Frequency-Dependent Thermal Response of the Charge System and the Restricted Sum Rules of $La_{2-x}Sr_xCuO_4$

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In $La_{2-x}Sr_xCuO_4$ (LSCO) the spectral weight $W = \int_0^\Omega \sigma_1^{ab}(\omega, T)d\omega$ [where $\sigma_1^{ab}(\omega, T)$ is the ab-plane conductivity] obeys the same law $W = W_0 - B(\Omega)T^2$ as in a conventional metal such as gold, for any Ω up to the plasma edge. However, in LSCO $B(\Omega)$ points toward correlation effects and, unlike in gold, is related to an energy scale $t_T \ll t_0 \sim W_0$. The Ferrell-Glover-Tinkham sum rule is fulfilled in LSCO superconductors for $\Omega \gtrsim 2000$ cm^{-1}.

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The optical properties of high-T_c cuprates, both in the normal and in the superconducting phase, are still extensively discussed in the literature. For $T > T_c$, an infrared conductivity $\sigma_1^{ab}(\omega)$ peaked at $\omega = 0$ and smoothly decreasing with ω supports one-component approaches [1]. In other experiments, contributions peaked at finite frequencies show up [2,3], which point towards charge localization and ordering. Below T_c, contradictory results are reported on the London penetration depth [4,5] extracted from $\sigma_1^{ab}(\omega)$.

Therefore, recent works have been often focused on a model-independent quantity such as the spectral weight

$$W(\Omega, T) = \int_0^\Omega \sigma_1(\omega, T)d\omega \qquad (1)$$

and on its behavior in different spectral ranges. For $\Omega \rightarrow \infty$, the sum rule on the real part of the optical conductivity $\sigma_1(\omega, T)$ requires that $W(\Omega, T)$ is independent of temperature. However, there are a few special cases where "restricted sum rules" can be considered. In metals $W(\omega_p)$, where ω_p is the plasma frequency which approximately coincides with the minimum in the reflectivity (plasma edge), is expected to be nearly independent of T [6]. Another example is the Ferrell-Glover-Tinkham (FGT) sum rule which predicts that the W lost at low energy when a superconductor is cooled below T_c is recovered in the δ function at $\omega = 0$.

In cuprates such as $Bi_2Sr_2CaCu_2O_{8+y}$ (BSCCO) and $YBa_2Cu_3O_{7-y}$ the restricted sum rules have been investigated by several groups [7–10]. In $La_{2-x}Sr_xCuO_4$ (LSCO), a similar study on the in-plane $\sigma_1^{ab}(\omega)$ has recently appeared [5], while a previous work was focused on the c-axis conductivity [11]. In the present Letter we study the behavior of $W(\Omega, T)$ in LSCO. In the normal phase, starting from the sum rule restricted to ω_p, we observe topic differences between LSCO, BSCCO, and conventional metals, which lead us to identify two different energy scales for the charge system in the cuprates. In the superconducting phase we find that the FGT sum rule holds only if the frequency range is extended well above 2000 cm^{-1}.

The reflectivity $R_{ab}(\omega)$ of the two LSCO single crystals (a superconductor with $x = 0.12$ and a nonsuperconducting metal with $x = 0.26$) were measured with respect to that of a gold film (between 15 and 12 000 cm^{-1}) and a silver film (up to 20 000 cm^{-1}), both of which evaporated *in situ* onto the sample. The reflectivity of gold was then measured with respect to a platinum mirror, both in order to correct for its ω dependence in the near infrared and to compare the response of LSCO at $x = 0.26$, which is often indicated as a "normal metal" with that of a good conventional metal. The optical configuration for measuring $R_{ab}(\omega)$ in LSCO is shown in the inset of Fig. 1(a). The radiation impinges under an incidence angle of 8° on the surface of the crystal. By use of a four-circle diffractometer and a laser we determined for $x = 0.12$ a miscut of $\theta = 1.0° \pm 0.5°$ with respect to an ideal ab plane. Therefore, we used a polarizer to align the electric field orthogonally to the miscut plane. We show elsewhere [12] that, under these conditions, the relative deviation with respect to the ideal reflectivity of the ab plane is

$$\frac{\Delta R_{ab}(\omega)}{R_{ab}(\omega)} \simeq \sqrt{2(1-\eta)}\,\frac{1 - R_{ab}^2(\omega)}{R_{ab}(\omega)}\,\theta^2 g(\omega). \qquad (2)$$

Here, $\eta = (I_p - I_u)/(I_p + I_u)$, as I_p (I_u) is the intensity of the field component parallel (orthogonal) to the polarizing direction. It is plotted in the inset (gray lines) for both the polyethylene and the KRS-5 device here used. Moreover,

$$g(\omega) = \left[\frac{-2\omega}{\pi\epsilon_2^{ab}}\wp\int_0^\infty \frac{-(\epsilon_1^{ab})^2/2\epsilon_1^c}{\omega'^2 - \omega^2}\,d\omega' + \frac{1}{2}\right]. \qquad (3)$$

$\Delta R_{ab}(\omega)/R_{ab}(\omega)$ turns out to be [12] on the order of 0.001 at 100 cm^{-1}, much smaller than the experimental noise. In fact, no signature of the c-axis phonons appears in the $R_{ab}(\omega)$ of the $x = 0.12$ sample (see the top inset of Fig. 1). In previous measurements on the ac surface of the same sample, reported in Ref. [3], a dip from such a phonon appeared around 470 cm^{-1} [13]. In that case, however, the commercial polyethylene polarizer was used in its whole transmittance range. As shown in the inset, η drops to 0.93 at that frequency, causing a 4% deviation from the real reflectivity of the a axis. Below

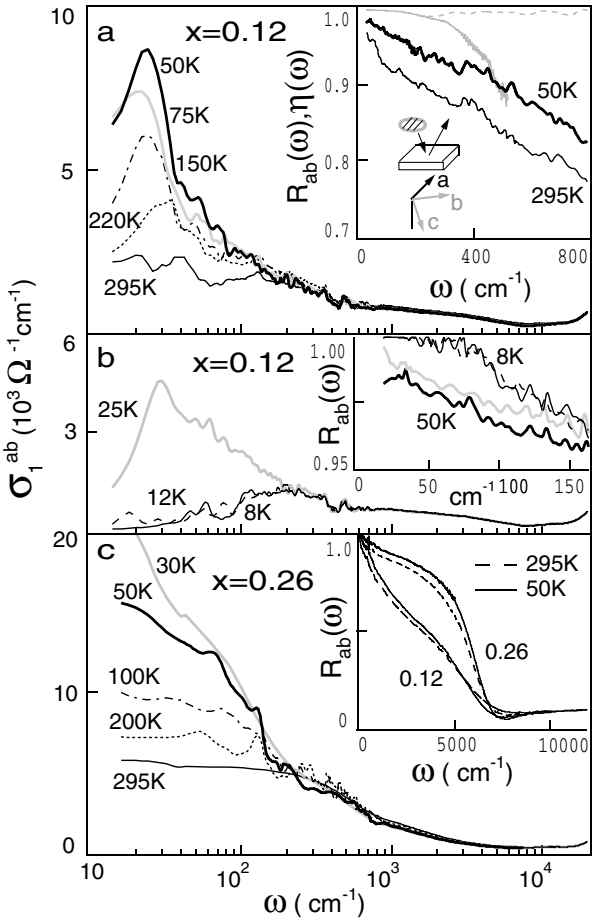

FIG. 1. Optical conductivity, from the reflectivity data reported in the inset, of the underdoped crystal $x = 0.12$ above T_c (a) and below T_c (b) compared with that of the nonsuperconducting metal $x = 0.26$ (c). The insets show the corresponding R_{ab}: in the far infrared (FIR) for $x = 0.12$ (a) above and (b) below T_c; in the whole energy range for both $x = 0.12$ and 0.26 (c). In the inset of (a) the gray lines plot the efficiency η of the polarizers employed in the experiment: polyethylene (solid line) and KRS-5 (dotted line).

200 cm^{-1}, where $\eta > 0.99$, the results of Ref. [3] on this one and other samples were not affected by the c-axis response. This is confirmed by the results with the present safe procedure, which was applied to both $x = 0.12$ and 0.26. In the former one the in-plane conductivity $\sigma_1^{ab}(\omega)$, once extracted from the $R_{ab}(\omega)$ extrapolated to $\omega = 0$ by a Drude-Lorentz fit, shows again [Fig. 1(a)] the T-dependent resonance at $\simeq 30$ cm^{-1} reported in Ref. [3] for this and other LSCO samples. The resonance is not observed in the nonsuperconducting metal with $x = 0.26$ [Fig. 1(c)]. A discussion of the FIR peak and of other details of the LSCO conductivity is reported in Refs. [3,14]. They are not relevant to the present study of the spectral weight in LSCO, a quantity insensitive to narrow spectral features in the far infrared.

In both samples of Fig. 1, the screened plasma frequency $\tilde{\omega}_p$ obtained from the condition $\epsilon_1(\omega) \simeq 0$ (for a scattering rate $\Gamma \ll \tilde{\omega}_p$) is 6100 ± 150 cm^{-1}, independent of T within errors. This is in agreement with the value (6300 ± 100 cm^{-1}) extracted from a Drude fit in LSCO films with different doping [4]. However, in order to include the whole free-carrier contribution in Eq. (1), we followed Ref. [15] and extended the integration limit Ω to the ω_p corresponding to the minimum in the reflectivity (plasma edge). In the inset of Fig. 1(c), this gives 6800 cm^{-1} for both samples. In conventional metals W exhibits a temperature dependence

$$W(\Omega = \omega_p, T) \simeq W_0 - BT^2, \tag{4}$$

where W_0 accounts for all the carriers in the conduction band, while B depends crucially on the density of states at the Fermi energy $\rho(E_F)$. In a tight-binding approach *both W_0 and B depend on the same hopping rate t_0*. Equation (4) is verified in gold, as one can see from our data in Fig. 2(c) where $\omega_p = 20\,500$ cm^{-1} (from the zero crossing of ϵ_1).

It has been found that Eq. (4) holds also for a high-T_c superconductor such as BSCCO [8,15]. Here, Figs. 2(d) and 2(e) show that this behavior is verified also in LSCO, both for $x = 0.26$ and $x = 0.12$. One may ask if these findings are sufficient to extend the above tight-binding approach, characterized by a single energy scale t_0, to cuprates. To obtain deeper insight, we notice that for LSCO, based on the good fits in Figs. 2(d) and 2(e), the above T^2 dependence holds [16] not only at ω_p, but also

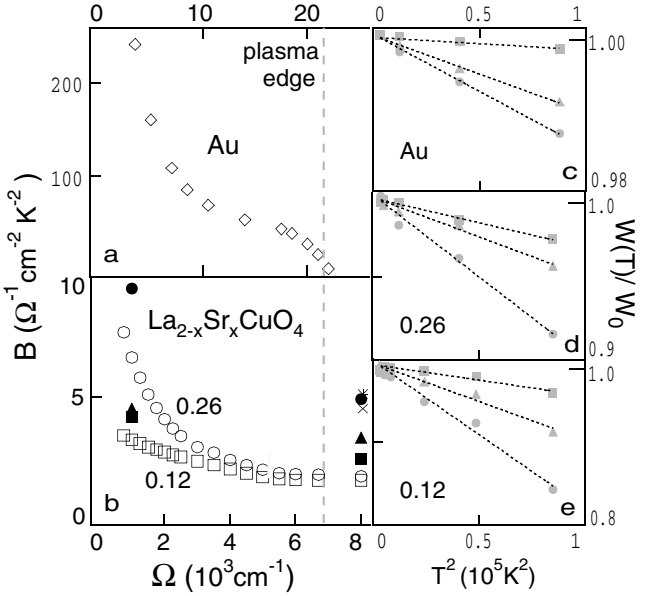

FIG. 2. The coefficient $B(\Omega)$ in Eq. (4) is plotted for gold (a), and LSCO with $x = 0.12$ and 0.26 (b), as extracted from plots like those in (c), (d), and (e), respectively. Therein, gray squares refer to $\Omega = \omega_p$, triangles to $\Omega = 0.5\omega_p$, and circles to $\Omega = 0.2\omega_p$. In (b), B values obtained from the existing data on $Bi_2Sr_3CaCu_2O_{8+y}$ with different y and T_c are reported for comparison: full symbols are from Ref. [7] (circles, $T_c = 70$ K; triangles, 80 K, squares, 63 K); the star ($T_c = 88$ K) and the cross (66 K) are extracted from the data of Ref. [8].

for lower values of Ω (provided that they are higher than the highest phonon frequency, ~ 700 cm^{-1}). Therefore, we can write for both gold and LSCO

$$W(\Omega, T) \simeq W_0 - B(\Omega)T^2. \quad (5)$$

The frequency-dependent coefficient $B(\Omega)$, which we introduce through Eq. (5), describes the "thermal response" of the carriers. It can be evaluated at any Ω as done in Figs. 2(c)–2(e). The resulting values are reported in the left panels of the same figure. In gold (a), all T-dependent mechanisms are confined at $\omega \lesssim \omega_p$ and at the plasma edge, $B \simeq 0$. In both LSCO samples, on the contrary, at the edge B is still much different from zero [$B(\omega_p) = 1.7\ \Omega^{-1}\,\mathrm{cm}^{-2}\,\mathrm{K}^{-2}$]. (When evaluating these figures one should consider that the B scale for gold is larger by more than a factor of 10 than in LSCO, as $W_0 \propto \omega_p^2$.) The result at ω_p is not surprising, in view of the correlation effects that, in LSCO, may extend the T dependence of the carrier response up to energies on the order of the Hubbard splitting U. One should then observe similar effects in other cuprates. Indeed, by using the data of Refs. [8,15] on five BSCCO samples with different T_c's, one obtains the B values shown for comparison in Fig. 2(b). All of them, at the BSCCO $\omega_p \sim 8000$ cm^{-1}, are even higher than here found in LSCO.

One may ask if the predictions of the noninteracting, tight-binding model for the Cu-O square lattice are compatible with these results. For the present purpose one can use a simplified one-band picture and obtain

$$W(\Omega = \omega_p, T) = \frac{\pi e^2 a^2}{2\hbar^2 V} K, \quad (6)$$

where K is the kinetic energy of the carriers, a is the Cu-O plane lattice parameter, and V is the LSCO cell volume. In this framework, Eq. (4) derives directly from the Sommerfeld expansion of the Fermi distribution function [17] which, in a first approximation, also gives

$$B(\Omega = \omega_p) \simeq \frac{\pi e^2 a^2}{2\hbar^2 V} \frac{\pi^2 k_B^2}{6} \rho(E_F) \equiv A \frac{\pi^2}{6} \rho(E_F). \quad (7)$$

In two dimensions one may introduce the simplifying assumption of a rectangular density of states, so as $\rho(E_F) = \rho(E) = (4t_T)^{-1}$, where t_T is the hopping rate. Then one finds $t_T = \pi^2 A/[24B(\omega_p)] = 22$ meV which corresponds to a bandwidth $8t_T = 176$ meV. By applying the same procedure, even smaller values for t_T can be extracted from the data [8,15] reported in Fig. 2 for $Bi_2Sr_2CaCu_2O_{8+y}$. On the other hand, applying to the present data Eq. (6), one obtains $W_0 \simeq 240$ meV for $x = 0.12$ and 350 meV for $x = 0.26$. This provides the hopping rate related to the full bandwidth, which we call t_0. As in any hopping model $t_0 \lesssim W_0 \lesssim 2t_0$, t_0 is in qualitative agreement both with estimates for the Cu-O planes from photoemission data (250–300 meV) [18] and with energy band calculations (430 meV) [19]. However, t_0 is larger, by 1 order of magnitude, than the above t_T obtained from the temperature dependence of W. In the noninteracting description, the two values should be the same. The present inconsistency shows once again that a simple hopping model cannot describe the electrodynamics of the Cu-O planes. One could perform more reliable tight-binding calculations, including the effects of next-nearest neighbor hopping rate t', to obtain a different value of $\rho(E_F)$ and hence of t_T. However, it is unlikely that such corrections may increase t_T by an order of magnitude. On the other hand, the possibility that a Van Hove singularity in $\rho(E)$, close to the Fermi level, may play a major role in the observed T dependence of W, can be excluded. It would imply that t_T might change very strongly when passing from $x = 0.12$ to 0.26, in contradiction with the present results at $\Omega \sim \omega_p$.

In summary, our results indicate a coexistence of *two different energy scales* in Eq. (5), t_0 and t_T. The former one is related to the width of the broad conduction band built up either directly by doping or by doping-induced transfer of spectral weight from the high-energy bands [20]. In turn, t_T seems to control the transfer of spectral weight that is triggered by temperature. From this point of view, one may notice that a similar energy scale is involved in pseudogap formation [1]. However, as the latter phenomenon is restricted to underdoped compounds, that hint should be supported by analyzing the difference in the low-energy thermal response between 0.12 and 0.26, which clearly appears in Fig. 2(b).

The behavior of $B(\Omega)$ for $x = 0.12$ in Fig. 2 deserves a few further comments. As the T dependence of the response is concentrated below ~ 4000 cm^{-1}, the Drude term vanishes at frequencies definitely lower than the pseudoplasma edge at ~ 6000 cm^{-1}. This may explain why this energy is basically insensitive to the number of carriers (in the inset of Fig. 1(c) it is the same for $x = 0.12$ and 0.26). A large part of the T-independent spectral weight W_0 may be ascribed to the midinfrared band peaked at ~ 0.5 eV, directly observed in the semiconducting phase of several cuprates [20] and usually included in the multicomponent models of $\sigma_1^{ab}(\omega)$ as a T-independent component [21].

The behavior of the spectral weight in the superconducting phase has been studied in the sample with $x = 0.12$ and, for comparison, in two LSCO single crystals with $x = 0.10$ and 0.15. Their raw data are reported in Refs. [22] and [3], respectively. We plot in Fig. 3 the difference $W_n - W_s$ between the spectral weight in the normal phase at 50 K and that at a T well below T_c. The right-hand panel shows plots of $(\pi/2)\omega\sigma_2^{ab}(\omega)$, where σ_2^{ab} is the imaginary part of the in-plane conductivity and is approximately constant, as expected, for $\omega \leq 250$ cm^{-1}. Its limit for $\omega \to 0$ gives the spectral weight which, below T_c, condenses at $\omega = 0$ [7,8]. In Fig 3, it coincides for the three samples with the difference $W_n - W_s$ for $\Omega \gtrsim 2000$ cm^{-1}. As the gaplike feature in Fig. 2(b) appears around 200 cm^{-1}, in LSCO the energy range involved in the FGT sum rule is much larger than

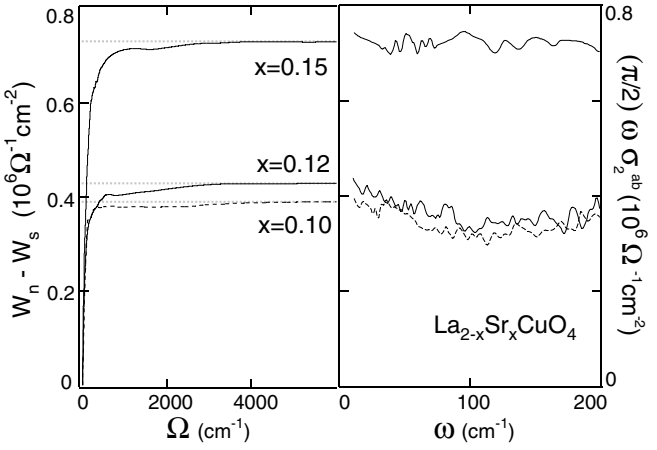

FIG. 3. In the left panel, the difference $W_n - W_s$ between the spectral weight calculated from $\sigma_1^{ab}(\omega)$ at 50 K and that at $T < T_c$ is plotted vs the integration limit Ω for $x = 0.15$ ($T_c = 41$ K and $T = 23$ K), $x = 0.12$ ($T_c = 29$ K and $T = 12$ K), and $x = 0.10$ ($T_c = 27$ K and $T = 16$ K). In the right panel $(\pi/2)\omega\sigma_2^{ab}$ is approximately independent of ω for the three samples, as expected, and for $\omega \to 0$ provides the spectral weight of the condensate.

expected for a conventional superconductor, as reported for other hole-doped cuprates [8].

From $W_n - W_s$ one can also extract the London penetration depth λ_L. For the three crystals with $x = 0.10, 0.12$, and 0.15 of Fig. 2 one obtains 295, 280, and 215 nm, respectively. These values are in good agreement with a previous optical determination in LSCO with $x = 0.15$ [4] and also with recent muon-spin-rotation measurements [23].

In conclusion, we have used model-independent quantities to compare the infrared response of an underdoped LSCO superconductor and a nonsuperconducting LSCO crystal (indicated in the phase diagram of LSCO as a normal metal) with that of a conventional metal such as gold. In all three samples, the spectral weight $W(\Omega, T)$ follows the quadratic law $W = W_0 - B(\Omega)T^2$ for any Ω lower than ω_p. This allows one to introduce a useful quantity, the thermal response $B(\Omega)$. In gold, $B(\omega_p)$ is reduced to a vanishingly small fraction of its low-ω value, while in both LSCO samples and in BSCCO $B(\omega_p)$ is much different from zero. This confirms that the behavior of cuprates is dominated by correlation effects, which extend the energy scale of the restricted sum rule much beyond the plasma edge. We have then applied a single-band hopping model to verify whether W_0 and B are controlled by the same energy scale, as predicted for normal metals. The result clearly indicates the coexistence of two different energy scales in both LSCO samples, t_0 and t_T. t_0 is consistent with the bandwidth of photoemission experiments and scales with doping, while t_T is smaller by 1 order of magnitude. When lowering the temperature, t_T controls the transfer of spectral weight in the Drude term towards low frequency. In underdoped samples like the present one with $x = 0.12$, this may compete with the opposite transfer corresponding to the opening of a pseudogap [1] since it has the right size ($\sim$20 meV or 200 K). This may explain the much smaller variation of B for low Ω at 0.12 than at 0.26, where no pseudogap phenomena are observed. Concerning the superconducting phase, the spectral weight lost below T_c at $\omega > 0$ is fully recovered, within errors, by the weight condensed at $\omega = 0$ in a spectral range of about 0.5 eV. This value is lower than in cuprates with higher T_c's, but higher by 1 order of magnitude than in conventional superconductors. The London penetration depth depends on doping and is consistent with muon-spin-rotation values.

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