Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica C 408–410 (2004) 721–724
PHYSICA C
www.elsevier.com/locate/physc

Energy scales of the excitations associated with superconductivity: an analysis of the infrared–visible in-plane response of $Bi_2Sr_2CaCu_2O_{8+\delta}$

A.F. Santander-Syro [a], R.P.S.M. Lobo [a], N. Bontemps [a,*], Z. Konstantinovic [b], Z.Z. Li [b], H. Raffy [b]

[a] *Laboratoire de Physique du Solide, CNRS UPR 5, Ecole Supérieure de Physique et Chimie Industrielles de la Ville de Paris, 24 rue Lhomond, 75231 Paris cedex 5, France*

[b] *Laboratoire de Physique des Solides, CNRS UMR 8502, Université Paris-Sud, 91405 Orsay cedex, France*

Abstract

The *ab*-plane infrared and visible (3 meV–3 eV) response of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) thin films has been measured between 300 and 10 K for different doping levels. In the superconducting state, dramatic differences appear between the underdoped and optimally/overdoped regimes regarding the electrodynamics of the formation of the superfluid condensate. In the optimally doped and overdoped regimes, the superfluid grows up by removing states from energies below 60 meV. This energy is of the order of a few times the superconducting gap. In this respect, optimally doped and overdoped Bi-2212 exhibit a conventional behavior. In the underdoped regime, states extending up to 2 eV, far beyond any conventional scale for a BCS-like mechanism, contribute to the superfluid. The spectral weight change, below the critical temperature and beyond the intraband transitions, may be assigned to a change of electronic kinetic energy ~1 meV, a figure which addresses the issue of a kinetic energy driven mechanism.

PACS: 74.25.−q; 74.25.Gz; 74.72.Hs
Keywords: Properties of type I and type II superconductors; Optical properties; Bi-based cuprates

In cuprate superconductors, the pairing mechanism remains an open question. One clue is the typical energy scale of the excitations responsible for pairing. Infrared (IR) and visible spectroscopy measures the charge density distribution as a function of energy, through the investigation of the area under the frequency (ω) and temperature (T) dependent optical conductivity $\sigma_1(\omega, T)$. This area, known as the spectral weight W, is defined as:

$$W = \int_{0^+}^{\omega_c} \sigma_1(\omega, T)\, d\omega \quad (1)$$

where ω_c is a cut-off frequency. When integrating from zero to infinite frequency, this spectral weight should be conserved. Ferrell, Glover and Tinkham (FGT) noted that, in the superconducting state, the spectral weight ΔW lost from the finite frequency conductivity is retrieved in the spectral weight W_s of the $\delta(\omega)$ function centered at zero frequency, representing the condensate [1]. ΔW is approximately equal to W_s (the so-called FGT sum rule) when the cut-off frequency ω_c in Eq. (1) covers the spectrum of excitations responsible for the pairing mechanism. In conventional superconductors, this occurs at an energy corresponding roughly to 4–8Δ (Δ is the superconducting gap) [1]. Assuming a similar behavior in cuprates, the FGT rule should be exhausted at $\hbar\omega_c \sim 0.1$–0.2 eV, as a typical maximum gap value in these d-wave superconductors is roughly 25 meV [2]. Lately, ellipsometric measurements

* Corresponding author.
E-mail address: nicole.bontemps@espci.fr (N. Bontemps).

0921-4534/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2004.03.052

[3] and ellipsometric + IR reflectivity experiments [4] showed that in-plane spectral weight was lost in the visible range, which raised the question of an anomalous in-plane energy scale, but without direct evidence that this spectral weight is indeed transferred into the condensate.

The data presented in this paper address this specific issue. We report on the investigation of the FGT sum rule in three carefully selected thin films from the Bi-2212 family, probing three typical locations in the phase diagram: the underdoped (UND), the optimally doped (OPT) and the overdoped (OVD) regimes. A detailed study of the spectral weight changes as the temperature goes from well above T_c down to $T \ll T_c$ allows to work out the FGT sum rule with well controlled error bars. We find that within these error bars, retrieving the condensate spectral weight in the OVD and OPT samples requires integrating up to an energy of the order of 0.1 eV (800 cm^{-1}), i.e. a conventional energy scale. In the UND sample, about 30% of the FGT sum rule is still missing at 1 eV, and the integration must be performed up to at least 16,000 cm^{-1} (2 eV), an energy scale much larger than typical boson energies in a solid, and ~100 times larger than the maximum gap. We derive the associated change of the in-plane kinetic energy.

Among 13 samples investigated, three were selected for this work. The selection procedure and criteria are described in Ref. [5]. The thin films were epitaxially grown by r.f. magnetron sputtering on (1 0 0) $SrTiO_3$ substrates heated at temperatures $\gtrsim 700$ °C. The various doping levels (UND and OVD) were obtained by post-annealing the films in a controlled atmosphere [6]. Our films critical temperatures are 70 K (B70KUND), 80 K (B80KOPT) and 63 K (B63KOVD). The reflectivities, taken at typically 15 temperatures (10–300 K) and at quasinormal incidence (~8°), were measured in the spectral range [30–7000] cm^{-1} with a Fourier Transform spectrometer (Bruker IFS-66v), supplemented with a standard grating spectrometer in the range [4000–28000] cm^{-1} (Cary-5).

It is known that temperature changes of the optical response in the mid-infrared and the visible ranges are small, but cannot be neglected. Yet, as suggested in Ref. [7], most studies rely on a single spectrum at one temperature in the visible range. We did monitor the temperature evolution of the reflectivity spectra in the full available range. This is obviously important if one is looking for a spectral weight transfer originating from (or going to) any part of the *whole* frequency range.

Fig. 1(a) shows two reflectivity curves (at $T = 250$ K and $T = 10$ K) of the B70KUND sample. This is an example of the typical spectra we have measured. The signal-to-noise ratio is unprecedented, and relative variations of the reflectivity of less than 0.2% can be measured in the infrared [Fig. 1(b)] and the visible (not shown). In the far-infrared [inset, Fig. 1(a)], the three

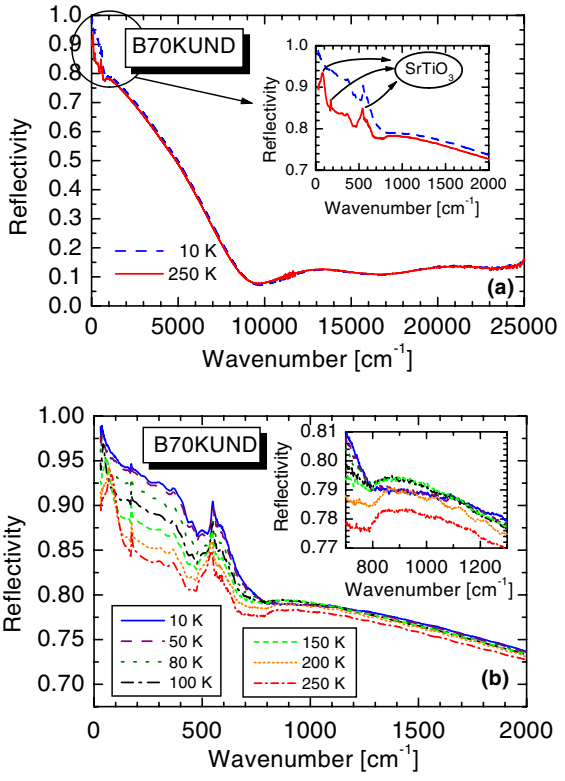

Fig. 1. (a) Reflectivity of the B70KUND sample in the whole experimental range, at high (250 K) and low (10 K) temperatures. The inset shows the variation of the reflectivity in the far-infrared, and the phonon peaks from the substrate. (b) Temperature changes of reflectivity in the far-infrared range for the B70KUND sample. The spectral range 700–1300 cm^{-1} is zoomed in the inset. Note that relative variations of the reflectivity of less than 0.2% can be resolved.

phonon peaks coming from the underlying substrate are clearly visible, specially at high temperatures (or low doping), when the system is less metallic.

The contribution of the substrate to the experimentally measured reflectivity precludes the Kramers–Kronig analysis in such thin films. In order to extract the optical functions intrinsic to Bi-2212, we simulated its dielectric function at each temperature and doping level using Drude–Lorentz oscillators (thus warranting causality). We then modelled the reflectance of the film on top of the substrate, using the optical constants of $SrTiO_3$ that were experimentally determined at each temperature [5,8]. The fit yields a valuable extrapolation of the conductivity in the low energy range ($\omega < 30$ cm^{-1}, not available experimentally) [9,10], which is important in the evaluation of the spectral weight.

Fig. 2 shows the conductivity spectra for the B70KUND, B80KOPT and B63KOVD samples, at some selected temperatures. The superconducting transition is marked, for the overdoped sample, by a decrease

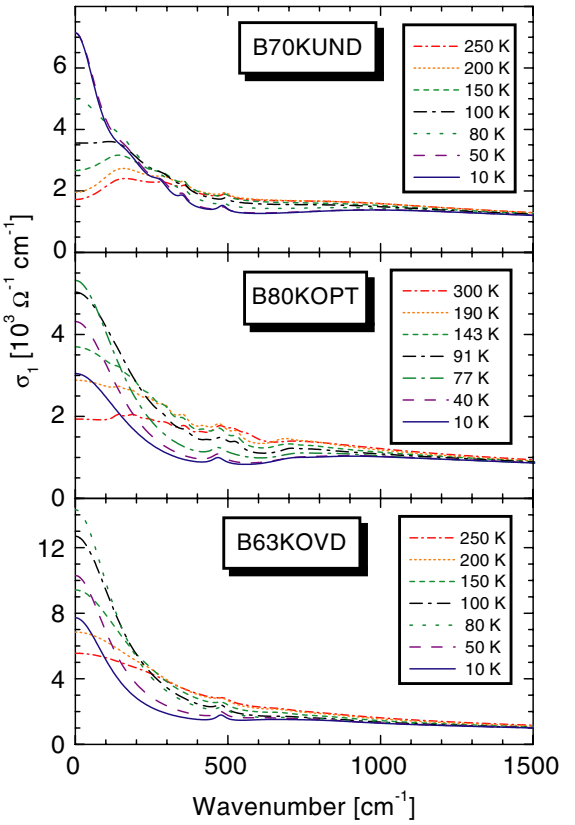

Fig. 2. Selected conductivity spectra for the B70KUND (upper), B80KOPT (middle) and B63KOVR (lower) samples. For the B70KUND sample, in the spectral range shown, the spectra at 50 and 10 K are indistinguishable. The error bars in the conductivity spectra are $\Delta\sigma/\sigma \lesssim 10\%$ for $\hbar\omega > 30$ cm^{-1}, and $\Delta\sigma/\sigma \sim 20\%$ for $\hbar\omega < 30$ cm^{-1} [5,11].

of the conductivity over the spectral range shown in Fig. 2, so that a clear loss of spectral weight, associated with the formation of the zero-frequency condensate, is observed in this spectral range. In contrast, the low frequency ($\hbar\omega \lesssim 100$ cm^{-1}) conductivity of the underdoped sample does not decrease when temperature decreases below T_c. Beyond this energy scale, the normal- and superconducting-state conductivities cross, and there is no a clear loss of spectral weight within the spectral range shown in the figure. A quantitative analysis is needed in this case, based on the FGT sum rule.

From an experimental point of view, the FGT sum rule usually compares the change $\Delta W = W(T_A \geqslant T_c) - W(T_B < T_c)$ (Eq. (1)) and the superfluid spectral weight W_s. W_s was determined for $T < T_c$ at low frequencies, within the measured spectral range, by looking at the region where the real part of the dielectric function $\varepsilon_1(\omega)$ behaves linearly when plotted versus $1/\omega^2$ (London approximation). The slope is directly related to the superfluid spectral weight W_s through the "London" frequency $\Omega_L = c/\lambda_L$, where λ_L is the London penetration depth. At $T_B = 10$ K, for instance, we find $\Omega_L = 7200$, 2900 and 2350 cm^{-1} for the UND, OPT and OVD samples respectively [11]. The values for the OPT and OVD samples are in fair agreement with those reported in the literature [12]. There are no reliable data on the absolute value of the London penetration depth for underdoped samples [13].

Fig. 3 shows the ratio $\Delta W/W_s$ for the samples studied in this work. In the UND sample, we find that at energies as large as 1 eV (8000 cm^{-1}), $\Delta W/W_s \sim 0.65 \pm 0.18$ (details about the evaluation of the error bars are given in Ref. [5]). It approaches 1 at ~16,000 cm^{-1}. A large part (~30%) of the superfluid weight in the underdoped regime thus builds up at the expense of spectral weight coming from high energy regions of the optical spectrum ($\hbar\omega \geqslant 1$ eV). Because of our error bars, we cannot make a similar statement for the OPT and OVD samples, where the sum rule may be exhausted at roughly 500–1000 cm^{-1}. Our results for the OVD and OPT samples thus do not contradict earlier similar work in $YBa_2Cu_3O_{7-\delta}$ (Y-123) and $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2212) [14]. Underdoped Y-123 showed a conventional behavior, possibly because only one spectrum is usually recorded in the visible range which is precisely the energy range which matters in this case.

One interpretation of the sum rule violation can be made in the context of the tight-binding Hubbard model. The relation between the low-frequency spectral weight and the kinetic energy E_{kin} per copper site is [7]:

$$\frac{\Delta W}{W_s} - \frac{4\pi c}{137\hbar}\frac{a^2}{V}\frac{1}{\Omega_L^2}(E_{kin,s} - E_{kin,n}) = 1 \qquad (2)$$

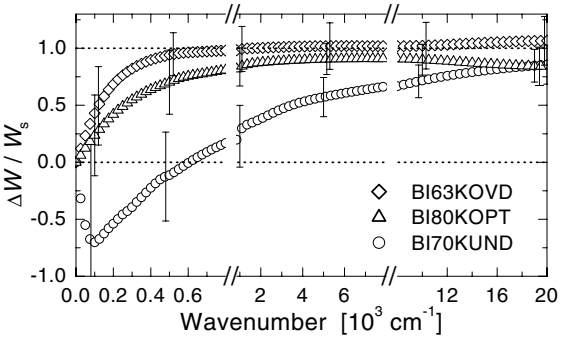

Fig. 3. Ratio $\Delta W/W_s$ versus frequency showing the exhaustion of the FGT sum rule at conventional energies for the OVD (diamonds, right error bars) and OPT (triangles, middle error bars) samples. An unconventional (~16,000 cm^{-1} or 2 eV) energy scale is required for the UND sample (circles, left error bars). $T_A = 80$, 91 and 80 K for the OVD, OPT and UND samples, respectively. For all the samples, $T_B = 10$ K (see text). Note that the frequency scale changes at 800 and 8000 cm^{-1}.

where a is the (average) lattice spacing in the plane and V is the volume per site (SI units). This relation means that a breakdown of the FGT sum-rule up to an energy $\hbar\omega_c$ of the order of the plasma frequency ($\sim$1 eV for Bi-2212) is related to a change in the carrier kinetic energy $\Delta E_k = E_{\mathrm{kin,s}} - E_{\mathrm{kin,n}}$, when entering the superconducting state. According to our results in the UD sample (Fig. 3), $\Delta W/W_s = 0.65 \pm 0.18$ at 1 eV, which yields $\Delta E_k = 1.1 \pm 0.3$ meV per copper site. This is a huge kinetic energy gain, $\sim$ 15 times larger than the condensation energy U_0. For optimally doped Bi-2212, $U_0 \simeq 1$ J/g at $\approx$0.08 meV per copper site [15].

Fig. 4 shows the temperature changes in kinetic energy per charge carrier (relative to the 10 K kinetic energy) as calculated from the infrared (0–1 eV) changes in spectral weight (Eq. (2)). This figure shows the kink resulting in a decrease of 1 meV in the superconducting state, consistent with the experimental results of Ref. [4]. Note that it is the analysis of the IR spectral weight together with the superfluid weight that actually tell that such extra transfer is used to build-up the superconducting condensate (Fig. 3).

Various scenarios are consistent with our results. Most of them (but not all) propose indeed a superconducting transition driven by an in-plane kinetic energy change: holes moving in an antiferromagnetic background [16], hole undressing [17], phase fluctuations of the superconducting order parameter in superconductors with low carrier density (phase stiffness) [18], and quasiparticle formation in the superconducting state [19]. There is a quantitative agreement between our results and those of the hole undressing and quasiparticle formation scenarios.

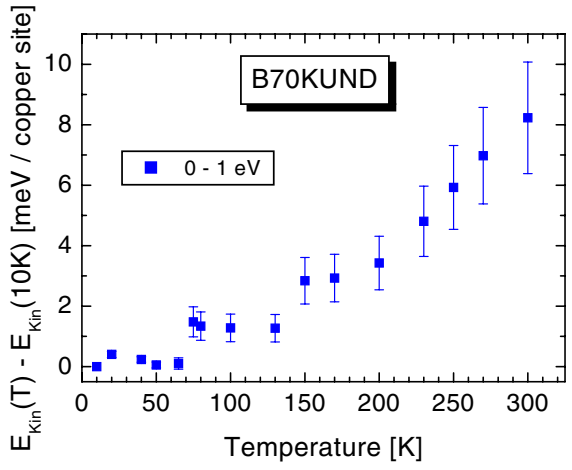

Fig. 4. Temperature changes in kinetic energy per charge carrier, as calculated from the infrared (0–1 eV) changes in spectral weight (see Eq. (2)). The kinetic energy at 10 K is taken as the ground energy. The 1 eV frequency cut-off can be changed from 0.8 to 1.2 without altering the main features (in particular the 1 meV kink at T_c).

In conclusion, we have have found for the in-plane conductivity of the underdoped Bi-2212 a large ($\sim$30%) transfer of spectral weight from regions of the visible–ultraviolet spectrum to the superfluid condensate. This corresponds to a kinetic energy lowering of $\sim$1 meV per copper site. The very large energy scale required in order to exhaust the sum rule in the underdoped sample cannot be related to a conventional bosonic scale, hence strongly suggests an electronic pairing mechanism.

Acknowledgements

AFSS thanks Colciencias and Ministère Français des Affaires Etrangères (through the Eiffel Fellowships Program) for financial support. RPSML acknowledges the financial support of CNRS-ESPCI.

References

[1] R.A. Ferrell, R.E. Glover, Phys. Rev. 109 (1958) 1398;
M. Tinkham, R.A. Ferrell, Phys. Rev. Lett. 2 (1959) 331.
[2] See e.g. Ch. Renner et al., Phys. Rev. Lett. 80 (1998) 149;
M. Randeria, J.C. Campuzano, <cond-mat/9709107>.
[3] M.R. Rübhausen et al., Phys. Rev. B 63 (2001) 224512.
[4] H.J.A. Molegraaf et al., Science 295 (2002) 2239.
[5] A.F. Santander-Syro et al., in: I. Bozovic, D. Pavuna (Eds.), Superconducting and Related Oxides: Physics and Nanoengineering V, Proc. SPIE 4811, 2002, pp. 48–59.
[6] Z. Konstantinovic, Z.Z. Li, H. Raffy, Physica B 259–261 (1999) 569.
[7] D. van der Marel et al., Strong Correlation in the High T_c Era, Lecture Notes, Trieste Miniworkshop, ICTP, Trieste (Italy), 17–28 July 2000.
[8] The best description of our data was obtained by assuming no backward reflection from the rear of the substrate (i.e., assuming an infinitely thick substrate).
[9] M.A. Quijada et al., Phys. Rev. B 60 (1999) 14917.
[10] A.F. Santander-Syro et al., Phys. Rev. Lett. 88 (2002) 097005.
[11] A.F. Santander-Syro et al., Europhys. Lett. 62 (2003) 568.
[12] G. Villard et al., Phys. Rev. B 58 (1998) 15231.
[13] D. Di Castro et al., Physica C 332 (2000) 405.
[14] D.N. Basov et al., Phys. Rev. B 63 (2001) 134514-1.
[15] J.W. Loram et al., Physica C 341–348 (2000) 831.
[16] J. Bonca, P. Prelovsek, I. Sega, Phys. Rev. B 39 (1989) 7074;
E. Dagotto, J. Riera, A.P. Young, Phys. Rev. B 42 (1990) 2347;
T. Barnes et al., Phys. Rev. B 45 (1992) 256.
[17] J.E. Hirsch, Phys. Rev. B 62 (2000) 14487;
J.E. Hirsch, Phys. Rev. B 62 (2000) 14498.
[18] T. Eckl, W. Hanke, E. Arrigoni, <cond-mat/0207425>.
[19] M.R. Norman, C. Pépin, Phys. Rev. B 66 (2002) 100506(R).