Thermodynamic Evidence for a Density-of-States Peak near the Fermi Level in $YBa_2Cu_3O_{7-y}$

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Thermodynamic properties such as the specific-heat discontinuity at the transition temperature (T_c), $\Delta C/T_c$, and the zero-temperature critical field, $H_c(0)$, of oxygen-deficient $YBa_2Cu_3O_{7-y}$ are analyzed to show that, within the framework of the BCS formalism, the density of states (DOS) at the Fermi level is peaked at $y=0$. The energy dependence of the DOS is considered for several models and found to be consistent with the Fermi level lying close to a two-dimensional van Hove singularity.

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To understand the origin of high-temperature superconductivity and other anomalous properties of the cuprates, a model based on the close proximity of the Fermi level (ε_F) to a quasi-two-dimensional van Hove singularity (vHs) in the density of states (DOS) $N(\varepsilon)$ has been suggested [1-7]. Recently, in Y-Ba-Cu-O, the predicted [8-10] X-shaped Fermi surface feature in the antibonding band formed from the CuO_2-Y-CuO_2 bilayer, which defines the vHs in this material, seems to have been observed in angle-resolved photoemission spectroscopy [11]. On the other hand, theoretically it has been pointed out that several adverse factors such as interlayer coupling [7] (3D effects), impurity (dopant) scattering, and other effects [6] may severely reduce the effectiveness of the vHs. Evidently the credibility of the van Hove model for high-T_c superconductivity would be greatly enhanced by a direct experimental observation of the DOS peak associated with the vHs near the Fermi level in a T_c-optimized Cu-oxide superconductor such as $YBa_2Cu_3O_7$.

In this Letter, we derive valuable information on the DOS that is directly responsible for the high-temperature superconductivity in $YBa_2Cu_3O_{7-y}$ from the measurements of thermodynamic quantities such as specific-heat jump ΔC at T_c and the zero-temperature critical field $H_c(0)$. Thermodynamic properties can provide a reliable comparative measurement of the DOS at the Fermi level, $N(\varepsilon_F)$. Furthermore, being a measure of the condensation energy, these quantities represent a selective measure of the partial DOS that is directly relevant to superconductivity. For oxygen-deficient $YBa_2Cu_3O_{7-y}$, we will show that the DOS is sharply peaked as a function of y with the DOS $N(\varepsilon_F)$ and T_c maximum at $y=0$. As y increases, the DOS decreases rapidly, suggesting the existence of a vHs near the Fermi level for $YBa_2Cu_3O_7$.

Within the framework of the BCS formalism, the specific-heat jump at T_c can be calculated from the following formula [12]:

$$\Delta C(\delta)=A^2B^2k_B^2T_c\langle N(\delta)\rangle_{k_BT_c}, \tag{1}$$

where $A^2=-d[\Delta(T)/\Delta(0)]^2/d(T/T_c)$ at $T=T_c$, $B^2=[\Delta(0)/k_BT_c]^2$, $\Delta(T)$ is the temperature-dependent energy gap function, and the thermally averaged DOS is given by

$$\langle N(\delta)\rangle_{k_BT}=\int_{-\infty}^{\infty}N(\varepsilon)d\varepsilon(-df/d\varepsilon). \tag{2}$$

In Eq. (2), $N(\varepsilon)$ is the energy-dependent normal-state DOS (the quasiparticle energy ε is measured with respect to the initial location of the Fermi level), δ ($\varepsilon_F=\delta$) defines the Fermi level position relative to the DOS peak as a result of varying the concentration of charge carriers, for example, and f denotes the Fermi distribution function.

In the standard BCS treatment, $N(\varepsilon)$ is assumed to be a constant independent of energy, N_0. Then Eq. (1) for the specific-heat jump simplifies to [12] $\Delta C=9.4k_B^2T_cN_0$, where T_c is obtained from the standard BCS formula for T_c, $A=1.74$, $B=1.76$, and $\langle N(\varepsilon)\rangle_{k_BT_c}$ reduces to the constant DOS, N_0. However, if the DOS function is energy dependent, an appropriate form of $N(\varepsilon)$ has to be used in calculating ΔC_p and T_c. In the case of vHs, and if the Fermi level is located at the singularity,

$$N(\varepsilon)=N_0\ln(W/|\varepsilon|), \tag{3}$$

where $2W$ is the bandwidth. The value of the specific-heat discontinuity at T_c can be calculated numerically using the standard BCS treatment. The result can be written as $\Delta C(\delta)=10.25k_B^2T_c\langle N(\delta)\rangle_{k_BT_c}$ where the parameter A [see Eq. (1)] is found to be 1.74, the same as the standard BCS case and essentially independent of δ. The parameter B is 1.84 for $\delta=0$ and decreases towards 1.76 as δ increases. The value of $B=1.84$ for the vHs case is consistent with a recent study [13] of the effect of energy-dependent DOS on the values of B, assuming $N(\varepsilon)\sim|\varepsilon|^\alpha$. The vHs case corresponds to the case of $\alpha\lesssim 0$. To include the effect of mass enhancement, $\Delta C(\delta)$ can be expressed as the following:

$$\Delta C(\delta)=10.25k_B^2T_c\frac{B^2(\delta)}{B^2(0)}\langle N(\delta)\rangle_{k_BT_c}(1+\lambda_{e\text{-ph}}), \tag{4}$$

where the effective electron-phonon coupling strength $\lambda_{e\text{-ph}}$ is defined to take into account the effect of energy-dependent DOS over the phonon cutoff energy at the Fermi level [4,6].

Experimental results of direct and indirect measurements on $\Delta C/T_c$ for high-quality oxygen-deficient $YBa_2Cu_3O_{7-y}$ polycrystalline samples ($0<y<0.43$) have been reported recently [14,15]. In Fig. 1, the mean-field values of $\Delta C/T_c$ at zero magnetic field are plotted as a function of T_c which is in turn a function of oxygen deficiency y. The open circles represent data of direct measurements [14] of the specific heat by using a

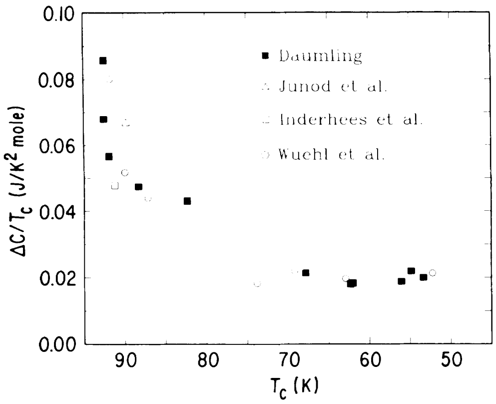

FIG. 1. Results of indirect (Däumling) and direct (Wühl *et al.*, data multiplied by 2) measurements on $\Delta C_p/T_c$ at zero magnetic field as a function of T_c for oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ polycrystals. The data for fully oxygenated single crystals (by Inderhees *et al.*) and polycrystals (by Junod *et al.*) are also included for comparison.

continuous-heating adiabatic calorimeter. For comparison, early results on fully oxygenated single crystals [16] and polycrystals [17] are also included in the figure (open squares and triangles). The solid squares are the values derived from reversible magnetization [15] of polycrystalline $YBa_2Cu_3O_{7-y}$. As shown in Fig. 1, the data for the direct and indirect measurements qualitatively agree and show that $\Delta C/T_c$ [i.e., $N(\varepsilon_F)$ in accordance with Eq. (1)] decreases rapidly with decreasing T_c in the range of small y (i.e., $0<y\leq 0.1$). For $0.1<y<0.5$, $\Delta C/T_c$ decreases fairly slowly with decreasing T_c. Quantitatively, the two sets of data differ roughly by a factor of 2 which we briefly discuss next. Direct measurements may underestimate the specific-heat discontinuity at T_c due to sample inhomogeneity. However, Wühl *et al.* [14] discard the possibility by demonstrating the validity of the Ehrenfest relation which is a thermodynamic rule that links the specific-heat data self-consistently with results of their measurements on thermal expansion and the pressure dependence of T_c. Another possible source of discrepancy may stem from the fact that Wühl *et al.* assume that, in their data analysis [14], the normal-state heat-capacity background is equal to that of nonsuperconducting Zn-doped $YBa_2Cu_3O_{7-y}$. There are also some uncertainties in the procedure of determining $H_c(T)$ (and thus $\Delta C/T_c$ at T_c) from the reversible magnetization data using the Ginzburg-Landau equations. Cross-checks with results on single crystals and aligned polycrystals suggest, however, that the fitting procedures used to derive H_c and ΔC are self-consistent and reliable [15]. In view of the good agreement between the single-crystal data and the results of the indirect measurement, we will concentrate our DOS analysis on the data of Däumling. In our attempt to determine the energy dependence of DOS from the specific-heat-jump data, this quantitative difference between the data by Wühl *et al.* and others will not alter our qualitative conclusion.

Another important consideration in analyzing the $\Delta C/T_c$ data is based on the fact that the vacant oxygen sites are ordered on the Cu-O chains in many of the $YBa_2Cu_3O_{7-y}$ samples. Such defect ordering can have a profound effect on T_c and other properties [18,19]. The well-established observation [20] of two plateaus in the T_c vs y plot for slowly cooled samples is a manifestation of the phase separation of the various ordered phases as a function of y and ordering kinetics. In order to minimize the complication arising from the effects of oxygen ordering the samples used in both the direct and indirect measurements of $\Delta C/T_c$ were quenched from 400–650 °C (single-phase field of ortho I) to liquid-nitrogen temperature or room temperature. The results of T_c measurements [15] as a function of y show that, except for a relatively sharp drop in T_c around $y=0.1$ from the fully oxygenated sample, the value of T_c decreases approximately as a linear function of y for $0.1<y<0.5$. The fact that the second T_c plateau is replaced by an approximately linear oxygen-deficiency dependence of T_c in these quenched samples suggests that the oxygen-ordered phase separation problem has been reduced significantly. In the work by Wühl *et al.* [14], $y=0.1$ was assumed for the fully oxygenated sample and values of y were determined indirectly. According to the direct measurements of y on the samples for the magnetization measurements [15], the fully oxygenated sample corresponds to $0<y<0.05$. To avoid this uncertainty in y, we choose to analyze $\Delta C/T_c$ as a function of T_c instead of y (see Fig. 1).

The data in Fig. 1 show that $\Delta C/T_c$ decreases sharply from its T_c-optimized value with a relatively small change in T_c. The consistency of this trend independently of whether it is derived from calorimetry or magnetization allows us to assume that a real effect in terms of a variation of DOS at the Fermi level is being measured, rather than some extrinsic phenomenon such as sample inhomogeneity, disorder, etc. An analysis of the experimental data for ΔC and T_c in terms of the calculated results should lead to the Fermi-energy dependence of DOS, $N(\varepsilon_F)$.

In Fig. 2, the $\Delta C/T_c$ data are compared with the numerically calculated results for a BCS van Hove model by using Eqs. (2)–(4). The bare DOS function used in the calculation is based on the DOS expression for a two-dimensional vHs [i.e., Eq. (3)]. Its logarithmic energy dependence is shown in the inset of Fig. 2 (dot-dashed curve) as a function of Fermi level shift δ from the vHs. The DOS normalization constant N_0 is chosen as 1 $eV^{-1}spin^{-1}$ so as to preserve unit norm. Also shown in the inset is the corresponding thermally averaged DOS at $T=T_c$, $\langle N(\delta)\rangle_{k_BT_c}$. The values of $\langle N(\delta)\rangle_{k_BT_c}$ compare favorably with those determined from other measurements [6]. The values of T_c as a function of the Fermi level position can be calculated as previously reported

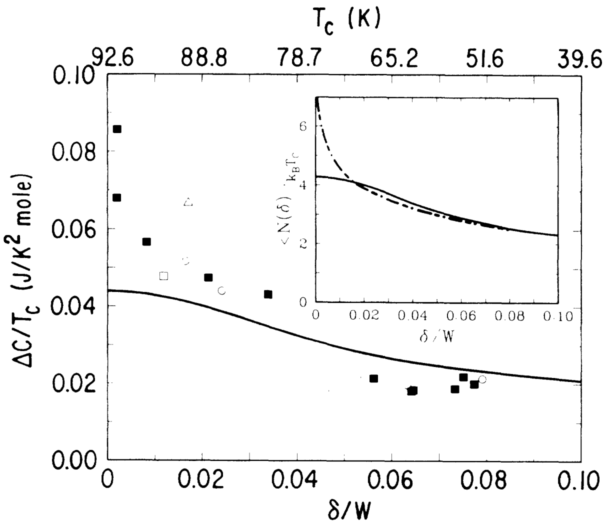

FIG. 2. $\Delta C/T_c$ as a function of T_c and the Fermi level shift δ normalized with the half bandwidth W. The solid curve is based on the vHs model ($W=0.5$ eV, $\hbar\omega_c=0.065$ eV). Inset: dot-dashed curve is the bare DOS based on Eq. (3), the 2D van Hove model with $N_0=1$ eV $^{-1}$spin^{-1}; solid curve is the corresponding thermally averaged DOS at $T=T_c$, $\langle N(\delta)\rangle_{k_BT_c}$.

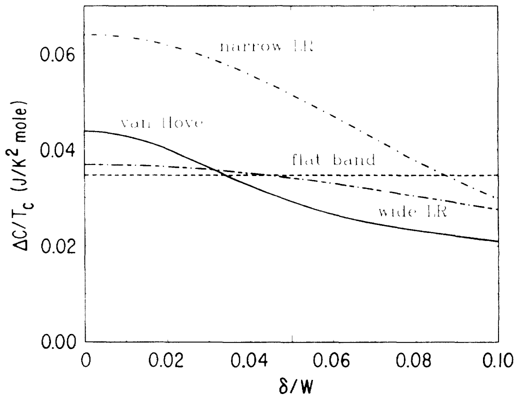

FIG. 3. Calculated $\Delta C/T_c$ as a function of δ/W, based on various DOS models: $N(\varepsilon)=N_0\ln(W/|\varepsilon|)$ for the van Hove model, and $N(\varepsilon)=(N_0/\pi)(\omega_{\rm LR}^2/\omega_{\rm LR}^2+\varepsilon^2)$ for the Lorentzian models. For the van Hove case, the following parameters are chosen for the $YBa_2Cu_3O_{7-y}$ system [4]: $N_0=1$ eV^{-1}spin^{-1}, $W=0.5$ eV, $\omega_c=0.065$ eV. For the Lorentzian models, the same values for W and ω_c are used, except N_0 is adjusted to give the same total number of states as the van Hove case. Narrow-Lorentzian-DOS-peak model: $\omega_{\rm LR}=0.05$ eV, $N_0V=0.083$; wide-Lorentzian-DOS-peak model: $\omega_{\rm LR}=0.097$ eV, $N_0V=0.13$.

[4,6]. The results of the T_c calculation are also shown in Fig. 2 (the upper abscissa). As shown in Fig. 2, in terms of the van Hove model, the calculated BCS curve for $\Delta C/T_c$ is basically capable of describing the observed magnitude of $\Delta C/T_c$ and its T_c dependence for $T_c \lesssim 90$ K. The variation of the $\Delta C/T_c$ data with T_c (and thus δ/W) mainly reflects the energy dependence of a vHs peak in DOS plus a small correction of mass enhancement $(1+\lambda_{e\text{-ph}})$.

However, the experimental data for $T_c > 90$ K suggest a T_c dependence of $\Delta C/T_c$ slightly stronger than that predicted by the simple BCS curve of the vHs model. To improve this situation, several functional forms of $N(\delta)$ were used to calculate $\Delta C/T_c$ as a function of δ/W with the constraint that $T_c=92.5$ K with the ε_F at the DOS peak. The numerical results presented in Fig. 3 clearly indicate that the BCS van Hove model provides the best approximation to the observed T_c dependence. It is important to point out that, for the same experimental range of T_c (90 K $> T_c >$ 40 K), the wide-Lorentzian-DOS-peak model predicts a much weaker T_c dependence of $\Delta C/T_c$ than that of the vHs model. On the other hand, the narrow-Lorentzian-peak model can provide about the same amount of the dynamical range in $\Delta C/T_c$ as the van Hove model, but with a wrong curvature and a too high overall magnitude in the $\Delta C/T_c$ vs δ/W plot. The calculated results presented in Fig. 3 thus suggest that further improvement in the agreement between experiment and the van Hove model should be derived from effects beyond the energy dependence of the DOS function. One such possibility is to include the enhancement effect from strong electron-phonon coupling.

The strong-coupling correction to the BCS values of $\Delta C/T_c$ has been extensively discussed and numerically calculated [21] using the Eliashberg theory. The enhancement factor η^2 can be defined as follows:

$$\frac{\Delta C}{T_c}=\left(\frac{\Delta C}{T_c}\right)_{\rm BCS}\eta^2\,, \qquad (5)$$

where $(\Delta C/T_c)_{\rm BCS}$ is the BCS value with correction due to the effective mass renormalization included [Eq. (4)]. In this work, we have calculated η^2 as defined in Eq. (5) by numerically solving the standard Eliashberg equations as described in detail in Ref. [21]. In our calculation, an energy-dependent DOS for the van Hove model [i.e. Eq. (3)] is used. The vectors describing the gap and Z factor are substituted into a generalization of the Bardeen-Stephens form for the free energy [21]. The specific-heat jump at T_c may then be calculated by a single numerical differentiation. In Fig. 4, the calculated results are compared with the experimental data. In terms of the overall T_c dependence, the agreement between theory and experiment is quite reasonable. In particular, the curve for $N_0=0.7$ corresponds to a value for $\langle N(\delta)\rangle_{k_BT_c}$ of about 2.9 eV^{-1}spin^{-1}, for $T_c=92.5$ K, in reasonable agreement with the values estimated from other experiments [6].

In spite of the apparent agreement between the experiments and the van Hove model, the fitting of experimental data with theory is not unique because of the slowly divergent nature of the 2D vHs and the large scatter in the available data. Our preliminary investigation indicates that the effect of including a constant DOS back-

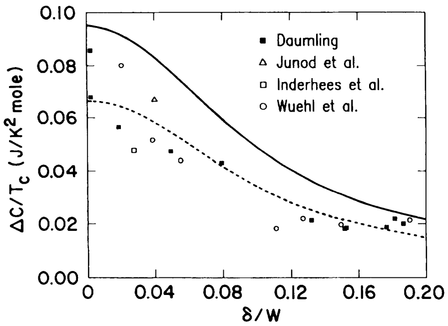

FIG. 4. $\Delta C/T$ as a function of δ/W. $\lambda_{e\text{-ph}}=0.4$, $W=0.5$ eV, $\omega_E=0.06$ eV (Einstein phonon mode) and $\mu^*=0$. $N_0=1$ eV^{-1}spin^{-1} (solid curve) and $N_0=0.7$ eV^{-1}spin^{-1} (dashed curve).

ground, and a variation in bandwidth in our calculations of $\Delta C/T_c$ does not change our qualitative conclusion. An alternative to understand the $\Delta C/T_c$ data is to suggest an impurity band, induced by hole doping, located in the Hubbard gap. If this is true, the energy dependence of $N(\varepsilon)$ should be Lorentzian. As discussed earlier, our preliminary $\Delta C/T_c$ calculation using a Lorentzian $N(\varepsilon)$ and comparable band-structure parameters (i.e., $W=0.5$ eV, with or without a constant DOS background) results in a poorer agreement with the experimental data than that achieved with the vHs model. Furthermore, it is important to point out that a model based on a very narrow impurity band is inconsistent with many of the experimentally observed band-structure features and marginal-Fermi-liquid behavior [6].

For the near-stoichiometric compositions (i.e., $0 \lesssim y \lesssim 0.05$, and $T_c \gtrsim 91$ K), the data for each group shown in Fig. 1 suggest a sharp rise in $\Delta C/T_c$ (for example, the solid-square data points only). This effect might be attributable to a chain contribution to $\Delta C/T_c$, which falls off rapidly with increasing y due to chain fragmentation and formation of localized states.

In conclusion, from thermodynamic quantities such as $\Delta C/T_c$, one can deduce important information about the density of states at ε_F that is directly relevant to high-temperature superconductivity. For the oxygen-deficient $YBa_2Cu_3O_{7-y}$ superconductors, the $\Delta C/T_c$ data suggest that $N(\varepsilon_F)$ is peaked at $y=0$ and its energy dependence is consistent with the 2D vHs model.

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Note added.—Recently, supporting specific-heat-jump data on two more materials have come to our attention. The overdoped Tl 2:2:0:1 system [22] shows a decreasing $\Delta C/T_c$ with decreasing T_c, complementing the present data on underdoped Y-Ba-Cu-O samples, while the La-Sr-Cu-O system [23] shows a positive correlation between the specific-heat jump and T_c over both underdoped and overdoped regions.

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