Kinetic energy change with doping upon superfluid condensation in high-temperature superconductors

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In conventional BCS superconductors, the electronic kinetic energy increases upon superfluid condensation (the change ΔE_{kin} is positive). Here we show that in the high critical temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$, ΔE_{kin} crosses over from a fully compatible conventional BCS behavior ($\Delta E_{kin}>0$) to an unconventional behavior ($\Delta E_{kin}<0$) as the free carrier density decreases. If a single mechanism is responsible for superconductivity across the whole phase diagram of high critical temperature superconductors, this mechanism should allow for a smooth transition between two such regimes around optimal doping.

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One of the fundamental predictions of the BCS theory is that the kinetic energy of the charge carriers increases upon condensation in the superconducting state, while the interaction energy decreases and overcompensates the kinetic energy increase, resulting in a net energy gain. The value of this condensation energy is easily determined, for instance, from the value of the thermodynamical critical field, but the respective changes in kinetic and interaction terms are not easily accessed. In fact, the change in kinetic energy in "conventional" BCS superconductors has never been determined experimentally. This change is of the order of $(\Delta/E_F)^2$, where Δ is the energy gap and E_F the Fermi energy. It is exceedingly small for a typical low-temperature superconductor, of the order of 10^{-6} to 10^{-8}.

The situation is much more favorable in high critical temperature superconductors (HCTS, cuprates), where the gap is larger and the Fermi energy smaller, so that the change in kinetic energy, if it is to conform to the predictions of the BCS theory, should be of the order of 10^{-3} to 10^{-2}, a change that has become accessible experimentally.[1–3] However, the mechanism for HCTS is still under debate and the change in kinetic energy could well be different from that predicted by BCS, including in sign.

It is of particular interest to investigate the case of overdoped high-temperature superconductors. There is a general belief that in the overdoped range, the cuprates can be described in their normal state as Fermi liquids. Thus it is conceivable that in this regime, condensation is of the BCS kind, and if it is, according to the above considerations regarding orders of magnitude, the change in kinetic energy should be large enough to be measured, allowing a quantitative comparison between theory and experiment.

Our analysis shows that the change in kinetic energy in overdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) having $T_c=63$ K is indeed compatible with the predictions of the BCS theory, both in sign and in size. The latter result appears in the data in our previous papers, but was not explicitly mentioned.[2,3] This is in contrast with the change of kinetic energy in optimally doped, and definitely in underdoped Bi-2212, which has been found to be of the opposite sign.[1–3] We observe that going from the overdoped to the underdoped regime, the change in kinetic energy is actually progressive, going through zero not far from optimum doping. This progressive change strongly suggests that there is in the cuprates a smooth transition from a conventional mode of condensation in the overdoped regime to an unconventional mode in the underdoped one.

We note in this context that, whereas the separation between kinetic and potential energies can be worked out in the Fermi liquid framework[4] (overdoped cuprates), this separation may be a more complex issue in strongly correlated non-Fermi-liquid materials (underdoped cuprates).[5]

We recall that from measurements of the reflectivity, one can derive the real part $\sigma_1(\omega)$ and the imaginary part $\sigma_2(\omega)$ of the optical conductivity. The single band sum rule[6] writes:

$$\int_0^\infty \sigma_{1,xx}(\omega)d\omega = \frac{\pi e^2 a^2}{2\hbar^2 V} E_K, \tag{1}$$

where e is the electron charge, a the in-plane lattice constant, and V the volume of the unit cell. E_K is given by

$$E_K = \frac{2}{a^2 N}\sum_k \frac{\partial^2 \epsilon_k}{\partial k_x^2} n_k, \tag{2}$$

where N is the number of k vectors, ϵ_k is the dispersion from the kinetic energy part of the Hamiltonian, and n_k is the momentum distribution function.

In a nearest neighbor tight binding model, the kinetic energy is related to E_K:

$$E_{kin} = -E_K. \tag{3}$$

From numerical calculations, it was shown that relation (3) is still valid (however, within ~50% for the size of the changes upon condensation) when taking into account the second nearest neighbor hopping with a value $t'/t=-0.27$ relative to the nearest neighbor term.[7]

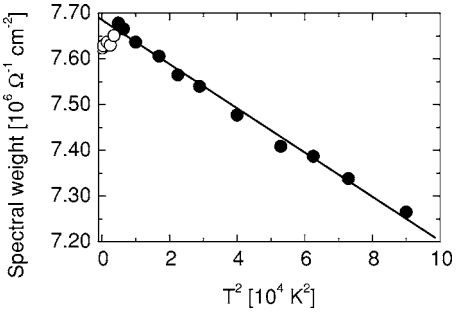

FIG. 1. Spectral weight of the overdoped Bi-2212 sample, integrated up to 1 eV, plotted vs T^2, from Ref. 3. Closed symbols: spectral weight in the normal state, open symbols: spectral weight in the superconducting state, including the weight of the superfluid. The errors in the *relative* variations of the spectral weight are of the size of the symbols.

The optical conductivity is generally derived experimentally from a Kramers-Kronig transform of the reflectivity,[8] or by fitting the reflectivity,[2,3] or more accurately by a combination of ellipsometric measurements in the visible supplemented by infrared and visible reflectivity.[1] Two difficulties arise when computing the spectral weight defined in Eq. (1), related to the limits of the integral: (i) one has to choose a cutoff frequency Ω_c in order to avoid including interband transitions which are irrelevant to the calculation of the kinetic energy, and (ii) the optical conductivity cannot be derived starting from zero: one is restricted at best to the experimental lowest frequency.

The choice of the high-frequency cutoff is a difficult problem: it is generally agreed to select a cutoff significantly below the energy of the charge transfer band, located at typically 1.5 eV. Therefore according to the authors, $\Omega_c \sim 0.6-1.2$ eV.[1–3,9] We have calculated the spectral weight for various cutoff energies in this range. It changes with the cutoff but the trend as a function of doping is robust. In the following, we will show data for a 1 eV cutoff. The uncertainty on the temperature changes of the spectral weight is $\sim 0.3\%$ in this range.[10] The low limit can be dealt with by fitting the reflectivity and using the deduced optical conductivity in order to extrapolate to zero.[2,3] In the superconducting state, the spectral weight includes the superfluid weight which is extracted from the data[11] or inferred from the fit.[2,3]

We show in Fig. 1 the change of spectral weight as a function of T^2, for an overdoped Bi-2212 sample, after reconstructing the optical conductivity through a well-controlled fitting procedure from the reflectivity of a thin film.[3,10] The spectral weight integral [Eq. (1)] has been extended up to 1 eV (8000 cm^{-1}). In the normal state, it is linear in T^2. The change from room temperature down to T_c is about 5%. At T_c, a change in *sign* of the slope of the temperature dependence of the integral, corresponding to an increase in kinetic energy, is observed very clearly. By extrapolating the temperature dependence in the normal state down to $T=0$ following the T^2 behavior found above T_c, one can obtain the value $\Delta E_{kin}/E_{kin}^N$ of the difference between the kinetic energy in the normal and superconducting states in that limit. We find that it is of about 1%.

According to BCS theory, the increase in kinetic energy in the superconducting state per unit volume is given by

$$\Delta E_{kin} = \frac{\Delta^2}{\mathcal{V}} - \frac{\mathcal{N}(0)\Delta^2}{2}, \tag{4}$$

where $\mathcal{N}(0)$ is the density of states at the Fermi level, and $\mathcal{V}$ the interaction parameter. Because $\mathcal{N}(0)\mathcal{V}$ is in any case substantially smaller than unity, we neglect at first the second term of the right-hand side. We then obtain

$$\frac{\Delta E_{kin}}{E_{kin}^N} \approx \frac{1}{\mathcal{N}(0)\mathcal{V}}\left(\frac{\Delta}{E_F}\right)^2, \tag{5}$$

where E_{kin}^N is the kinetic energy in the normal state at $T=0$. The quantity $\Delta E_{kin}/E_{kin}^N$ is precisely that measured experimentally following the procedure described above. Taking the values $\Delta = 20$ meV and $E_F = 500$ meV,[12] we obtain $\mathcal{N}(0)\mathcal{V} \approx 0.16$, not an unreasonable value. A slightly higher value of 0.2 is obtained by taking into account the condensation energy, i.e, the second term of the right-hand side of Eq. (4), as measured, for instance, by Loram.[13] The measured change in kinetic energy for this overdoped sample is thus in good agreement with BCS theory, both in sign and in value.

We now turn to a comparison between the behavior of the overdoped sample, and that of optimally and underdoped samples. In the normal state, the change in kinetic energy with temperature is somewhat smaller (4%) but close to that of the overdoped sample.[1–3] However, upon condensation, there is now a relative decrease in kinetic energy of about -0.2% for close to optimally doped[1] or about 0 within the error bars,[2,3] and of -0.5%[1,14] or -0.7%[3] for underdoped samples. These values were obtained by noting that the normal state spectral weight follows a T^2 dependence from room temperature down to 90–100 K for the optimally doped and underdoped samples of Ref. 1, and down to $\sim T_c$ for the optimally doped sample of Ref. 3, whereas its value saturates below 150 K for the underdoped sample of Ref. 3. We extrapolated the normal state spectral weight down to $T=0$, using the T^2 behavior for the first three samples and the saturated value for the latter underdoped sample from Ref. 3.

The transition between the BCS and unconventional regimes thus appears to be progressive: Fig. 2 shows the change ΔE_{kin} (in meV/Cu) as a function of $(p-p_{opt})$,[15] through

$$\frac{T_c}{T_{c,opt}} = 1 - 86.2(p - p_{opt})^2, \tag{6}$$

where p is the charge per Cu atom, and p_{opt} corresponds to the maximal critical temperature $T_{c,opt}$.[16]

The case of the overdoped sample is clear. The kinetic energy increases in the superconducting state by an amount compatible with a BCS condensation. This result is in line with the observation that the full spectral weight in the superconducting state is recovered, within ΔE_{kin}, at an energy equal to a few times the gap, as shown in Refs. 2 and 3. By contrast, for the underdoped sample, the full spectral weight is clearly only recovered at energies of more than 1 eV, or about 40 times the gap, and the kinetic energy now decreases

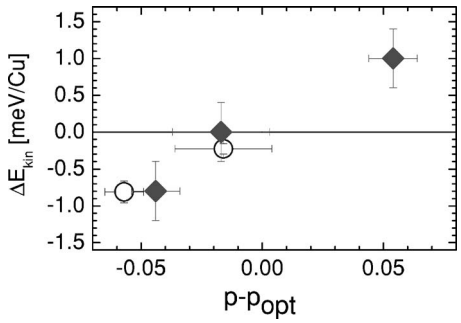

FIG. 2. Change ΔE_{kin} of the kinetic energy, in meV per copper site, calculated from Eqs. (1) and (3), vs the charge p per copper with respect to p_{opt} [Eq. (6)]. Full diamonds: data from Ref. 3, high-frequency cutoff 1 eV. Open circles: data from Ref. 1, high-frequency cutoff 1.25 eV. Error bars: vertical, uncertainties due to the extrapolation of the temperature dependence of the normal state spectral weight down to zero temperature; horizontal, uncertainties resulting from $T_c/T_{c,max}$ through Eq. (6) (see text). We have taken $T_{c,max}=(83\pm2)$ K for films and (91 ± 2) K for crystals.

in the superconducting state.[2,3] Both in terms of the change in kinetic energy and rate of recovery of the spectral weight, nearly optimum doped samples are intermediate between the overdoped and the underdoped ones: the change in kinetic energy is small. This doping dependence suggests a smooth transition from a BCS mode of condensation in the overdoped regime to a different mode in underdoped samples, as one would expect, for instance, in the case of a BCS to Bose-Einstein crossover.[17]

In the case of $YBa_2Cu_3O_{6+x}$ (YBCO), we are not aware of any measurement in overdoped samples. In underdoped $YBa_2Cu_3O_{6.6}$, an unconventional energy scale (of about 0.6 eV) for recovering the full spectral weight was found, whereas in optimally doped samples, the change in kinetic energy is definitely small.[18]

While much theoretical and experimental emphasis has been given in previous works to the unconventional behavior of the kinetic energy change ΔE_{kin} in underdoped samples, the full compatibility of the behavior of overdoped samples with a BCS mode of condensation has been so far overlooked. Most important, the sign and size of ΔE_{kin} upon condensation in the superconducting state and the rate of recovery of the spectral weight point simultaneously towards a progressive change in the condensation regime when going from underdoped to overdoped. Such an overall behavior shows that the high-T_c mechanism, if it is the same across the phase diagram, must allow for the observed transition from kinetic energy loss to kinetic energy increase as doping is increased.

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