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Universal trend in the heat capacity of $YBa_2Cu_3O_{7-x}$ near $T_c(x)$

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The reduction in transition temperature that occurs as oxygen is removed from $YBa_2Cu_3O_{7-x}$ is accompanied by a rapid decrease in the size of the heat-capacity anomaly at T_c. We treat the fluctuation effects in the context of XY-like behavior and demonstrate that their dependence on the transition temperature agrees in detail with a relationship between T_c and the hole concentration proposed by Schneider and Keller. Further, we show that this empirical relationship can be understood by combining scaling arguments with the nearly antiferromagnetic Fermi-liquid model of Monthoux and Pines.

Studies of reduced-oxygen-content $YBa_2Cu_3O_{7-x}$ have shown a dramatic reduction of the heat-capacity anomaly associated with the superconducting transition as oxygen is removed.[1–4] A consistent explanation has so far not been developed. Furthermore, fluctuations so dominate the behavior of the heat capacity near T_c that predictions which treat the anomaly as a mean-field jump are likely to be invalid.[5,6] In this paper we present an analysis based on XY critical fluctuations and two-scale factor universality as proposed recently by Schneider and Keller.[7] We show that the behavior of the critical amplitude agrees quantitatively with the reported trends in extreme type-II superconductors and suggests a connection to the strong-coupling theory of Monthoux and Pines.[8]

We have measured the heat capacity of a series of $YBa_2Cu_3O_{7-x}$ crystals prepared at Argonne National Laboratory (Au doped) and at the University of Illinois (no Au doping),[9,10] whose properties are listed in Table I. All but one of the crystals, sample No. 1, were annealed at Argonne National Laboratory in the same manner. Crystal No. 1 was annealed at Sandia National Laboratory under 1 kbar of O_2 pressure. Crystal No. 5 was not exposed to Au at any stage in its preparation. Even when the gold doped (3 at. % of the copper atoms substituted by gold atoms) and the undoped crystals were annealed simultaneously, the gold-free samples have transition temperatures which are 2–8 K higher. Note this is not in contradiction to other measurements, which demonstrate that gold impurities actually raise the transition temperature, because the oxygen contents could be different. In a previous paper we argued that the heat capacity of these samples reflects the intrinsic properties of the superconducting transition because of an absence of any systematic dependence of the transition width, shielding fraction, or Meissner fraction on the transition temperature.[4]

Heat-capacity data, as measured by a previously reported ac method on Au-doped samples, are shown in Fig. 1. All curves have been normalized to unity at 100 K. It was noted previously[4] that the amplitude of the heat-capacity anomaly in "fully oxygenated" gold-doped samples is generally 25% to 40% smaller than that of fully oxygenated non-gold-doped samples. However, when Au-doped samples are annealed in a 1-kbar atmosphere of oxygen the heat-capacity anomaly is nearly the same as that seen in non-Au-doped samples. Thus, the original discrepancy is resolved by incorporating a sufficient amount of oxygen into the gold-doped samples. As a further check, the heat-capacity anomaly in a reduced-

TABLE I. Parameters from a least-squares fit of the heat capacity as described in the text, Eq. (1). All parameters except T_c and t_0, which are in units of Kelvin, are in units of mJ g^{-1} K^{-1}.

Crystal No.	T_c	A	D	t_0	B_0	B_1	B_2
1[a]	91.69	1.17	4.98	0.0034	169.4	204	−80
2	90.79	1.05	3.75	0.0025	167.9	205	−21
3	89.44	0.85	1.88	0.0024	166.8	188	−50
4	88.12	0.65	1.63	0.0042	164.9	185	−64
5[b]	81.38	0.48	1.16	0.011	152.0	175	−53
6	77.4	0.39	1.28	0.0039	144.2	171	−50
7	75.87	0.27	0.87	0.0077	141.7	169	−25
8	59.4	<0.2	<0.3	0.002	97.0	155	N/A

[a] Annealed in 1 kbar O_2.
[b] Never in contact with gold.

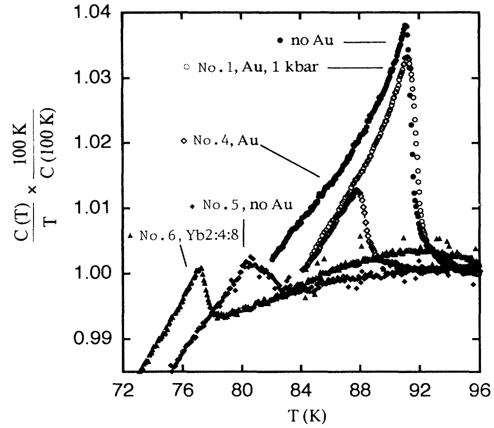

FIG. 1. Heat capacity divided by the temperature and the value of C/T at 100 K of a series of samples. The data on the highest-T_c sample with the largest anomaly were reported by Inderhees *et al.* in Ref. 12.

oxygen-content Au-free sample, No. 5, has been measured and shows a behavior consistent with the samples with gold impurities having the same T_c (Fig. 1).

The behavior of reduced-oxygen-content Y-Ba-Cu-O differs markedly from that seen in most doped superconductors. Indeed, the heat-capacity anomaly can be reduced significantly faster than the transition temperature upon the addition of magnetic impurities, when the Kondo temperature of the impurities is approximately the same as the superconducting T_c. Even then the reduction is more gradual than that observed here.[11] Heavy-fermion superconductors and highly anisotropic intercalated compounds are notable exceptions. A marked reduction in the size of the heat capacity in these materials can occur with only a slight reduction of T_c.

The heat capacity of fully oxygenated samples can be fit assuming either that the fluctuations are in the Gaussian or critical regimes. However, analysis of the field dependence of C_p, the magnetization and fluctuation conductivity are consistent only with a fully critical three-dimensional (3D) XY-like behavior.[12] Note that in the "intermediate critical region"[13] the superconducting transition belongs to the same universality class as the superfluid transition regardless of whether the order parameter has conventional s-wave or d-wave symmetry.[14] The fluctuation heat capacity in this universality class exhibits a nearly symmetrical logarithmic singularity at the transition; that is, $C_{\mathrm{fl}} \propto \ln|t|$ where $t=(T-T_c)/T_c$. The symbol t will be referred to as the reduced temperature. The approximation of a logarithmic divergence also admits the possibility of a step discontinuity at T_c. Many of the results reported, principally the T_c dependence of the amplitude of the fluctuations and the mean-field step, are relatively insensitive to whether the fluctuation contributions are treated as being Gaussian or critical.

One, of course, never actually observes an infinite heat capacity. This rounding can be best modeled by assuming that there is a maximum correlation length due to defects, and introducing an effective reduced temperature t^* which determines the distance from the true critical point.[15] The actual reduced temperature is related to t^* by $t^*=+[t^2+(t_0)^2]^{1/2}$. The two parameters $T_c(\xi_{\max})$ and t_0 are functions of the limiting size, $\xi_{\max}$. The fluctuation contribution to the heat capacity is then $\propto \ln(t^*)$. If this were the sole effect of rounding, this definition locates the transition temperature at the rounded maximum in C_p, which is at a lower temperature than the true transition temperature. The remanent of the mean-field step is also affected by inhomogeneities in the superconductor. The rounded mean-field step is arbitrarily modeled by the function $[1-\tanh(t/t_0)]/2$. Note, the same results are obtained even if the rounding of the mean step is allowed to be independent of the rounding of the fluctuation peak. In addition, because the fits are confined to regions and the superconducting transition, our neglect of the slope in the mean-field heat capacity below the transition is also not important.

The superconducting contribution is a small fraction of C_{tot} in the vicinity of T_c. The largest contribution to the heat capacity near the transition is from the phonon degrees of freedom. This will be assumed to be smooth at the transition temperature, and can easily be approximated by a second-order polynomial in the reduced temperature for temperatures near the superconducting transition. The normal electronic specific heat is a linear function of temperature and is thus accounted for by the polynomial during the fit.

With these basic elements it is now possible to fit all the heat-capacity data near the superconducting transition. We have performed a seven parameter fit of the data using

$$C_{\mathrm{tot}}=B_0+B_1 t+B_2 t^2+\left\{\frac{D}{2}\right\}\left[1-\tanh\left\{\frac{t}{t_0}\right\}\right] - A\ln(t^*)\ . \tag{1}$$

The seven free parameters are A, B_0, B_1, B_2, D, t_0, and T_c. C_{tot} has been assigned a value of 190 mJ g^{-1} K^{-1} at 100 K. In order to be consistent with a logarithmic fit A, the amplitude of the fluctuations, is taken to have the same value above and below the transition temperature ($A=A^-=A^+$). A standard iterative nonlinear fitting program was used to determine the parameters that minimize the sum of the squares of the residuals. An example of a typical fit is shown in the inset of Fig. 2. The values of the best fit parameters for all the samples are contained in Table I, including a single crystal[16] of $Yb_2Ba_4Cu_8O_{16}$ (sample No. 6). Only limits can be set on the parameters for sample No. 8. The most striking trend is that both the amplitude of the fluctuation contribution A and the step D decrease dramatically as the transition temperature is lowered. The step D initially falls only slightly faster than A. This implies that the shape of the heat-capacity anomaly remains relatively constant, so that approximating the fluctuation contributions by a logarithm remains as valid for lower-T_c samples as it is for fully oxygenated ones. This is also supported by similarities in the field-dependent heat capacity.[4,12] For all the samples examined there is no systematic dependence of t_0 on T_c;

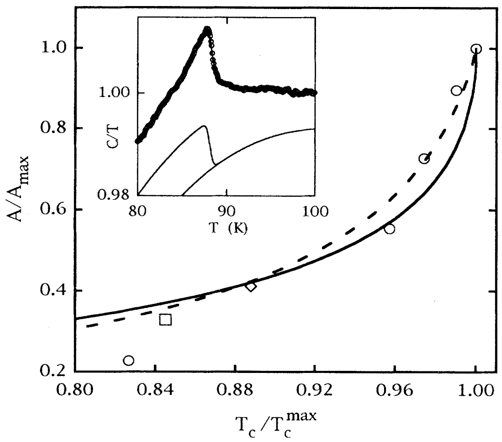

FIG. 2. A comparison between the measured and predicted ratio of the amplitude of the logarithmic term to its maximum value (taken to be that of sample No. 1). The solid line represents the prediction of the Schneider and Keller ansatz [Eq. (5)] given constant anisotropy and the dashed line, the result of the Monthoux-Pines T_c [Eq. (6)]. Sample No. 8 gives $A/A_{\max} \leq 0.18$ at $T_c/T_c^{\max}$. The diamond is sample No. 5 and the square is sample No. 6. Inset: An example of a typical fit (sample No. 4). The lower curves represent the smooth background and the step in the heat capacity associated with transition while the line through the data points is calculated with parameters presented in Table I.

thus, the reduction of A is not due to increased rounding. In any case the fitting procedure should correct for the effects of rounding.

Recently, Schneider and Keller[7] argued that many properties of extreme type-II superconductors follow from an unusual relationship between the transition temperature and $\lambda_{0,ab}$, the zero-temperature London penetration depth for fields along the c axis. A similar connection was first pointed out by Uemura *et al.*[17] An optimal composition for these materials is assumed to exist at which point T_c has its largest value $T_c^{\max}$ and the penetration depth, its smallest value, which we denote nonetheless as $\lambda_{0,ab}^{\max}$. The transition temperature for nonoptimal compositions can be written as

$$\frac{T_c}{T_c^{\max}} = 2\left[\frac{\lambda_{0,ab}^{\max}}{\lambda_{0,ab}}\right]^2\left[1-\frac{1}{2}\left[\frac{\lambda_{0,ab}^{\max}}{\lambda_{0,ab}}\right]^2\right] . \quad (2)$$

From this assumption a direct calculation of A is made possible by exploiting two-scale-factor universality.[18] The key element is a long-overlooked relationship among T_c, $\lambda_{0,ab}$, and the transverse, or phase, coherence length $\xi_{0,ab}^T$ which, for type-II superconductors in the intermediate XY critical regime, is given by

$$T_c = (6.24\times10^7\ \text{Å K})\xi_{0,ab}^T/\lambda_{0,ab}^2 . \quad (3)$$

A further result of hyperscaling is a relationship between the amplitude of the fluctuation heat capacity below T_c and the phase coherence length, which can be written as[19]

$$A^- = m_{ab}k_B R_T^3\left[m_c(\xi_{0,ab}^T)^3\right]^{-1} , \quad (4)$$

where $R_T \approx 0.8$ for the 3D XY model. If we ignore changes in the effective mass ratio with doping, $\xi_{0,c}^T$ is proportional to $\xi_{0,ab}^T$, and $\lambda_{0,ab}$ and $\xi_{0,c}^T$ can be eliminated from Eqs. (2)–(4) to give

$$\frac{A^-}{A_{\max}^-} = \left[1+\left[1-\frac{T_c}{T_c^{\max}}\right]^{1/2}\right]^{-3} . \quad (5)$$

In Fig. 2, we have plotted the predictions of Eq. (5) along with the measured values $A(T_c)/A(92\ \text{K})$ for the first seven samples listed in Table I. Including the effects of anisotropy changes, the same procedure predicts a faster reduction in A by a factor of $(m_{ab}/m_c)(m_c/m_{ab})_{\max}$.

Because of the large lattice background inherent in the high-temperature superconductors, the uncertainty in the values of A is quite large. One measure is to vary A so as to double the sum of the squares of the residuals while allowing all other parameters to vary. However, the parameters are strongly covariant, and this procedure predicts an uncertainty of 25% for sample No. 3 and up to 100% for samples with lower T_c. The conventional fitting routine returns very small standard errors, less than expected from the apparent scatter in the data. Thus we cannot objectively distinguish between the two models that are shown on Fig. 2.

Overall, the parabolic *ansatz* of Eq. (2) and the hyperscaling results provide a remarkably consistent picture for the reduction in the fluctuation amplitude, associating it with a significant increase in the coherence volume as T_c is lowered. As a further check on the applicability of hyperscaling, we eliminate the transverse coherence length between Eqs. (3) and (4), and use experimentally determined values of $\lambda_{0,ab} = 1480$ Å and $m_c/m_{ab} = 25$ to predict $A^- = 1.3\ \text{mJ g}^{-1}\text{K}^{-1}$ for 92-K samples.[20] This is in excellent agreement with the value of $A = 1.2\ \text{mJ g}^{-1}\text{K}^{-1}$ determined by fitting the heat capacity of sample No. 1.

The relationship expressed in Eq. (2) is quite unexpected from conventional theories of superconductivity. However, we will demonstrate that it follows from the nearly antiferromagnetic Fermi-liquid model of Monthoux and Pines,[8] when some simple scaling assumptions are made. In this model, a phenomenological susceptibility $\chi(Q)$ is constructed to correctly explain NMR Knight shift and relaxation data. A constant g measures the coupling between spin degrees of freedom and the quasiparticles, yielding an expression for T_c through the Eliashberg equations.[21] An expression relating T_c to g has been derived, reminiscent of the related BCS equation, which can be written as $T_c = \Gamma\exp(-1/\Lambda)$, where $\Lambda = 0.32N(0)g$, Γ is a magnetic energy, and $N(0)$ is the tunneling density of states at the Fermi surface. In analyzing reduced oxygen samples, Monthoux and Pines[22] made the remarkable observation that $g^2\chi(Q=0,T_c)$ appears to be constant. We assume that for this quasi-2D system, the density of states is simply proportional to the quasiparticle density n, so that we can write

$$\frac{T_c}{T_c^{\max}} = \exp\left\{\frac{1}{\Lambda_{\max}}\left[1-\left[\frac{n_{\max}[1+F_0^a(n_{\max})]}{n[1+F_0^a(n)]}\right]^{1/2}\right]\right\} . \quad (6)$$

Here, we have assumed that $\chi(Q=0,T_c)$ is proportional to $N(0)/(1+F_0^a)$, that we can express the pseudo-Fermi-liquid parameter $F_0^a(n)\approx fn/n_{\max}$, and that $\Lambda_{\max}$ is the coupling constant at $T_c^{\max}$. In their strong-coupling calculation, Monthoux and Pines obtain $\Lambda_{\max}=0.72$. In Fig. 3 we plot the ansatz equation (2), expressed in terms of the quasiparticle density ratio $n/n_{\max}$ along with the curve calculated from Eq. (6) with $f=-0.45$. The agreement is quite remarkable. As a further test, we have combined the critical-temperature ratio from Eq. (6) with Eq. (3) to calculate the heat-capacity ratio as in Eq. (5). This is plotted on Fig. 2 (dashed line). We caution that the uncertainty in the experimental data precludes any decision as to which curve is in better agreement with the experiment. As a final test, we calculate the susceptibility at T_c. The experimental ratio[23] is $\chi(T_c=60\text{ K})/\chi(T_c=90\text{ K})=0.25$; the model gives 0.27.

In summary, we have shown that the Schneider-Keller ansatz, combined with hyperscaling results, provides a detailed explanation for the strong decrease in the fluctuation amplitude observed in this cuprate superconductor. Because a consistent fit indicates that the fluctuation term is the largest contribution to the heat-capacity anomaly, it can be said that this ansatz gives a description of the reduction of the heat-capacity anomaly with a reduction of the oxygen content. Further, we have demonstrated that the Monthoux-Pines model is capable of reproducing the dependence of T_c on the quasiparticle density if the pseudo-Ferm-liquid parameter F_0^a increases from -0.4 at the optimal concentration through -0.16 for $T_c\approx 60$ K to zero for the concentration at which T_c vanishes.

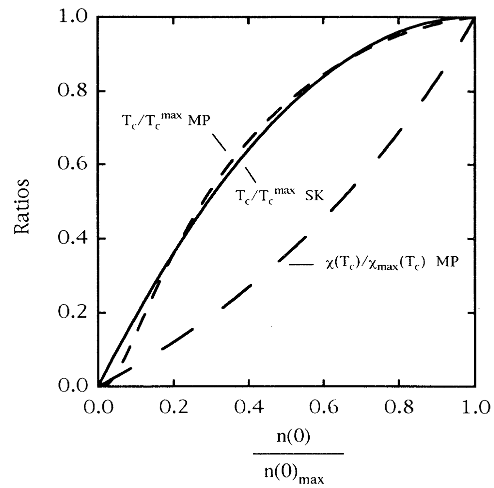

FIG. 3. A comparison of the functional form of the dependence of the transition temperature on the carrier density as predicted by the Monthoux-Pines model and the approximation by Schneider and Keller.

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