Nodes of the superconducting gap probed by electronic Raman scattering in HgBa$_2$CaCu$_2$O$_{6+\delta}$ single crystals

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Abstract. – Pure electronic Raman spectra with no phonon structures superimposed to the electronic continuum are reported, in optimally doped HgBa$_2$CaCu$_2$O$_{6+\delta}$ single crystals ($T_c = 126$ K). As a consequence, the spectra in the $A_{1g}$, $B_{1g}$ and $B_{2g}$ symmetries, including the crucial low-energy frequency dependence of the electronic scattering, are directly and reliably measured. The $B_{2g}$ and, most strikingly, the $B_{1g}$ spectra exhibit a strong intrinsic linear term, which suggests that the nodes are shifted from the [110] and [110] directions, a result inconsistent with a pure $d_{x^2-y^2}$ model.

Since the last few years, identifying the symmetry of the pairing state has been the expected major step towards an understanding of high-$T_c$ superconductivity. The controversy between $s$-wave or $d$-wave pairing is not, however, resolved: some experiments appear to advocate strongly in favor of a $d_{x^2-y^2}$ symmetry [1], whereas others seem to show a significant $s$-wave contribution [2]. With respect to this problem, inelastic light scattering has been shown to be a powerful tool because, besides probing the bulk (in contrast with photoemission and tunneling), the selection rules on the polarization of incoming and outgoing light make the spectra sensitive to the wave vector of the electronic excitations [3]-[6]. Usual theoretical approaches of electronic Raman scattering ignore other excitations such as phonons. The experimental major difficulty lies, however, in the fact that in La$_{2-x}$Sr$_x$CuO$_4$, YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123), Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) and Tl$_2$Ba$_2$CuO$_{6+\delta}$ the phonons mask the electronic excitations, which hampers an accurate determination of their spectrum in the superconducting state [7]-[14].

In this letter, we report for the first time pure —no phonon structures superimposed— electronic Raman spectra in HgBa$_2$CaCu$_2$O$_{6+\delta}$ (Hg-1212) single crystals. This compound belongs to the new mercury family where the phonons do not mask the low-energy electronic spectrum for electric fields within the planes [15], [16]. Its crystallographic structure is purely tetragonal ($^4D_{2h}$) [17], which allows an unambiguous comparison with theoretical calculations.

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based on tetragonal symmetry. Hg-1212 is, therefore, particularly well suited for the study of the superconducting gap. Our most striking result is that the low-frequency behavior of the $B_{1g}$ spectrum displays a quasi-linear dependence; this has not been reported so far, presumably because the determination of the spectrum in this frequency range is usually hindered by phonons. Such an observation strongly suggests that the nodes are shifted from the [110] and [101] directions, a conclusion at odds with the generally accepted $d_{x^2-y^2}$ gap symmetry. We believe that our new and unambiguous experimental data should be taken into account in any theoretical approach of high-$T_c$ superconductors.

Raman spectra have been obtained from high-quality single crystals of Hg-1212. The crystals were grown by a single-step synthesis as previously described for Hg-1223 [18]. They are perfect parallelepipeds with typical $0.5 \times 0.5 \text{ mm}^2$ cross-section and thickness $0.3 \text{ mm}$. The crystals were characterized by X-ray diffraction and energy dispersive X-ray analysis [18]. The [100] crystallographic direction lies at $45^\circ$ of the edge of the square and the [001] direction is normal to the surface. DC magnetic susceptibility measurements performed with a SQUID magnetometer yield $T_c = 126 \pm 1 \text{ K}$.

The measurements were performed with a standard Raman set-up using a single channel detection and the $\text{Ar}^+$ laser $514.52 \text{ nm}$ line [19]. The spectral resolution was set at $3 \text{ cm}^{-1}$. The crystals were mounted in vacuum ($10^{-5} \text{ mbar}$) on the cold finger of a liquid-helium cryostat. The temperature was controlled by a Si diode located inside the cold finger. The incident laser power density onto the crystal surface was kept below $15 \text{ W/cm}^2$ in order to avoid heating of the crystal during the low-temperature runs. The incidence angle of the incoming light was $60^\circ$ and the scattered light was collected along the normal to the crystal surface. The polarizations of the incident and scattered lights are denoted in the usual way. $x$: [100] ($a$ axis), $y$: [010], $z$: [001] ($c$ axis), $x'$: [110], $y'$: [110]. In order to compare our experimental data with theoretical calculations [5], [6], [20], the pure $B_{2g}$ ($xy$) and $B_{1g}$ ($x'y'$) symmetries are needed. This requires that the incident electric field lie within the $xy$-plane. The incident angle being non-zero, the crystal must be rotated by $45^\circ$ after measuring in the $B_{2g}$ channels in order to get the $B_{1g}$ spectrum. The impact of the laser beam onto the crystal surface was precisely located in order to probe the same crystal area for the three symmetries. Finally, a very weakly diffusive spot was carefully chosen for each crystal to minimize the amount of spurious elastic scattering.

The raw Raman spectra at $T = 13 \text{ K}$ of the Hg-1212 single crystals for the $A_{1g} + B_{1g}$, $B_{1g}$ and $B_{2g}$ symmetries are displayed in fig. 1a). Remarkably and in sharp contrast with Y-123 and Bi-2212 [9], [13], no Raman active mode hinders the $B_{1g}$ and $B_{2g}$ spectra. Weak peaks are seen at 388 and $576 \text{ cm}^{-1}$ in the $A_{1g}$ spectrum but their energy location is such that no correction is actually needed to discuss the electronic spectra [21]. Note that the residual elastic scattering below $50 \text{ cm}^{-1}$ is only seen in the $A_{1g}$ spectrum and is very weak. Therefore, we are in a position to turn immediately to the analysis of the data without dealing with the delicate handling of “phonon subtraction”.

Two well-marked maxima are observed around $530 \text{ cm}^{-1}$ and $800 \text{ cm}^{-1}$ for the $A_{1g}$ and $B_{1g}$ symmetry, respectively. The ratio of the peak energies is $\sim 1.5$, while it was found $\sim 2$ for Bi-2212 and Y-123 [9], [13]. No clear maximum appears in the $B_{2g}$ symmetry, for which, actually, the scattered intensity levels out smoothly around $530 \text{ cm}^{-1}$. The intrinsic (e.g., after subtracting the dark current of the photomultiplier) scattered intensities in $A_{1g}$, $B_{1g}$ and $B_{2g}$ symmetries drop close to a zero count rate at zero frequency whereas, in Bi-2212, a trend towards finite intensity was claimed to be observed in $A_{1g}$ symmetry [9]. We note that in Bi-2212 the presence of numerous phonon structures at low frequency especially in $x'x'$ polarizations ($xx$ in the notation of ref. [9]) makes it difficult to estimate quantitatively the electronic scattered intensity. In this respect, we believe that our data are more reliable.

Figure 1b) displays the imaginary part $\text{Im}[\chi(\omega, T = 13 \text{ K})]$ of the electronic response
functions at $T = 13$ K associated with the $A_{1g} + B_{1g}$, $B_{1g}$ and $B_{2g}$ symmetries. They were obtained from the raw spectra after subtracting the residual Rayleigh scattering, and correcting for the thermal Bose-Einstein factor $1 + n(\omega) = [1 - \exp(-\hbar\omega/k_BT)]^{-1}$. The dashed lines in fig. 1 b) are the imaginary part $\text{Im}[\chi(\omega, T = 150 \text{ K})]$ of the response functions at $T = 150$ K displayed for clarity after smoothing the spectra. Note that the three response functions vanish at zero frequency. The main new observations which emerge from fig. 1 b) are: i) The $B_{1g}$ response function exhibits a clear decrease of the electronic scattering rate at low energy with respect to the normal state, unlike the $A_{1g}$ and the $B_{2g}$ response functions where the difference is small. ii) The normal-state intensity is recovered for all symmetries beyond the maximum. iii) The two distinct maxima observed for both $A_{1g}$ and $B_{1g}$ symmetries disappear above $T_c$. iv) The scattered intensity in the $B_{1g}$ channel exhibits a quasi-linear increase.

Our experimental data are of special interest in the low-frequency regime. Indeed the $B_{1g}$ and $B_{2g}$ symmetries are the ones which are expected to have the most different behavior ($\omega^3$ and $\omega^2$, respectively) in the $d_{x^2-y^2}$ model. Two fits have been performed for each symmetry: a first one to a power law $\omega^\alpha$ and a second one to the simple polynomial function $b\omega + c\omega^3$. The $\alpha$ exponents calculated below 300 cm$^{-1}$ for $A_{1g}$, $B_{2g}$ and $B_{1g}$ symmetries are $1.3 \pm 0.3$, $0.8 \pm 0.2$, $1.5 \pm 0.5$, respectively. The power law fit shows clearly that the low-energy range of the $B_{1g}$ spectrum does not display an $\omega^3$-dependence, in contrast to the claim of ref. [5], [6], [20]. A linear $\omega$-dependence in the low-frequency regime is quite compatible with our three response functions. In the second fit the ratio $\tau = b/(c\omega^2)$, which gives the relative weight of the linear and the cubic variation, is $\tau = 2 \pm 1$, $4 \pm 1$, $3.3 \pm 0.7$ and $3.4 \pm 0.5$ at 300, 400, 500 and 600 cm$^{-1}$, respectively, much larger than an earlier estimate [14]. This provides quantitative evidence for the predominance of the linear part compared to the cubic part especially for the $B_{1g}$ symmetry. We suspect that the $\omega^3$ fit to previous experimental measurements is less reliable due to the phonon background [9], [13].

We now turn to the comparison of our data with existing theories. In the limit where the superconducting coherence length is much smaller than the optical penetration depth, the
imaginary part of the unscreened response function for \( T \to 0 \) is given by [3]

\[
\text{Im}[\chi(\omega, T \to 0)] = \frac{2\pi N_F}{\omega} \text{Re} \left( \frac{\gamma_k |\Delta_k|^2}{(\omega^2 - 4|\Delta_k|^2)^2} \right) \frac{1}{k}.
\] (1)

\( N_F \) is the density of states for both spin orientations at the Fermi level, and the brackets indicate an average over the Fermi surface. \( \Delta_k \) stands for the superconducting, \( k \)-dependent gap. \( \gamma_k \) is the Raman vertex.

Obviously, our results cannot be accounted for with an isotropic gap combined with a cylindrical Fermi surface. Several \( \Delta_k \) and \( \gamma_k \) distributions have been proposed to reproduce the electronic excitations. Taking a Gaussian distribution of \( \Delta_k \)'s [4], [8], we obtain for the \( A_{1g} \) and \( B_{1g} \) spectra the fits shown in fig. 1 b). We have added an \( \omega^{1/2} \) function to the bracketed expression at energies greater than the \( \Delta_k \) values, in order to mimic the asymptotic recovery of the normal-state behavior. The low-energy part of the response function in \( B_{1g} \) symmetry is not satisfactorily described by this type of calculation and moreover this numerical fit does not yield any information on the gap symmetry.

We have then attempted to fit our \( A_{1g}, B_{1g} \) and \( B_{2g} \) response functions with the calculations of Devereaux et al. for a \( d_{x^2-y^2} \) gap [20] which were found to describe satisfactorily the Bi-2212 results. After adjusting the relative energy location of the maxima in \( A_{1g} \) and \( B_{1g} \), we find a fair agreement with our data in the linear dependence of the low-energy part of the \( A_{1g} \) and \( B_{2g} \) symmetries (see fig. 2). However, the low-frequency behavior of the theoretical \( B_{1g} \) spectrum is incompatible with our experimental results. This was already clear from the above discussion of the exponents and of the ratio of the linear and cubic contributions. We have also done the calculation for the simplest \( s \)-wave anisotropic gap \( \Delta(\theta) = \Delta_0 + \Delta_1 \cos^2 \theta \), not finding a satisfactory agreement because no hint of a threshold corresponding to the minimum gap is seen in our data.

Let us, therefore, consider the implications of our experimental findings. We analyze first the \( B_{1g} \) and \( B_{2g} \) symmetries, which are easier to interpret due to simple symmetry considerations and are not affected by screening, in contrast with the \( A_{1g} \) symmetry. In the \( B_{1g} \) case, the Raman vertex \( \gamma_k \) is zero by symmetry for \( k_x = k_y \), hence the electronic scattering is insensitive
to the gap structure around 45°; in contrast, the \( k_x \approx 0 \) and \( k_y \approx 0 \) regions do contribute, giving weight to the gap \( \Delta_0 \) in these directions. Conversely, in the \( B_{2g} \) case, the Raman vertex \( \gamma_k \) is zero by symmetry for \( k_x = 0 \) or \( k_y = 0 \), and non-zero elsewhere, hence provides weight in the \( k_x = k_y \) direction. In the \( d_{x^2-y^2} \) pairing state, these considerations imply that the \( B_{1g} \) symmetry is insensitive to the nodes at 45° (hence the \( \omega^3 \) dependence) and displays a maximum at 2\( \Delta_0 \), whereas the \( B_{2g} \) symmetry exhibits a linear frequency dependence (because it probes the nodes) and a smeared gap. An inescapable consequence of the linear low-frequency dependence is the existence of a density of states which increases linearly with frequency, most naturally due to nodes in the gap. Since these nodes are probed in both \( B_{1g} \) and \( B_{2g} \) symmetries, they cannot be (only) located in the 45° direction.

It could be argued that impurities are responsible for the observed low-frequency density of states in the \( B_{1g} \) channel. Devereaux [22] has shown that, for a \( d_{x^2-y^2} \) gap, impurities induce for \( B_{1g} \) a linear rise of the electronic scattering at low frequency, crossing over to the \( \omega^3 \) dependence at higher frequency. However, the linear behavior in \( B_{1g} \) extends in our experiment up to 600 cm\(^{-1} \), yielding a crossover energy \( \omega^* \sim (\Gamma\Delta)^{1/2} \) of order 600 cm\(^{-1} \). In the most favorable case of unitary scatterers [22], this would imply a scattering rate \( \Gamma \) of order of the gap \( \Delta \) itself. Such a high scattering rate should strongly reduce the critical temperature, in contradiction with the optimal 126 K critical temperature of our samples. Therefore, this explanation looks unlikely. We believe that our data are representative of a pure compound and that the linear contribution found in the \( B_{1g} \) spectrum is intrinsic.

We are thus left with the conclusion that the nodes are shifted from the 45° direction. Hg-1212 being tetragonal, we cannot ascribe this to an orthorhombic distortion as could be the case in Y-123. We, therefore, explore this shift more quantitatively. As a first approach, we take the simple model \( \gamma_{B_{1g}} \sim \cos 2\theta, \gamma_{B_{2g}} \sim \sin 2\theta \) for the Raman vertices [5], [6] and a cylindrical Fermi surface. We start by using a “toy model” where we compute the \( B_{1g} \) and \( B_{2g} \) spectra for an order parameter \( \Delta(\theta) = \Delta_0 \cos(2\theta - 2\alpha) \) obtained by artificially rotating the \( d_{x^2-y^2} \) one by an angle \( \alpha \). This is intended to check the sensitivity of the Raman spectra to the nodes location (note that a 22.5° rotation would naturally make \( B_{1g} \) and \( B_{2g} \) identical). We find that a rotation by \( \alpha \approx 10^\circ \) is barely noticeable in the spectra: the linear rise at low \( \omega \) produced in \( B_{1g} \) by this rotation is comparable to the experimental accuracy. This suggests that the shift of the nodes away from 45° is quite sizeable.

Because of the tetragonal symmetry, one node located at \( \theta_0 \) (\( \neq 45^\circ \) or \( 0^\circ \)) implies 8 nodes at \( \pm\theta_0 + n\pi/2 \) (\( n = 0, 1, 2, 3 \)). A very simple model corresponding to this situation is \( \Delta(\theta) = \Delta_0 [\cos(4\theta) + s] \) with \( 0 \leq s \leq 1 \), an order parameter which has the \( A_{1g} \) symmetry [23]. The gap has a maximum \( \Delta_0 (1 + s) \) for \( \theta = 0 \), seen in \( B_{1g} \), and a secondary maximum \( \Delta_0 (1 - s) \) for \( \theta = \pi/4 \), seen in \( B_{2g} \), while the node lies at \( \theta_0 = (1/4) \arccos(-s) \). This model could also be loosely called a \( g \)-wave model or a (super) extended \( s \)-wave model (in contrast to the \( d \)-wave model, which has the \( B_{1g} \) symmetry). With one more parameter we might decouple the position of the nodes and the size of the gap maxima. We choose the parameter \( s \) to account for the relative peak positions in \( B_{1g} \) and \( B_{2g} \) (inasmuch as we consider that \( B_{2g} \) has a very broad peak around 500 cm\(^{-1} \)). It can be seen in fig. 2 that the \( B_{1g} \) and \( B_{2g} \) spectra calculated in this framework for \( s = 0.2 \) (giving \( \theta_0 = 25^\circ \)) are in good agreement with experiment for the low-frequency behavior. The discrepancy at high frequency, most conspicuous in \( B_{2g} \), is assigned to finite electronic scattering rate in the normal state. This should be also accounted for, but this is beyond the scope of this letter. In order to remove the singularities at the gap maxima, a smearing function with width proportional to frequency [22] has been incorporated in the calculation.

Our model explains the different positions of the \( B_{1g} \) and \( B_{2g} \) peaks (also found in Bi-2212) by the gap anisotropy. This leads us to try and connect the position of the peak found in
$A_{1g}$ symmetry to the other peaks. The $A_{1g}$ symmetry is screened and the peak position can not be related directly to $\Delta(\theta)$. Since a constant vertex is completely screened, the simplest model giving a non-zero result for $A_{1g}$ is $\gamma_{A_{1g}} \sim \cos 4\theta$. However, in our one-parameter model, the position of the nodes is imposed by the relative peak position in $B_{1g}$ and $B_{2g}$. This leads to the $\gamma_{A_{1g}} \sim \cos 4\theta$ being essentially zero at the nodes, and yields a very small low-$\omega$ linear contribution in contrast with experiment. We have thus included higher harmonics. The calculation shown in fig. 2 is done with $\gamma_{A_{1g}} \sim \cos 4\theta - 3\cos 8\theta$. The agreement is quite satisfactory both with respect to the low-$\omega$ behaviour and the peak position. However, it is clear that this could even be improved in a more complicated two-parameter model for $\Delta(\theta)$, decoupling the node position and the gap maxima, and also including a \(\theta\)-dependence for the density of states.

In conclusion, we have presented, for the first time, pure electronic Raman spectra of Hg-1212 single crystals. Our most significant result is the observation of an intrinsic linear $\omega$-dependence, not only in the $B_{2g}$ spectrum, but also in the $B_{1g}$ spectrum. This is an important clue in order to locate the nodes, which was not reported so-far in other compounds presumably because the experimental determination of the low-frequency regime is usually hampered by phonons. Our observations advocate in favor of a shift of the nodes from the $[110]$ and $[1\bar{1}0]$ directions, which is inconsistent with the simple $d_{x^2-y^2}$ model.

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REFERENCES

[1] Wollman D. A. et al., Phys. Rev. Lett., 74 (1995) 797.
[2] Sun A. G. et al., Phys. Rev. Lett., 72 (1994) 2267.
[3] Klein M. V. and Dierker S. B., Phys. Rev. B, 29 (1984) 4976.
[4] Dierker S. B. et al., Phys. Rev. Lett., 50 (1983) 853.
[5] Deveraux T. P. et al., Phys. Rev. Lett., 72 (1994) 396.
[6] Deveraux T. P. and Einzel D., Phys. Rev. B, 51 (1995) 16336.
[7] Cooper S. L. et al., Phys. Rev. B, 37 (1988) 5920; Cooper S. L. et al., Phys. Rev. B, 38 (1988) 11934.
[8] Hackl R. et al., Phys. Rev. B, 38 (1988) 7133.
[9] Stauffer T. et al., Phys. Rev. Lett., 68 (1992) 1069.
[10] Leach D. H. et al., Solid. State Commun., 88 (1993) 457.
[11] Nemetschek R. et al., Phys. Rev. B, 47 (1993) 3450; Gasparov L. V. et al., unpublished.
[12] Chen X. K. et al., Phys. Rev. Lett., 73 (1994) 3290.
[13] Krantz M. and Cardona M., J. Low Temp. Phys., 99 (1995) 205.
[14] Strohm T. and Cardona M., cond-mat/9609143.
[15] Sacuto A. et al., Physica C, 259 (1996) 299.
[16] Xingjiang Zhou et al., Phys. Rev. B, 54 (1996) 6137.
[17] Cantoni M. et al., Physica C, 215 (1993) 11.
[18] Colson D. et al., Physica C, 233 (1994) 231; Bertinotti A. et al., Physica C, 250 (1995) 213.
[19] Sacuto A. et al., Phys. Rev. B, 52 (1995) 7619.
[20] Deveraux T. P., J. Supercond., 8 (1995) 421; Deveraux T. P. et al., Phys. Rev. Lett., 72 (1994) 3291.
[21] The 576 cm$^{-1}$ peak shows a phonon asymmetric lineshape with an antiresonance on the high-energy side. This is characteristic of the interference between an electronic continuum and a single phonon state. Such Fano lineshape has already been detected in Y-123 and Bi-2212 for the $B_{1g}$ normal mode in the vicinity of the gap structure maximum [7], [10].
[22] Deveraux T. P., Phys. Rev. Lett., 74 (1995) 4313.
[23] An order parameter with $B_{1g}$ symmetry (changing sign under $\pi/2$ rotation) would imply 12 nodes.