PHYSICAL REVIEW B **66**, 140501(R) (2002)

Condensation energy and high-T_c superconductivity

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(Received 14 July 2002; published 2 October 2002)

From an analysis of the specific heat of one of the cuprate superconductors it is shown that even if a large part of the experimental specific heat associated with the superconducting phase transition is due to fluctuations, this part must be counted when one tries to extract the condensation energy, E_{cond}, from the data. Previous work where the fluctuation part was subtracted has resulted in an incorrect estimation of E_{cond}.

DOI: 10.1103/PhysRevB.66.140501 PACS number(s): 74.25.Bt, 74.20.Mn, 74.72.−h, 74.40.+k

In conventional metals superconductivity has been understood to result from an effective attractive interaction between electrons. This simultaneously causes a reduction of the interaction energy and an increase of the kinetic energy when the material becomes superconducting. For high-T_c superconductors, and in particular for the cuprate family, it has been proposed that the opposite situation could exist, where the superconducting state is accompanied by a reduction of the charge-carrier kinetic energy.[1–4] Experimental investigations of the kinetic-energy component perpendicular to the superconducting planes of the cuprate high-T_c superconductors have previously demonstrated that the kinetic-energy reduction perpendicular to the layers is far too small to account for the condensation energy,[4–6] which ruled out interlayer tunneling (ILT) as a mechanism of superconductivity.[6–12] Although evidence was subsequently reported[13,14] that the c-axis kinetic energy is reduced in the superconducting state in a number of cases, the amount of energy is orders-of-magnitude smaller than earlier estimates of the condensation energy.[4–6]

Later experiments have identified two contributions to the internal energy of cuprate superconductors: (i) From a reanalysis of inelastic neutron-scattering data it was concluded that the ab-plane spin-correlation energy was lowered by an amount which may be sufficient to account for the condensation energy,[15] and (ii) an even larger lowering of ab-plane kinetic energy was measured with optical spectroscopy.[16] Since spin correlations result from exchange interactions, which in turn reflect the spin-dependent virtual motion of electrons, these two channels of condensation energy may have at least in part the same microscopic origin.

However, the analysis providing the condensation energy from specific data has been questioned in 1999 by Chakravarty, Kee, and Abrahams[1] (hereafter CKA), who stated that "the attempt to extract the condensation energy from the specific heat data runs into ambiguity, except within a mean field treatment. In the presence of fluctuations, superconducting correlations, which can primarily be of in-plane origin, contribute to the energy and significantly to the specific heat of the normal state." In order to resolve this ambiguity, CKA proposed to "subtract the fluctuation effects and to use the remainder as an effective specific heat from which to extract the c-axis contribution to the condensation energy. The rationale is that free energy can be decomposed into a singular and a non-singular part. The universal singular part is more sensitive to collective long-wavelength fluctuations, while the non-singular part is dominated by short distance microscopic pairing correlations." Subtracting the fluctuation led CKA to a value of the condensation energy which was 40 times smaller than the value obtained in Refs. 4–6.

Here we demonstrate that the analysis of CKA was internally inconsistent. If carried out correctly, the subtraction of fluctuation energy makes only a factor of 2 to 3 difference compared to Refs. 4–6. Moreover, we show that it is overwhelmingly natural to count also the fluctuation contribution in the condensation energy.

The condensation energy E_{cond} is the internal energy of the equilibrium phase relative to the internal energy of the normal state. The former is the experimentally observed phase, which is superconducting for $T<T_c$, whereas the latter corresponds to the state where all superconducting correlations have been suppressed in the sense that the two-particle correlation function tends to zero as a function of the "center-of-mass" variable over a range no greater than a few times the interparticle spacing. In the remainder of this paper we will use the subindex n to indicate the thermodynamic quantities corresponding to this normal state. In any superconductor long-range phase coherence is only present for $T<T_c$. In BCS theory long-range phase coherence and pair correlations become nonzero simultaneously for $T\leqslant T_c$. Knowledge of equilibrium and normal specific heat for $T<T_c$ then suffices to determine E_{cond}. On the other hand, pair correlations can, in principle, still exist for temperatures above the transition temperature, and indeed such correlations are often associated with the pseudogap phenomenon in underdoped cuprates. A measurement of the internal energy, released when the superconducting state is formed out of the normal state, should now also include the pair correlations which already exist above the superconducting phase transition. Since our discussion is most easily formulated in terms of the entropy, let us remind the reader that the entropy follows uniquely from the specific heat according to the relation

$$S(T)=\int_0^T \frac{C(T')}{T'}dT'. \tag{1}$$

If the temperature dependence of the specific heat is known in equilibrium and in the normal state, the free- and internal

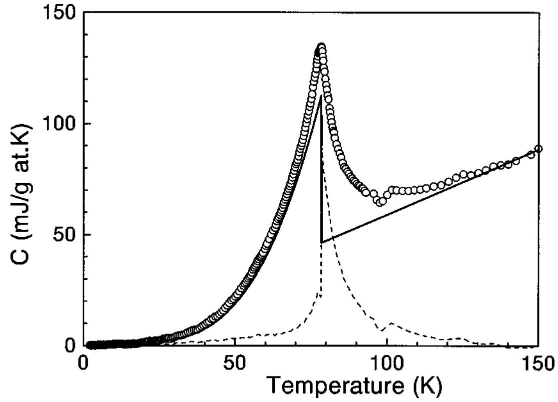

FIG. 1. Circles: Electronic specific-heat data of Tl2201. Dashed curve: Singular (fluctuation) contribution, parametrized as $C_{sing} = g_{\pm}/t$, where $t = |1 - T/T_c|$ ($T_c = 79$ K, $g_+ = 2.38, g_- = 0.74$). Solid curve: Electronic specific heat with the singular contribution subtracted.

energy differences can be calculated directly using the relations

$$F_n(T) - F(T) = \int_T^\infty [S_n(T') - S(T')] dT', \tag{2}$$

$$E_n(T) - E(T) = \int_T^\infty [C(T') - C_n(T')] dT'. \tag{3}$$

The integration limits ensure that $\lim_{T\to\infty} F(T) = F_n(T)$ and $\lim_{T\to\infty} E(T) = E_n(T)$, in accordance with the assumption that for $T \to \infty$ all superconducting correlations vanish. The condensation energy corresponds to the zero-temperature energy difference $E_{cond} = E_n(0) - E(0) = F_n(0) - F(0)$. This positive energy can be obtained either by integrating the specific-heat difference

$$E_{cond} = \int_0^\infty [C(T) - C_n(T)] dT \tag{4}$$

or by integrating the entropy difference

$$E_{cond} = \int_0^\infty [S_n(T) - S(T)] dT. \tag{5}$$

The fact that Eq. (4) and Eq. (5) should give the same value provides, as we will see, an important consistency check. CKA (Ref. 1) questioned the analysis providing the condensation energy, and provided a different analysis where a Gaussian fluctuation contribution was subtracted from the experimental data. In Fig. 1 the fit obtained by CKA to the specific heat of Tl2201 to two-dimensional Gaussian fluctuation plus nonsingular parts is reproduced. We will indicate with an asterisk thermodynamic quantities from which the fluctuations have been subtracted. CKA calculated both results with $[E_n(0) - E^*(0) = 25$ mJ/g at.] and without $[E_n(0) - E(0) = 825$ mJ/g at.] subtracting the singular part. The latter corresponds to the earlier estimates in Refs. 4–6. Following the basic idea of the ILT theory, CKA now equate the ''subtracted'' value of the condensation energy to the decrease of the *c*-axis kinetic energy in the superconducting state, δK. Finally they use the standard relation[6–14] between δK and the *c*-axis penetration depth λ_c,

$$\frac{c^2}{8\lambda_c^2} \approx \frac{\pi e^2 d^2}{2Ad\hbar^2} \delta K. \tag{6}$$

Their resulting estimate of λ_c is much larger than the value $\lambda_c \simeq 1$ μm derived previously in the context of ILT. Vice versa, the implication was that the condensation energy is approximately 40 times smaller than earlier estimates, which had not corrected the specific heat for the singular part.

The main source of this huge difference is the difficulty in determining the ''normal'' thermodynamic quantities. The experimental questions include not only how but also *whether* the ''normal'' state can be reached as a function of temperature, or indeed anything else, in other words, whether or not a parameter exists that can be tuned to lower the energy of the normal state below that of the equilibrium superconducting state so that it can be accessed without losing its fundamental character. Quite generally such a parameter does not always have to exist. For a weak-coupling superconductor a magnetic field would suffice. In most cuprate superconductors the required magnetic fields are beyond experimental reach, but Zn ions substituted for planar Cu may serve as an alternative for suppressing superconductivity.[17,18,19] However, for the cuprates there is reason to believe that several ''normal'' states are competing with the superconducting one (e.g., stripe, flux-phase, normal). In this case the field (or Zn doping) required to mute superconductivity could be enough to rearrange the order between these ''normal'' states, thus revealing the ''wrong'' one when superconductivity gets suppressed. Thus we are confronted with the difficult situation that the normal-state entropy is not an experimental quantity and can only be determined based on theoretical considerations and/or by extrapolating the normal-state dependence as was indeed done in Ref. 1, providing us, as we have seen, with estimates of condensation energy differing by a factor of 40.

However, the situation isn't as bad as it looks. We can use our knowledge of thermodynamics to constrain the possible behavior of $S_n(T)$: Both $S(T)$ and $S_n(T)$ are subject to the $2d$ and $3d$ law of thermodynamics. We can also use the reasonable assumption that for temperatures high enough, all superconducting correlations cease to exist, causing S_n and S to become equal in that limit. The circumstance that $F(T)$ corresponds to the equilibrium state implies that for any temperature $F_n(T)$ has to be larger than $F(T)$. The corresponding constraints on the entropy are, in the same order,

$$dS_n/dT > 0,$$

$$S_n(0) = S(0) = 0,$$

$$S_n(\infty) = S(\infty),$$

$$\int_0^T S_n(T') dT' \leq \int_0^T S(T') dT' + E_{cond}. \tag{7}$$

In Fig. 2 the entropy is plotted as a function of temperature. The condensation energy in this plot corresponds to the area

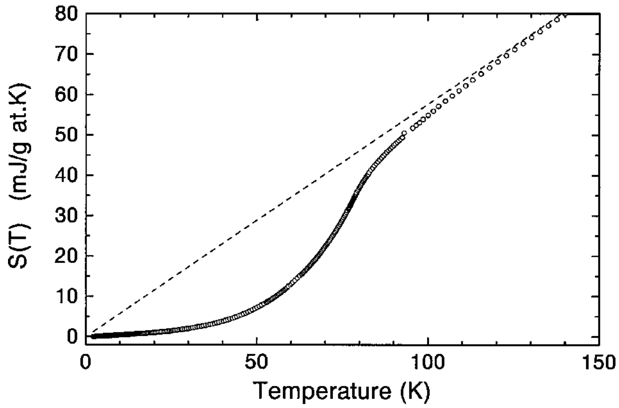

FIG. 2. Experimental entropy versus temperature. Dashed curve: Normal entropy with $\gamma = 0.576$ mJ/G at. K^2

between the equilibrium entropy $[S(T)$: circles$]$ and the normal entropy $[S_n(T)$: dashed curve$]$. A condensation energy which is 40-times smaller than the earlier estimates of the condensation energy[4–6] would require that the area enclosed by $S_n(T)$ and $S(T)$ is also 40-times smaller than in Fig. 2. Due the constraints of Eq. (7), $S_n(T)$ would almost coincide with $S(T)$. $S_n(T)$ then has a sharp bend at T_c, which would correspond to a pathological phase transition of the normal state in close proximity to the real superconducting phase transition.

Let us now return to the analysis by CKA. If we calculate the entropy by integrating $C^*(T)/T$ with the singular part subtracted, we obtain the curve indicated with circles in Fig. 3. Above the phase transition $S^*(T)$ approaches a linear temperature dependence with a negative offset, given by $S^*(T) = \gamma T - S_0$. We notice that the corrected entropy $S^*(T)$ and the normal entropy do not merge above T_c, causing the integral $E^*_{cond} = \int_0^\infty [S_n(T) - S^*(T)]dT$ to diverge. We see that subtracting the singular part has the effect that two procedures by which the condensation energy can be calculated provide opposite results:

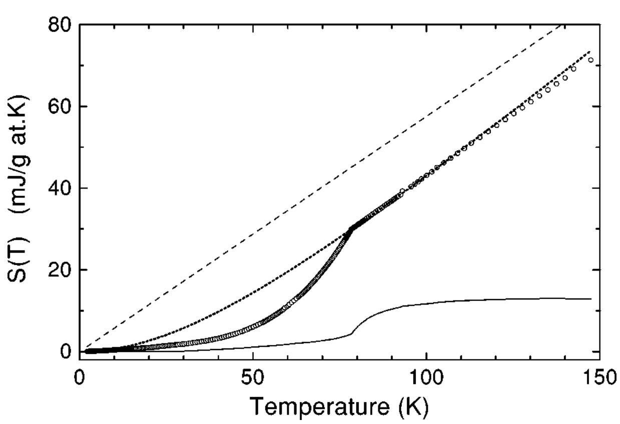

FIG. 3. Circles: Corrected entropy versus temperature $S^*(T) = S(T) - S_{sing}(T)$, following the procedure of Ref. 1 where the singular contribution was subtracted. Dashed curve: Normal entropy, $S_n(T)$, same as in Fig. 2. Dotted curve: "Normal" entropy, $S_n^*(T)$, fitted to the $T > T_c$ region of the corrected entropy curve. Solid curve: Singular contribution to the entropy $S_{sing}(T)$.

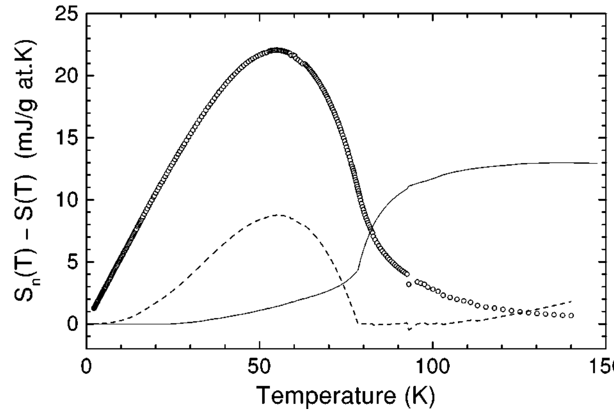

FIG. 4. Circles: Normal-state entropy minus experimental entropy. Solid curve: Singular contribution to the entropy. Dashed curve: "Normal" entropy $S_n^*(T)$, minus the corrected entropy $S^*(T)$.

$$E_{cond} = \int_0^\infty [C(T) - C_n(T)]dT = 25 \text{ mJ/g at.},$$

$$E_{cond} = \int_0^\infty [S_n(T) - S(T)]dT \to \infty.$$

This inconsistency does not arise in the earlier estimates of the condensation energy:[4–6] The fact that $S_n(T)$ and $S(T)$ merge above T_c in Fig. 2 guarantees that the same value of E_{cond} is obtained with the two different formulas.

Following a recent suggestion by Abrahams[20] the CKA analysis can be improved by adopting a specific-heat exponent η different from 1 below T_c. We must also take into account that the entropy above for $T > T_c$ approaches $S^*(T) = \gamma T - S_0$. A simple analytical expression with these two properties is

$$S_n^*(T) = S_0 \left\{ \left[1 + \left(\frac{T}{T_0} \right)^\eta \right]^{1/\eta} - 1 \right\}. \quad (8)$$

We have tried to fit different values for η. If we choose $\eta \geq 2.5$ the "normal" entropy $S_n^*(T)$ becomes smaller than the experimentally measured $S(T)$ for temperatures below 40 K. Although such a possibility cannot be excluded by the thermodynamical constraints of Eq. (7), from a microscopic perspective it looks suspicious that the entropy of the (gapped) superconducting state could exceed that of the normal state. To avoid this, we have adopted the value $\eta = 2.0$. The best fit in the region between T_c and 110 K was obtained with $S_0 = 34.85$ mJ/g at. K and $T_0 = 50$ K. In Fig. 3 we display the singular contribution to the entropy $S_{sing}(T)$, the corrected entropy $S^*(T) = S(T) - S_{sing}(T)$, and the normal-state entropy $S_n^*(T)$. Note that if indeed it would be justified to subtract the singular contribution, the presence of a negative offset in the entropy implies that this "normal" state would have a pseudogap.[5,17]

In Fig. 4 we display both $S_n(T) - S(T)$ and the quantity which corresponds to the improved version of the CKA analysis, $S_n^*(T) - S^*(T)$. We see that with the improved CKA analysis the difference entropy between the normal and

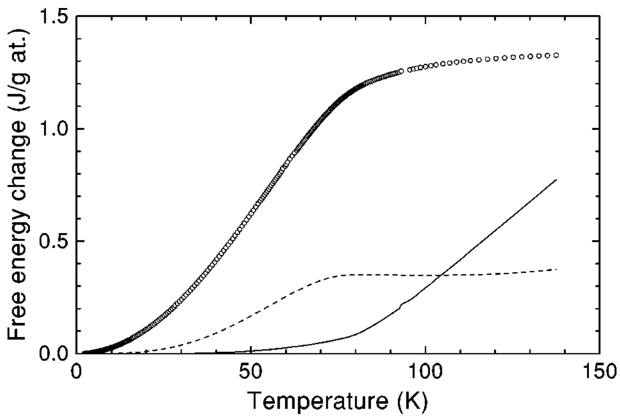

FIG. 5. Integrated entropy differences of Fig. 4. Circles: $\int_0^T [S_n(T') - S(T')] dT'$. Dashed curve: $\int_0^T [S_n^*(T') - S^*(T')] dT'$. Solid curve: Singular contribution to the free energy.

superconducting states indeed becomes zero above T_c. We carried the analysis of the specific heat one step further, and calculated the free-energy difference curves. These are displayed in Fig. 5. The corrected CKA analysis thus provides a condensation energy of 0.35 J/g at. This value is about 30% of the condensation energy from direct integration of the total entropy of Fig. 2 which gives $E_{cond} = 1.3$ J/g at. We see that even if it would be justified to subtract the fluctuations, the correct analysis would still reduce the condensation by a factor of 2 or 3, not by a factor of 40 as stated in Ref. 1.

However, removing the singular contribution from the experimental data comes with a penalty: As a reminder that a fluctuation contribution has been subtracted in the CKA analysis, we have displayed in Figs. 3–5 its contribution to the entropy and the free energy. We see that the fluctuation entropy has a conspicuous step at T_c, which indicates that these fluctuations are intimately connected to the superconducting phase transition. The fact that the fluctuation specific heat is strongly peaked at the phase transition implies that there is an additional reduction of the internal energy due to the fluctuation contribution. Hence it would seem to be overwhelmingly natural to count this part when one estimates the energy by which the superconducting state is stabilized relative to competing (nonsuperconducting) phases.

In conclusion, we have shown that in the original analysis of CKA, i.e., subtraction of a fluctuation contribution to the specific heat, a corrected entropy below T_c was used which does not match the value used above T_c. This internal inconsistency was the main reason why the condensation energy was estimated a to be factor-of-40 smaller than the value obtained in earlier publications. This problem could have been fixed by letting the specific-heat exponent be less than one at low temperatures. We have repeated the CKA analysis with this fix, resulting in a condensation energy which is ten times as large. However, it seems overwhelmingly natural to include the contribution of the fluctuations in the analysis, because experimentally the fluctuation contribution to the internal energy appears to be intimately linked to the superconducting phase transition. This results in a condensation energy of approximately 1.3 J/g at. for optimally doped Tl2201.

We gratefully acknowledge stimulating discussions with K. A. Moler, S. Kivelson, J. Zaanen, S. Chakravarty, H.-Y. Kee, and E. Abrahams during the preparation of this paper.

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[19] In cuprate superconductors Zn ions substituted for planar Cu act as unitary scatterers and strongly reduce T_c by pair breaking, thus exposing the normal-state electronic specific heat to lower temperatures. Zn doping fully oxygenated Y-123 [$YBa_2(Cu_{1-y}Zn_y)_3O_{6.95}$] reveals a T independent $C(T)/T$ to low temperatures with no indication of a pseudogap (Ref. 18). In contrast, Zn doping of Y-124 [$YBa_2(Cu_{1-y}Zn_y)_4O_8$] exposes a pseudogap T dependence for $C(T)$ to low temperatures [J. W. Loram *et al.* (unpublished)]. In both cases the T dependencies of $C(T)$ below T_c $(y=0)$ are in excellent agreement with that deduced from the entropy conservation arguments discussed above. This suggests that Zn doping has little effect on the normal-state electronic specific heat and provides a good approximation to the underlying $C(T)$ of the non-Zn-doped material.
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