

## Anomalous Temperature Dependence of the Work Function in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We report the experimental observation of a discontinuous change in slope at  $T_c$  of the temperature dependence of the work function of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . We interpret this effect as a superconductivity-induced temperature dependence of the chemical potential. Using a general thermodynamic relation for second-order phase transitions and published values of the specific heat jump, we extract a value for  $d \ln T_c / dn$ , with  $n$  the charge carrier density. This value is consistent with hole-type superconductivity.

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An important issue in the discussion about the microscopic mechanism of high- $T_c$  superconductivity [1] is the question whether or not a large fraction of the valence electrons is involved in the superconducting state. The classification by Uemera *et al.* [2] of the superconducting cuprates together with  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_4$ , Chevrel phase, organic, and heavy-fermion superconductors in a single class of "exotic" superconductors with a  $T_c/T_F$  ratio between 0.01 and 0.06, seems to justify an approach based on the former assumption. Here  $T_F$  enters only as the relevant kinetic energy scale of the charge carriers derived from the London penetration depth, and it may or may not have a physical meaning as a parameter in a Fermi-liquid approach. Directly related to this issue is the degree of localization of Cooper pairs, and the question as to what extent incoherent pairing may persist in the metallic state. Globally this problem can be accessed by considering the ratio  $\xi_0^d n$ , with  $\xi_0$  the physical length scale of a Cooper pair,  $d$  the dimensionality of the system, and  $n$  the density of charge carriers. For a two-dimensional (2D) Fermi liquid this number  $\propto (T_c/T_F)^{-2}$ . Hence it is of considerable interest to have an experimental tool with which one can determine the degree of participation of valence electrons in the ground state of a superconductor.

One possible experimental probe, which has received little attention so far, is the temperature dependence of the chemical potential  $\mu$ . In a recent publication [3] we showed that  $d\mu/dT$  should have an anomaly near the phase transition given by the general thermodynamic relation

$$\left. \frac{(d/dT)(\mu_n - \mu_s)}{c_n - c_s} \right|_{T=T_c} = \frac{d \ln T_c}{dn}, \quad (1)$$

where  $c_n$  and  $c_s$  indicate the specific heat in the normal and superconducting state, respectively. This equation is applicable to any second-order phase transition irrespective of the underlying mechanism. In earlier publications a similar relationship has already been pointed out using specific microscopic models based on a 2D BCS real-space pairing model of fermions [4] and bosons [5]. The results of these microscopic models can be shown to agree with Eq. (1) [3].

Because a change in  $\mu$  is caused by an increase of the surface charge, it is exactly matched by a change of work function, where the work function is defined as the energy difference between the vacuum level directly outside the sample surface and the Fermi level. Apart from the chemical potential, the work function also has a contribution from the surface dipole layer, which depends on the surface electronic structure and (if present) adsorbates.

One of the most sensitive techniques for measuring changes in the work function is the vibrating Kelvin probe method [6]. Here the sample forms a parallel plate capacitor with a reference material (in our case Au). If the distance between the plates is varied, a current will be induced in the wire connecting the plates due to the work-function difference between the two plates. This current can be nulled using a variable voltage source in series with the capacitor. In the nulled state the voltage  $V_{fb}$ , applied to the reference material, is equal to the difference in work function of the sample and the reference plate:

$$-eV_{fb} = W_{\text{sample}} - W_{\text{reference}}. \quad (2)$$

We performed our experiments with a home-built Kelvin probe, based on a previous design by Besocke [6]. This probe was added to a standard vacuum chamber which has a facility for x-ray photoelectron spectroscopy (XPS). The base pressure of the chamber is  $4 \times 10^{-11}$  mbar. A copper block mounted on a continuous flow cryostat was cooled below 10 K. This cold finger acts as a cryopump, due to which the pressure drops quickly below the detection limit of  $3 \times 10^{-11}$  mbar. Therefore measurements were taken only while the cold finger was below 20 K. The sample block on a rotatable manipulator is connected through a thermal weak link (a copper braid) to the cold finger, allowing a slow and gradual ramp through  $T_c$  with about 100 K per hour. The null voltage was controlled by a feedback loop with a time constant of approximately 5 sec. A computer was used to continuously monitor and store the value of the null voltage.

To obtain large clean surfaces we prepared thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with the *in situ* pulsed laser-deposition technique. Directly after growth in the deposition chamber the films were transported under ultrahigh vacuum (UHV) conditions to the measurement chamber. The

process of transferring the samples to the (already cold) sample holder took less than 10 min. Surface cleanliness of each sample was checked with XPS after the work function experiments were completed. We avoided exposure of the sample surfaces to x rays prior to the work-function measurements, as ionizing radiation could in principle influence the surface dipole. The XPS core level spectra were characteristic of good clean stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  surfaces. In spite of our *in situ* preparation technique, traces of carbon and BaO were still present at the surface [7]. X-ray diffraction analysis of the films after the work-function measurements showed that all films were highly *c*-axis oriented. We measured three samples (*A*, *B*, and *C*) with  $T_c$ 's of  $91.5 \pm 0.3$ ,  $87.5 \pm 1.0$ , and  $90.5 \pm 0.3$  K, respectively, as determined from the four terminal resistivity. In order to reach a noise level of about  $20 \mu\text{V}$  in the work-function measurements we have to use a large sample area ( $\approx 1 \text{ cm}^2$ ). For each sample approximately five temperature scans were made. The data points were accumulated in temperature intervals of 2 K.

As one measures a work-function *difference* with the Kelvin probe, we made a separate determination of the work function of the Au reference electrode, by measuring the low-energy cutoff of the secondary electron spectrum with the XPS facility. The measured value of 4.2 eV was added to the work-function difference resulting in the values displayed in the inset of Fig. 1. The values are scattered over 0.2 eV, probably due to small differences in preparation and transport conditions. Also the three curves do not have exactly the same slope. Although these differences may seem small, they become significant on the meV scale, where we will focus our discussion. We tentatively attribute the variation in slope to slight changes in average sample composition, with the possible presence of traces of secondary phases, in particular in sample *B* which has a significantly reduced  $T_c$ .

However, we are mostly interested in changes of the work function at  $T_c$ . If  $\mu$  changes at the transition temperature, this should give the same effect for all samples more or less independent of the exact condition of the surface. In order to separate the superconductivity-induced changes from the background, we subtracted a straight line from the original data such that a zero slope was obtained above  $T_c$ . In the main body of Fig. 1 we display  $-W$  with the background subtracted. As

$$\delta\mu/q + \delta W/q_e = 0, \quad (3)$$

with  $q$  the carrier charge and  $q_e$  the charge of an electron, this corresponds to the chemical potential of the electrons. We see that there is a sudden change of slope of the work function at about 90 K. For sample *B* the kink appears a few kelvin below the kink in samples *A* and *C*, in accordance with the lower  $T_c$  obtained from resistivity experiments. Therefore we assign this kink to anomalous behavior of the chemical potential at  $T_c$ . For

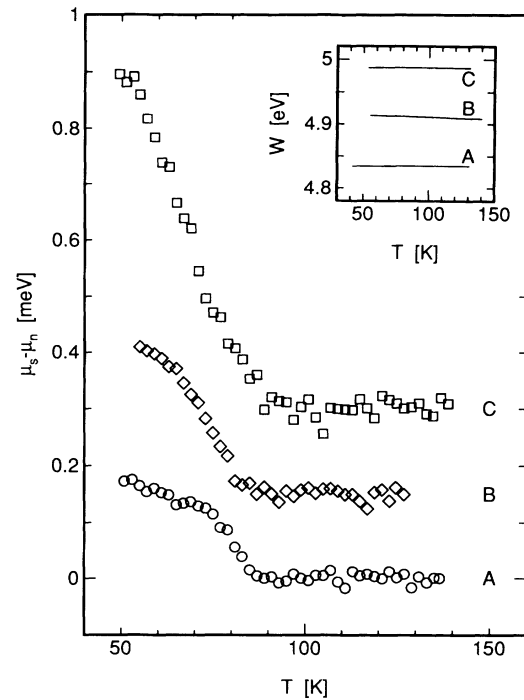


FIG. 1. Temperature dependence of the chemical potential of three different samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Plotted along the vertical axis is  $-\Delta W = \Delta\mu$ . Each curve represents the accumulation of data in approximately five successive temperature scans. The curves were given arbitrary vertical offsets and a straight slope was subtracted. Inset: Absolute value of the work function of each sample vs temperature.

all samples the kink appears to be 2 K below the value of  $T_c$  as determined from resistivity measurements. This reflects a difference in temperature between the sample block (where the Pt thermometer is situated) and the spring-loaded sample, a problem which is difficult to avoid as the samples have to be transported under UHV conditions. The jump in the first derivative of the chemical potential is the same within 10% accuracy for the three samples and equals

$$\left. \frac{d(\mu_n - \mu_s)}{dk_B T} \right|_{T=T_c} = 0.12 \pm 0.02. \quad (4)$$

Before we embark on a deeper analysis of our observations, using Eq. (1), let us first consider two alternative explanations. First of all one could speculate that it is a "spurious" effect caused by physisorption of adsorbate molecules. Adsorbate induced changes of work function are of the order of 0.1 to 1 eV for a monolayer coverage. At a pressure of  $1 \times 10^{-11}$  mbar and a cooling rate of 40 s/K one may expect changes of 0.04 meV/K due to physisorption, which is also the scale of the changes displayed in Fig. 1. Although such effects may well contribute to the background temperature dependence, the kink must be of a different origin, as there is no physical ground for a correlation of such adsorption processes with the super-

conducting phase transition. A second possibility is a change in expansivity ( $\alpha \equiv d \ln V / dT$ ) at  $T_c$ . As the Fermi temperature of a 2D (or layered) free electron gas equals  $n/2\rho$ , with  $\rho$  the density of states per unit volume, we have  $d\mu/dV = -\mu/V$ , so there will be a contribution of  $\alpha$  to the change of chemical potential according to the relation  $d\mu/dT = -\mu\alpha$ . Hence a jump in  $\alpha$  implies a jump in  $d\mu/dT$ . The experimental value of the jump in  $\alpha$  at  $T_c$  is  $-2 \times 10^{-7} \text{ K}^{-1}$  [8], and from an analysis of the London penetration depth the Fermi temperature is estimated to be between 1000 and 2000 K [2]. As a result we can estimate that due to the lattice anomaly there is a contribution to the jump in  $d\mu/dk_B T$  of  $3 \times 10^{-4}$ , which is at least 2 orders of magnitude smaller than the effect displayed in Fig. 1.

We therefore attribute the observed anomaly to the temperature dependence of the chemical potential. It is interesting to see that the sign of the effect is opposite to the curves calculated in Ref. [4]. This is a natural consequence of the fact that the charge carriers are holes instead of electrons [see Eq. (3)]. Let us now further analyze the effect with the help of Eq. (1). Experimental values of the jump in the specific heat of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are in the range of  $5.5 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$  [9], or  $(0.33 \pm 0.06)k_B$  per unit of  $\text{CuO}_2$ . Combining our result of Eq. (4) with this value for the jump in specific heat we conclude that for these samples  $d \ln T_c / dn$  equals  $-0.36 \pm 0.09$ . The negative sign indicates an increase of  $T_c$  upon increasing the hole doping. Hence we conclude from our data that these samples are in the underdoped regime. In the overdoped regime the sign would be positive, whereas at optimal doping there would be no observable effect. Using some reasonable assumptions about the behavior of doping versus  $T_c$ , we conclude from our value of  $d \ln T_c / dn$  that the doping is close to optimal with  $T_c$  less than 5 K below its maximal value. However, a complete analysis of this point requires a set of values of  $T_c$  and  $d \ln T_c / dn$  obtained on samples covering the whole concentration range, which is the subject of future research.

In Fig. 2 we display  $\mu$  vs  $T$  in reduced units, using the average of the data sets of samples *A*, *B*, and *C*. For illustrative purposes a calculated curve is shown, using the 2D single-band negative- $U$  Hubbard model in the Hartree approximation [4]. The parameters in this model are the band filling  $n$  ( $\leq 2$ ) and the interaction  $g$ , which together determine the  $T_c/T_F$  ratio. For the curve in Fig. 2 we used  $n=0.6$ , and we adjusted  $g$  to get  $d(\mu_n - \mu_s)/dk_B T = 0.12$ , resulting in  $T_c/T_F = 0.085$ . More meaningful parameters can probably be extracted from a model where it is taken into account that doping starts from the Mott-Hubbard insulating state [10]. The  $T_c/T_F$  ratio obtained from the fit in Fig. 2 provides an effective Fermi temperature of 1070 K. From the analysis of the London penetration depth with 2D fermiology [11] one obtains  $T_F = 1350 \text{ K}$  for  $\lambda_L = 1500 \text{ \AA}$  [2]. This level of agree-

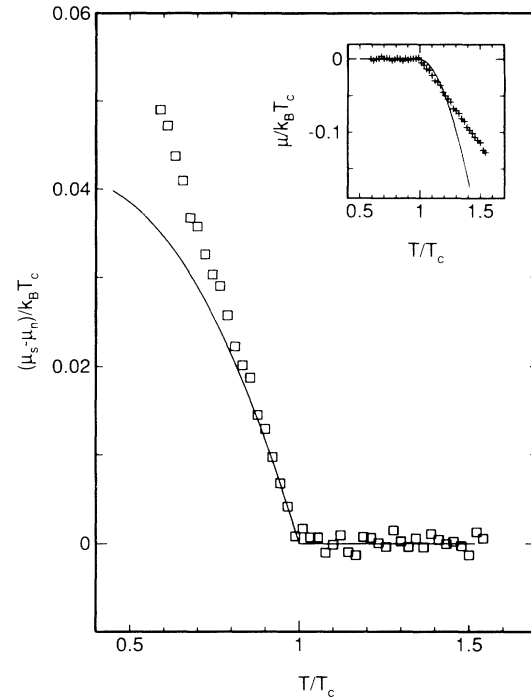


FIG. 2. Average over the experimental  $\mu(T)/k_B T_c$  curves of the three samples (squares) vs reduced temperature and a theoretical curve based on a 2D BCS local-pairing model (solid). Inset: The same experimental curve scaled with a factor  $-2$  and a different slope subtracted (crosses), together with the theoretical curve of  $\mu/k_B T_c$  for Bose condensation of noninteracting bosons (solid).

ment is probably better than we deserve given the model assumption of a 2D negative- $U$  Hubbard model, as well as a free electron analysis for analyzing  $\lambda_L$ . By combining the 2D BCS relation  $\xi_0^2 n_{\text{pair}} \approx 0.1 (T_c/T_F)^{-2}$  with our experimentally determined value of  $T_c/T_F$ , we conclude that the number of overlapping pairs is of the order 10 to 20. This is several orders of magnitude smaller than in classical BCS superconductors, indicating that a significant fraction of the valence electrons participate in the superconducting ground state.

Another well-known phenomenon where the chemical potential adjusts itself self-consistently if temperature is changed is Bose-Einstein condensation. Unfortunately we are not aware of any theoretical study of the interacting Bose gas where actual curves of  $\mu$  vs  $T$  are displayed. For the noninteracting case it is easy to calculate this function. In particular the 3D noninteracting Bose gas with an  $E \propto k^2$  dispersion is a textbook example, where  $\mu$  approaches zero from below for  $T$  approaching  $T_c$  from above. In this case  $\mu$  as well as  $d\mu/dT$  are continuous at the phase transition, and a jump occurs only in the second derivative versus  $T$ , as is shown in the inset of Fig. 2. Assuming a bosonic charge  $2|e|$  the (boson) chemical potential follows from the experimental data by reversing the sign and multiplying with a factor of 2 [see Eq. (3)].

As in this case  $\mu$  should be constant below  $T_c$ , we have to subtract a different linear background. The result is displayed in the inset. The qualitative difference between the two curves is at least in part due to the lack of realism in the assumed absence of boson-boson interactions. In fact, if preexisting local pairs would exist in the cuprates the interactions would be very strong due to the large spatial overlap between pairs mentioned above. However, it is questionable if under these conditions pairs are sufficiently stable to survive the phase transition. Nevertheless strongly localized pair fluctuations could be important, among other things resulting in a different phenomenology of the gap [12].

In conclusion, we have determined experimentally the temperature dependence of the work function of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and found an anomalous behavior at  $T_c$ . We interpret this as a superconductivity induced change in chemical potential. The value of the jump in  $d\mu/dT$  can be interpreted with an expression linking this effect to the specific heat jump and the density derivative of  $T_c$ . We arrive at a consistent picture where  $T_c$  of the samples is within a few kelvin from the maximum obtainable value in the hole-doped double-layer  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds.

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