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LETTER TO THE EDITOR

Normal state thermodynamics of cuprate superconductors

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Abstract. We propose an explanation of the pseudogap features discovered in the normal state specific heat and magnetic susceptibility of cuprates. We explain the magnitudes of the carrier specific heat and susceptibility as well as their universal scaling with temperature over a wide range of doping of $YBa_2Cu_3O_{7-\delta}$.

There is strong evidence for the normal state pseudogap in high-T_c cuprates from magnetic susceptibility [1], specific heat [2], angle-resolved photoemission (ARPES) [3], tunnelling [4], and some kinetic measurements [5]. One view supported by ARPES is that the gap reflects precursor superconducting correlations in the BCS-like state below some characteristic temperature T^* without long-range phase coherence [6]. Testing this hypothesis with specific heat [2] and tunnelling [4] data, it is found that this view cannot be sustained. In particular, there is no sign that the gap closes at a given temperature T^*, which rules out any role of superconducting phase or spin fluctuations [4]. On the other hand, the strong-coupling extension of the BCS theory based on the multi-polaron perturbation technique firmly predicts the transition to a charged Bose liquid in the crossover region of the BCS coupling constant $\lambda \simeq 1$ [7]. The (bi)polaronic theory of carriers in cuprates, confirmed by infrared spectroscopy [8] and by the isotope effect on the carrier mass [9], provides a natural microscopic explanation of the normal state gap [10]. Within the framework of the bipolaron theory, the ground state of cuprates is a charged Bose liquid of intersite bipolarons where single polarons exist only as excitations with an energy of $\Delta/2$ or more [11]. A characteristic temperature T^* of the normal phase is a crossover temperature of the order of $\Delta/2$ where the population of the upper polaronic band becomes comparable with the bipolaron density. Along this line the normal state kinetics of cuprates has been explained [12, 13] and a theory of tunnelling and photoemission (PES) has been developed [14].

In this letter, we find a universal temperature scaling of the specific heat and magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ and provide a microscopic explanation with bipolarons and thermally excited polarons. The central ideas of our model are as follows:

(i) Charge carriers are intersite real-space pairs of holes.
(ii) In addition to introducing hole charge carriers, doping also introduces considerable disorder and localized states. Owing to interparticle Coulomb repulsion [15], a localization well contains either a bipolaron or an unpaired polaron but not both. The interaction of polarons and bipolarons in the extended states is taken into account within the Hartree–Fock approximation and is included in their band dispersion.

(iii) At finite temperatures, a fraction of the carriers exist as unpaired hole polarons. These particles are responsible for the magnetic response of the system.

We also employ the simplification that the tunnelling probability between localization wells is negligible. This allows the partition function Z_l for the localized part of the system to be written as

$$Z_l = \prod_i Z_i$$
$$Z_i = 1 + 2\mathrm{e}^{(\mu - E_i)\beta} + \mathrm{e}^{2(\mu - E_i + \Delta/2)\beta} \tag{1}$$

where we have assumed the no double occupancy condition. Δ, μ and E_i are respectively the bipolaron binding energy, chemical potential and a single-particle energy level of the well, whilst $\beta = 1/k_B T$. The point to note about equation (1) is that the localized partition function cannot be factorized into a product of two particle and one particle partition functions. The physics of localized bipolarons and polarons is thus not separable implying that only one density of states (DOS) profile should be taken for localized particles. The density of localized particles is determined by

$$n_l = -\frac{\partial \Omega_l}{\partial \mu} \tag{2}$$

with $\Omega_l = -\beta^{-1} \log Z_l$. This gives

$$n_l = 2\int_{-\infty}^{0} \rho_l(E) f_l(E) \mathrm{d}E \tag{3}$$

where

$$f_l(E) = \{1 + g[\beta(E - \mu - \Delta/2)]\}^{-1} \tag{4}$$

with $g(\xi) = \exp(\xi)\cosh(\xi/2 + \beta\Delta/4)/\cosh(\xi/2 - \beta\Delta/4)$. $\rho_l(E)$ refers to the density of localized states per spin. We can then write for the number conservation condition:

$$2n_b + n_p + n_l = x \tag{5}$$

where $n_{b,p}$ is the density of delocalized bipolarons and polarons, respectively, and x the doping per unit cell. For $La_{2-x}Sr_xCuO_4$, x is given by the atomic concentration of Sr whilst in $YBa_2Cu_3O_{7-\delta}$, $x = 2(1 - \delta)/3$. The free particle density is given by

$$n_b = \int_0^{\infty} \mathrm{d}E \rho_b(E) f_b(E)$$
$$n_p = 2\int_0^{\infty} \mathrm{d}E \rho_p(E) f_p(E) \tag{6}$$

where $f_b(E) = \{\exp[\beta(E - 2\mu - \Delta)] - 1\}^{-1}$ and $f_p(E) = \{\exp[\beta(E - \mu)] + 1\}^{-1}$, so that equation (5) allows us to determine the chemical potential $\mu(T)$ if bipolaronic and polaronic DOS, $\rho_{b,p}(E)$, are known. The finite bipolaron bandwidth, the one-dimensional singularity of (bi)polaronic DOS [16] and a finite width of the localized tail give rise to a Schottky-like anomaly of the specific heat and a Curie-like temperature dependence of the susceptibility, which are observed at high temperatures in overdoped samples, as explained in [13]. Here we consider the underdoped region, where the potential wells are deep and impurity-scattering broadening of the Van Hove singularities (VHS) is large, due to ineffectiveness of a screening by carriers. The previous analysis [10, 14] showed that the characteristic width of the localized tails and VHS is about 20 meV. We can thus neglect any DOS structure for the relevant temperature range by taking $\rho_l(E) = \rho_p(E) = 2\rho_b(E) \simeq N(0)$ with $N(0)$ a single-particle DOS at the mobility edge, $E = 0$. The bipolaron chemical potential $2\mu + \Delta$ is then pinned at the mobility edge, giving $\mu = -\Delta/2$, as follows from equation (5) for $k_B T N(0) \ll 1$. This assumption greatly simplifies further calculations. Including the contribution of delocalized bipolarons, thermally excited polarons and localized carriers, we find a universal temperature scaling of the energy, $E(T) = f(\beta\Delta)$, which allows us to extract the normal state gap from the experimental specific heat, $C = \partial E/\partial T$, without any fitting parameters as shown in figure 1. In the low-temperature limit, $\beta\Delta \gg 1$ we get $g(\xi) \simeq \exp(2\xi)$ and a linear specific heat with an exponential correction

$$C \simeq k_B N(0)\beta^{-1}\left[\frac{\pi^2}{4} + \frac{(\Delta\beta)^2\chi(T)}{4\mu_B^2 N(0)}\right] \tag{7}$$

where $\chi(T)$ is the exponential spin susceptibility found below. This result is in contrast with an expectation that the specific heat of nondegenerate bipolarons is temperature independent above T_c. The random potential, as well as a low-dimensional DOS, pins the chemical potential at the mobility edge even in the normal state, so the bipolaron density (and hence the specific heat) is proportional to temperature. The latter leads to a temperature dependent Hall effect [12] and explains other anomalous kinetic properties of cuprates [17]. Half of the bipolaron binding energy $\Delta/2$, which is an energy gap between the bottoms of bipolaronic and polaronic bands, has been estimated from 400 K to 50 K depending on doping [13]. In this temperature range, one has to calculate $\gamma = C/T$ by numerical integration with the result shown in figure 1. There is a clear scaling of experimental γ with $\beta\Delta$ in a wide doping range of $YBa_2Cu_3O_{7-\delta}$. The corresponding values of Δ are shown in figure 2. They follow the same doping dependence as that determined phenomenologically [2] and are of the same order of magnitude. It should be noted though that the d-wave approach gives consistently higher gap values than those found here.

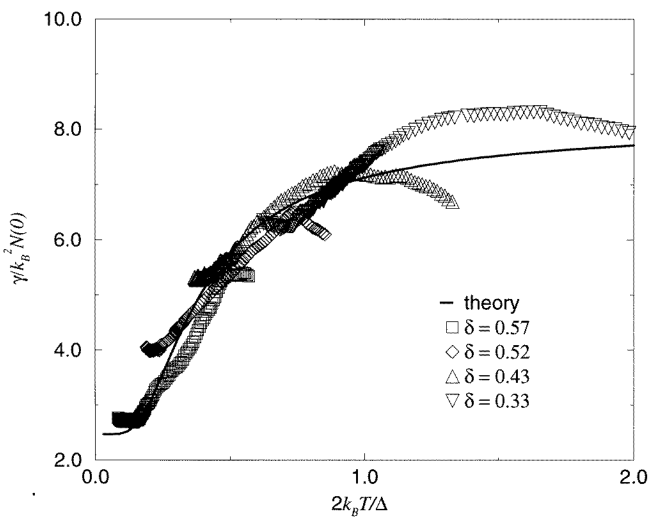

Figure 1. Universal scaling of $\gamma/k_B^2 N(0)$ with $2k_B T/\Delta$ compared with theory (curve) for $YBa_2Cu_3O_{7-\delta}$ ($N(0) = 1.17$ eV^{-1} per spin).

Following the analysis of [18], we compare γ with the differential magnetic susceptibility $\chi^* = \partial(\chi T)/\partial T$. The experimental data for $\chi^*(T)$ are perfectly consistent with our model. There are two contributions to the magnetic response, from delocalized (thermally excited) polarons, χ_p, and from localized ones, χ_l. For the first contribution we obtain, by the use of

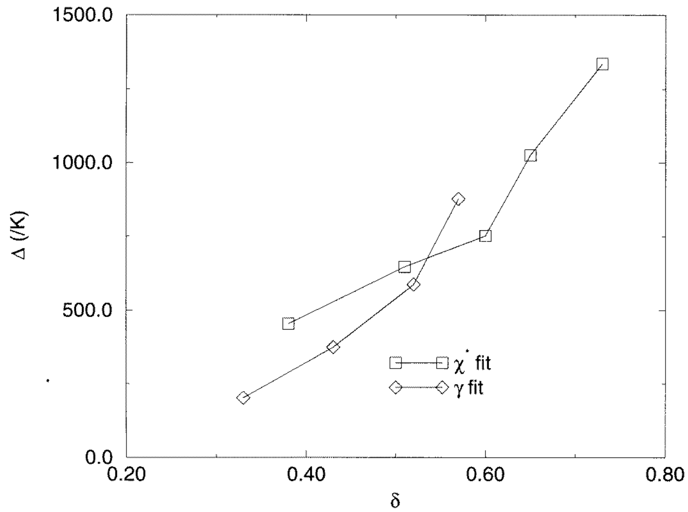

Figure 2. Theoretical normal state gap as a function of doping.

the Kubo formula for free fermion magnetization,

$$\chi_p(T) = 2\mu_B^2 N(0)[\exp(\beta\Delta/2) + 1]^{-1} \tag{8}$$

where μ_B is the Bohr magneton. The single-well partition function in an external magnetic field, H, is given by

$$Z_i = 1 + e^{2(\mu - E + \Delta/2)\beta} + e^{(\mu - E + \mu_B H)\beta} + e^{(\mu - E - \mu_B H)\beta}. \tag{9}$$

Differentiating twice, the corresponding Ω potential with respect to the magnetic field yields

$$\chi_l(T) = \mu_B^2 \beta \int_{-\infty}^{0} dE \rho_l(E) f_l^p(E) \tag{10}$$

where $f_l^p(E) = [1 + \exp(\beta\Delta/2)\cosh((E - \mu - \Delta/2)\beta)]^{-1}$ is the distribution function of localized polarons. If DOS is a constant, $\rho_l(E) = N(0)$, and temperature is low, $\beta\Delta \gg 1$, we obtain an exponential temperature dependence of the spin susceptibility as

$$\chi(T) = \chi_p(T) + \chi_l(T) \simeq 2\mu_B^2 N(0)(1 + \pi/4)\exp(-\beta\Delta/2). \tag{11}$$

The numerical integration of equation (10) for the entire temperature range, with the constant DOS, yields a universal scaling of χ^* as a function of $\beta\Delta$. This is nicely confirmed by experiment, as shown in figure 3. It is remarkable that, with about the same Δ and DOS (see figure 2), one can describe both the specific heat and spin susceptibility of underdoped $YBa_2Cu_3O_{7-\delta}$. This is at variance with some opinions that the experimental Wilson ratio is difficult to understand within the framework of our model. In fact, thermally excited polarons provide the spin susceptibility and a finite (temperature dependent) Wilson ratio close to the experimental one, while the binding energy of bipolarons is responsible for the normal state gap. Another strong indication of the existence of bipolarons comes from the resistive and thermodynamic measurements in the critical region. A divergent upper critical field was measured in many cuprates, as predicted by one of us [19], and the magnetic field dependence of the specific heat jump is just that of the charged Bose gas [20]. Recently, it has been established that there is a normal state gap in ARPES and SIN tunnelling, existing well above T_c irrespective of the doping level [21, 3, 4]. The 'Fermi surface' showed missing segments close to the points [21] where we expect the Bose–Einstein condensation [14]. A plausible explanation is that there are two liquids in cuprates, the normal Fermi liquid and the charged Bose liquid (this mixture has been theoretically discussed a long time ago [22]). A temperature independent paramagnetic background in the magnetic susceptibility (figure 3) might be due to a normal Fermi liquid component coexisting with the (bi)polarons, as suggested by several authors [23, 24, 25]. If a Fermi surface of the Fermi liquid is large then it is difficult to see how this scenario could explain the doping dependencies of dc and ac conductivity as well as of the magnetic susceptibility and carrier specific heat, which scales with doping. On the other hand, the single-particle spectral function of a pure bipolaronic system has been recently derived by one of us [14]. It describes the spectral features of tunnelling and photoemission in cuprates. Any single-particle spectral weight at the chemical potential appears in our model due to single polaronic states, localized by disorder inside the normal state gap. The model is thus compatible with the doping evolution of thermodynamic and kinetic properties.

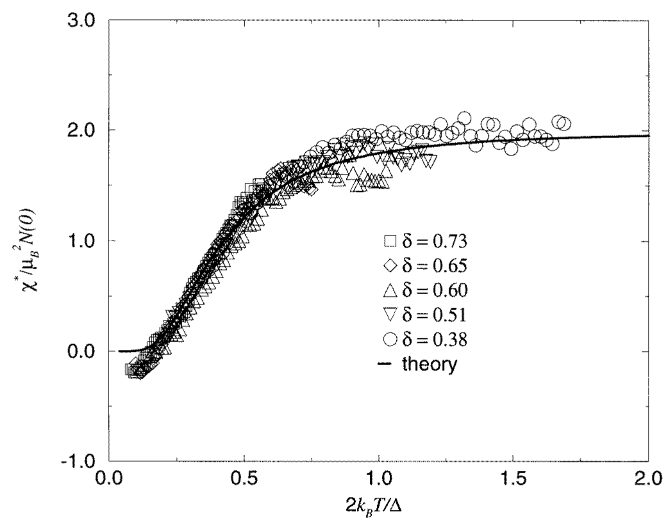

Figure 3. Universal scaling of the differential spin susceptibility, $\chi^*(T)/\mu_B^2 N(0) = (\chi^*_{\text{exp}} - 0.39 \times 10^{-4}$ emu mol$^{-1})/\mu_B^2 N(0)$ compared with theory (curve). For experimental data, see [18].

We may therefore conclude that the formation of real space pairs (bipolarons) above T_c and their partial localization by the random potential are essential features of the normal state thermodynamics of $YBa_2Cu_3O_{7-\delta}$ and other cuprates exhibiting similar normal state gap. In particular, a comprehensive study of the magnetic susceptibility of $La_{2-x}Sr_xCuO_4$ [23] and of the doping dependence of superconducting parameters in $HgBa_2CuO_{2+\delta}$ [26] has firmly confirmed the bipolaronic scenario. We have also fitted the specific heat and susceptibility of $La_{2-x}Sr_xCuO_4$ with bipolarons and thermally excited polarons in a wide range of doping [27]. Hence, the bipolaron theory can explain such non-Fermi-liquid features as a large carrier entropy, the gap above T_c, temperature dependences of γ and χ and their ratio in many cuprates.

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