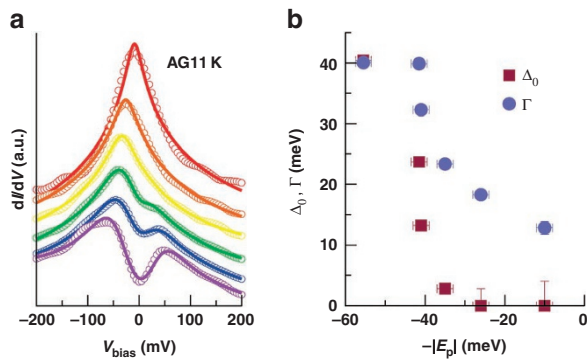
Figure 4 | Theoretical interpretation of Bi-2201 tunnelling spectra.
(**a**) Comparison of representative dI/dV curves in the as-grown sample
(circles) with fits based on a simple model (lines). The model involves a
2D tight-binding dispersion with a VHS, a d-wave BCS gap and a constant
scattering rate. The curves are offset vertically for clarity. (**b**) Squares
indicate amplitude of the BCS gap determined by the fits, as a function
of $-|E_p|$. When $\Delta_0 = 0$ (single-peak spectra), the model corresponds to
independent electrons that are subject to a constant scattering rate,
and the peak is the VHS. Circles indicate trend of the phenomenological
scattering rate Γ as a function of $-|E_p|$.

Discussion

In Bi-2212 and Bi-2223, the bilayer and trilayer compounds of
the same family, the spatial variations of the tunnelling spectra
have been ascribed to inhomogeneities of the doping level on a
nanometre scale[17]. In this scenario, the single-peak structure we
observe would correspond to extremely overdoped regions, which
are non-superconducting at 5 K. One thus expects that the pro-
portion of such spectra increases in samples with higher doping
levels. We have confirmed this by studying overdoped samples
with various doping levels. The STM observation of the VHS in a
low T_c cuprate superconductor provides a clear-cut experimental
answer to a long-standing theoretical question. Our results con-
firm that the STM tunnelling conductance is proportional to the
full-electron DOS, and not only to the 'superconducting DOS',
and disqualify qualitative arguments used to claim the opposite.
This must be taken seriously for the interpretation and modelling
of STM tunnelling spectra in materials with singularities in the
electron dispersion.

The appearance of the VHS as a sharp peak in Bi-2201 poses the
question of its signature in the spectra of other Bi-based cuprates.
It has been shown in refs 5–7 that the coupling to the (π,π) spin
resonance suppresses the VHS peak and gives rise to the strong dip
in Bi-2212 and Bi-2223 spectra. As suggested by ARPES[18] and our
measurements, if a dip is present in pure Bi-2201, it must be very
weak (Fig. 4a). Within a spin-fluctuation pairing scenario, we may
tentatively ascribe the low T_c of pure Bi-2201 and the absence of dip
in the DOS—hence the presence of the VHS—to a weak coupling
to spin fluctuations. Interestingly, in cation-doped Bi-2201, which
exhibit higher critical temperatures, the VHS has not been seen[19–21].

Our observation in the heavily overdoped sample (Fig. 3) con-
firms the presence of the pseudogap phase well to the overdoped
region in Bi-2201 (ref. 9). In a concurrent version of the phase dia-
gram without a pseudogap in the overdoped region, the gapped
spectra in Figure 3b would have to be interpreted as regions that
are superconducting at $T = 5\,K > T_c$ because of inhomogeneities. In
this scenario, a mechanism different from the pseudogap would be
needed to explain the anomalous large gap of ~30 meV, 30 times
larger than the expected value for a BCS superconductor with a T_c of
5 K. Furthermore, the observation of the coexistence of gapped and
un-gapped regions above T_c strongly supports the existence of the

pseudogap in the overdoped side and questions the universality of a
cuprate phase diagram, in which the pseudogap phase would cross
the superconducting dome.

Methods

STM measurements. STS measurements were performed in a home-built
STM placed in a low temperature and ultra-high-vacuum environment similar
to the one reported in ref. 22. The crystals were cleaved at room temperature in a
~10^{-9} mbar atmosphere, and immediately cooled down to 5 K. The bias voltage was
applied to the sample, while the ground electrode was a mechanically sharpened
iridium tip. The tunnelling current was 0.25 nA and the regulation bias was 0.4 V.
Conductance maps were obtained by numerical differentiation of the $I(V)$ curves.

Modelling of the spectra. The dI/dV curves were modelled as
the thermally broadened DOS, $dI/dV \propto \int d\omega[-f'(\omega - eV)]N(\omega)$,
where f is the Fermi function and $N(\omega)$ is the BCS DOS given by
$N(\omega) = \sum_k (-1/\pi)\mathrm{Im}\left[\omega - \xi_k + i\Gamma - |\Delta_k|^2 /(\omega + \xi_k + i\Gamma)\right]^{-1}$. The d-wave gap reads
$\Delta_k = \Delta_0(\cos k_x a - \cos k_y a)/2$, and for the dispersion we used the five-neighbor tight-
binding expression $\xi_k = 2t_1(\cos k_x a + \cos k_y a) + 4t_2 \cos k_x a \cos k_y a + 2t_3(\cos 2k_x a - \cos 2k_y a) + 4t_4(\cos 2k_x a \cos k_y a + \cos k_x a \cos 2k_y a) + 4t_5 \cos 2k_x a \cos 2k_y a - \mu$, with a
being the lattice parameter. The k-mesh involves 1,024×1,024 k points. The model
parameters were determined by least-square fits to the STM spectra. Given the
restricted energy range of the experimental data, the fits cannot reliably determine
the overall bandwidth controlled by t_1. We therefore kept t_1 fixed to the ARPES
value[10] $t_1 = -213$ meV for all spectra.

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Acknowledgments

Author contributions

A.P. and N.J. have performed the experiments. N.J. constructed the system. A.P. grew the samples and analysed the data. A.P. and C.B. have written the manuscript. N.J., and I.M.-A. helped refine the analysis and the manuscript. Ø.F. discussed the results and manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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