Crossover analysis of the heat capacity of $YBa_2Cu_3O_{7-x}$ near T_c: Evidence for XY-like critical behavior

George Mozurkewich
Research Staff, Ford Motor Company, Dearborn, Michigan 48121-2053

M. B. Salamon
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

S. E. Inderhees
Naval Research Laboratory, Washington, D.C. 20375-5000
(Received 13 September 1991; revised manuscript received 17 January 1992)

The heat-capacity anomaly of a largely untwinned single crystal of $YBa_2Cu_3O_{7-x}$ is reanalyzed by means of a crossover model. The conventional Gaussian-corrected BCS shape is shown to be inadequate to fit the data within ±4 K of T_c, a range much larger than estimated from the Ginzburg criterion. Improved fits in the vicinity of T_c were obtained using the approach of Chen, Albright, and Sengers, who introduced a crossover function to interpolate smoothly between critical and mean-field behavior. The best fit was obtained for the three-dimensional XY model, the expected "intermediate" critical behavior of a superconductor. From the crossover analysis, we estimate the zero-temperture coherence length to be $\xi_0 \simeq 12$ Å.

I. INTRODUCTION

The superconducting transition, unlike most second-order phase transitions, can usually be accurately described by the mean-field Ginzburg-Landau theory. The conventional explanation[1] for this rests on the Ginzburg criterion, a statement that critical effects are unimportant so long as the reduced temperature $\bar{t} \equiv (T/T_c)-1$ is much larger in magnitude than $\bar{t}_G$. The reduced Ginzburg temperature $\bar{t}_G$, the point at which the first-order fluctuation contribution to the heat capacity above T_c equals the mean-field heat capacity step ΔC, is given explicitly as[2]

$$\bar{t}_G = (1/32\pi^2)(k_B/\Delta C \xi_0^3)^2 , \quad (1)$$

where ξ_0 is the coherence length at zero temperature. For a conventional superconductor such as Sn, we have $\Delta C \simeq 1$ mJ/cm^3 K, $\xi_0 \simeq 2\times 10^{-5}$ cm, and $\bar{t}_G \simeq 10^{-14}$, clearly inaccessible. The situation is quite different for high-temperature superconductors, where $\Delta C \simeq 30$ mJ/cm^3 K^3, $\xi_0 \simeq 10^{-7}$ cm,[4] and $\bar{t}_G \simeq 10^{-3}$; fluctuations become significant within $\simeq 10\bar{t}_G$ or $\simeq 1$ K of T_c. Indeed, fluctuations have been observed as contributions to the heat capacity,[5] electrical conductivity,[6] and magnetic susceptibility[7] of $YBa_2Cu_3O_{7-x}$.

In a review of fluctuation effects in type-II superconductors, Fisher, Fisher, and Huse[8] (FFH) argued that the conventional Ginzburg criterion, Eq. (1), underestimates the width of the critical region by an order of magnitude. Higher-order contributions, it turns out, exceed the first-order Gaussian correction at $\bar{t}_G$. Thus, data within 10 K of the transition are likely to be within the crossover region between critical and mean-field behavior; neither mean-field nor critical-point expressions are appropriate. Yet, an accurate treatment of fluctuations can, through the exponents and amplitudes in both critical and mean-field regimes, provide information on the symmetry of the order parameter and the effective dimensionality of the system.

Recently, Chen, Albright, and Sengers (CAS),[9] and coworkers[10,11] proposed a workable scheme to treat crossover behavior in heat-capacity data. They introduce a Landau expansion of the free energy that incorporates a crossover function $Y(T)$. Far from T_c, $Y \to 1$, and the expansion reduces to the zero-field Ginzburg-Landau form. Near the critical point, Y vanishes in a way that reproduces both the critical behavior and corrections to scaling of a system of n degrees of freedom in d-dimensional space. This approach is particularly useful if, as argued by FFH, data for $YBa_2Cu_3O_{7-x}$ lie entirely in the crossover region.

In this paper, we analyze the heat-capacity data for $YBa_2Cu_3O_{7-x}$, measured previously on sample YC187 by Inderhees *et al.*[12] We proceed by demonstrating that the first-order (Gaussian) corrections to mean-field theory fail to describe data within 4 K of T_c, casting doubts on conclusions drawn from such analyses. Next, we follow the procedure of CAS to determine the best-fit parameters for various (n,d) models, for $d=3$, the presumed intermediate critical behavior as discussed by FFH. The fit for $n=2$, $d=3$ is statistically better than for either $n=1$ or $n=3$. Finally, we discuss the magnitudes of the fitting parameters and their connection to BCS theory and consider the Ginzburg criterion in the context of the CAS approach.

II. WIDTH OF THE CRITICAL REGIME

In the regime where Gaussian corrections to mean-field theory are sufficient, the heat capacity of a superconductor may be represented by[13]

$$C_p = \sum_{m=0}^{3} b_m \bar{t}^m + f\,\bar{t}^{-1/2}\ , \quad T > T_c\ ; \tag{2}$$

and

$$C_p = \sum_{m=0}^{3} b_m \bar{t}^m + 2^{3/2} f |\bar{t}|^{-1/2}/n + h_1 + h_2 \bar{t}\ , \quad T < T_c\ . \tag{3}$$

Here f is the amplitude of the fluctuation term (assuming that $d=3$), h_1, the mean-field step, and h_2, the slope of the mean-field heat capacity below T_c. The polynomial sum represents a smooth background variation that includes lattice, normal electronic, and addendum contributions.

The regime of validity for including only Gaussian corrections was found by applying the following principle: Both the values of the parameters and the goodness of fit should not depend on the domain of temperatures included, so long as that domain falls entirely within the range of validity of the functional form being tested. Any systematic variation of the parameters with domain size implies that the postulated fit is inadequate to model the data. Hence, Eqs. (2) and (3) (with various values of n) were fitted to the data by a linear least-squares method but excluding data close to T_c. Values of the sample variance s^2 (Ref. 14) were determined with all data points for which $|\bar{t}|T_c < T^*$ weighted to zero, while weighting to unity all other points. Figure 1 shows the dependence of f, h_1, and s^2 on the size of the excluded temperature range. The results are qualitatively the same for $n=1$, 2, and 3. For $T^* > 6$ K, f and h_1 behave rather erratically because the fluctuation contribution is not large enough to define a Gaussian term unambiguously. For $T^* < 4$ K, all three parameters vary smoothly; the increase in s^2 indicates that the Gaussian form is *not* obeyed. The decrease in f with decreasing T^* may indicate that $T^* < T_c|\bar{t}_G|$; i.e., that the system is in the crossover regime. Over no extended range of temperature does the Gaussian form provide a good fit to the data with parameters independent of T^*, except perhaps in the limited regime $4\ \text{K} < T^* < 6\text{K}$.

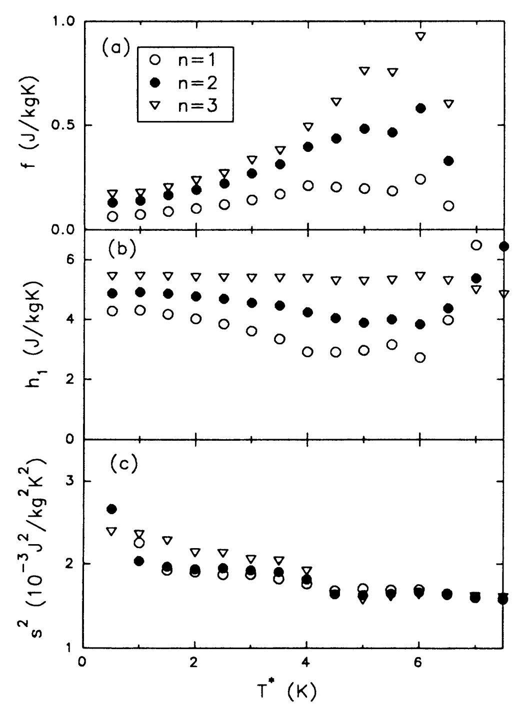

FIG. 1. Parameters of the Gaussian fit vs half-width T^* of the excluded temperature region. (a) Amplitude f of the Gaussian term; (b) magnitude h_1 of the mean-field-like step; and (c) sample variance s^2 (mean-square deviation per degree of freedom). Unity on this scale corresponds to an rms error of 0.03 J/kg K or 0.02% of the total heat capacity.

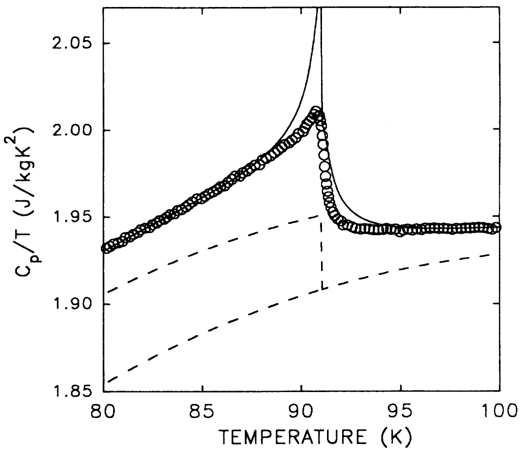

FIG. 2. Result of the Gaussian analysis for $T^*=5$ K (solid line) plotted through the data points. The dashed lines indicate the smooth polynomial background and that background plus mean-filed-like behavior. For clarity, only 25% of the data points used in the fit are shown.

Figure 2 shows the quality of the Gaussian fit for $n=2$ and $T^*=5$ K, along with the fitted polynomial background and mean-field-like contribution. This plot shows that the magnitude of the Gaussian contribution is quite large; even 10 K from T_c that contribution is $>30\%$ of the mean-field step. Thus, the reduction of s^2 for $T^* > 4$ K is not simply because the $\bar{t}^{-1/2}$ term is small in that region. As we will show below, the fitted background for $T^*=5$ K is quite similar to that obtained from the CAS fit, which gives credence to the physical significance of that background. For smaller T^* the Gaussian term decreases, as noted above, and the polynomial background increases to the point that data at lower temperature actually fall below the background.

We conclude that the Gaussian approximation (for $d=3$ and any n) is incapable of describing the heat-capacity data over the full range of $\bar{t}$. Consequently, a more complete analysis that correctly interpolates between mean-field-like and critical-like behavior is appropriate.

III. THEORY AND METHOD

The CAS method[9] constructs a renormalized form of the Landau free-energy functional, whose minimum with respect to the order parameter is capable of reproducing both mean-field behavior and critical divergences. To the usual Landau parameters (T_c, amplitude u of the term quartic in the order parameter, and overall amplitude c_t) are added the critical exponents and fixed-point value u^* of the appropriate (n,d) model. The method is implemented within the renormalization-group method by separating the critical part of the free energy into a mean-field part and a fluctuation part, both of which contain the rescaling length l. Because the physical free energy is independent of length scale, one is free to seek a particular value $l=l^*$, called the match point, at which the fluctuation part vanishes. The remainder has Landau-expansion form, but with the temperature, order parameter, and interaction strength u all renormalized, and with an additional term proportional to the square of the reduced temperature. To accomplish this, CAS introduce a crossover function $Y(l^*)=[u(l^*)-u^*]/[u-u^*]$, where $u(l=0)=u$ and $u(l=\infty)=u^*$. In the mean-field limit $Y\rightarrow 1$, while $Y\rightarrow 0$ in the vicinity of the true critical point. The match point can be related to the product of the correlation length and the physical wave-vector cutoff Λ, which therefore appears as a nonuniversal parameter in the problem. The mean-field-like critical free energy can then be written as

$$\frac{\Delta A(T,\Phi)}{RT_c}=\tfrac{1}{2}t|\Phi|^2Y^{(2-1/\nu-\eta)/\omega}+\frac{\bar{u}u^*\Lambda}{24}|\Phi|^4Y^{(1-2\eta)/\omega}-\frac{n\nu}{2\alpha\bar{u}\Lambda}t^2(Y^{-\alpha/\Delta}-1)\ . \tag{4}$$

Here we have $t=c_t\bar{t}$; $\bar{u}=u/u^*$; R, the gas constant; and ν, η, α, ω, and $\Delta=\omega\nu$ are the critical exponents. We can eliminate c_t, on which ΔA depends nonlinearly, in favor of an energy-scale variable A_0, by making the substitutions $\psi=\Phi/c_t^{1/4}$, $\lambda=\Lambda/c_t^{1/2}$, and $A_0=RT_cc_t^{3/2}$. In terms of these variables, Eq. (4) becomes

$$\frac{\Delta A(T,\psi)}{A_0}=\tfrac{1}{2}\bar{t}|\psi|^2Y^{(2-1/\nu-\eta)/\omega}+\frac{\bar{u}u^*\lambda}{24}|\psi|^4Y^{(1-2\eta)/\omega}-\frac{n\nu}{2\alpha\bar{u}\lambda}\bar{t}^2(Y^{-\alpha/\Delta}-1)\ . \tag{5}$$

The value l^* at which the fluctuation part of the free energy vanishes is contained implicitly in a pair of equations that Y must satisfy at each temperature:

$$Y'=0\ , \tag{6}$$

where

$$Y'\equiv Y\left[\frac{1+(\bar{u}-1)Y}{\bar{u}[1+(\Lambda/\kappa)^2]^{1/2}}\right]^{\omega} \tag{7}$$

and

$$(\kappa/\Lambda)^2=(\bar{t}/\lambda^2)Y^{(2-1/\nu)/\omega}+(\bar{u}u^*/2\lambda)|\psi|^2Y^{(1-\eta)/\omega}\ . \tag{8}$$

We will discuss below the relation between κ and the actual correlation length $\xi(T)$.

The fixed-point coupling constant u^* and the critical exponents depend on (n,d) and are given in Table I for various $(n,3)$. For each choice of n, $\bar{t}$, and the nonuniversal parameters A_0, T_c, $\bar{u}$, and λ, ψ takes on the value that minimizes $\Delta A(\psi)$, subject to the constraint of Eq. (6); i.e.,

TABLE I. Fixed points [Z. Y. Chen (private communication)] and exponents [J. C. LeGuillou and J. Zinn-Justin, J. Phys. (Paris) **46**, L137 (1985)] for (n,d) models with $d=3$.

n	1	2	3
u^*	0.472	0.422	0.379
ν	0.630	0.669	0.705
ω	0.79	0.78	0.78
η	0.031	0.033	0.033
$\alpha=2-3\nu$	0.110	−0.007	−0.115
$\Delta=\omega\nu$	0.498	0.522	0.550

$$\frac{d(\Delta A)}{d\psi}=0=\frac{\partial(\Delta A)}{\partial\psi}+\left[\frac{\partial(\Delta A)}{\partial Y}\right]\left[\frac{dY}{d\psi}\right]\ . \tag{9}$$

Explicit expressions for the required derivatives can be found in Appendix B of Ref. 10.

$\Delta A(T)$ was calculated by a numerical procedure. Values of ψ and Y were determined on a closely spaced temperature grid by subjecting them to a relaxational equation of motion in the $\psi-Y$ plane, with the driving forces determined by the degree to which the current values failed to satisfy Eqs. (6) and (9). At each step, the changes were therefore given by $\Delta|\psi|\propto -d(\Delta A)/d|\psi|$ and $\Delta Y\propto -Y'$. The procedure was continued until consistency was achieved; ΔA was then calculated from Eq (5). The process was repeated at each successive temperature with the previous values of ψ and Y as the starting point for the subsequent stage. The process was simplified above T_c by the requirement that $\psi=0$; note from Eq. (5), however, that $\Delta A\neq 0$ above T_c. Finally, the heat capacity was represented as

$$C_p=-T\frac{\partial^2(\Delta A)}{\partial T^2}+\sum_{m=0}^{3}b_m\bar{t}^m\ , \tag{10}$$

where the second derivative was computed numerically from closely spaced values of ΔA, and the sum represents all noncritical contributions.

For any choice of the nonlinear parameters, the corresponding linear parameters were found by an unweighted least-squares fit. A global minimum of s^2 was found by either a simplex method in the nonlinear parameters $\bar{u}$, λ, and T_c or by systematically exploring the space of nonlinear parameters.

IV. RESULTS

For fixed n and T_c, a contour plot of the sample variance s^2 in the $\bar{u}$-λ plane shows a sharp crevasse whose depth varies little along its length. Thus, there is an alternative coordinate system in which s^2 is independent of one coordinate. A convenient choice is the $\bar{u}\lambda-\bar{u}/\lambda$ system, with s^2 nearly independent of the latter coordinate.

TABLE II. Best-fit parameters of (n,d) models with $d=3$. No data points have been excluded from the fit in calculating s^2.

n	1	2	3
$10^3 s^2$(J/kg K)^2	12.0	6.0	9.3
$\bar{u}\lambda$	3.1 ± 0.2	0.98 ± 0.01	0.588 ± 0.002
$\bar{u}/\lambda$	$(8\pm2)\times10^{-2}$	$(5\pm5)\times10^{-4}$	$(2\pm1)\times10^{-4}$
T_c (K)	91.06 ± 0.01	91.04 ± 0.01	91.02 ± 0.01
A_0 (J/kg)	$153.\pm8$	77.1 ± 0.8	53 ± 3
b_0 (J/kg K)	174.4	173.1	172.4
b_1 (J/kg K)	196	203	207
b_2 (J/kg K)	−71.3	−67.8	−66.1
b_3 (J/kg K)	−42.2	−151	−232

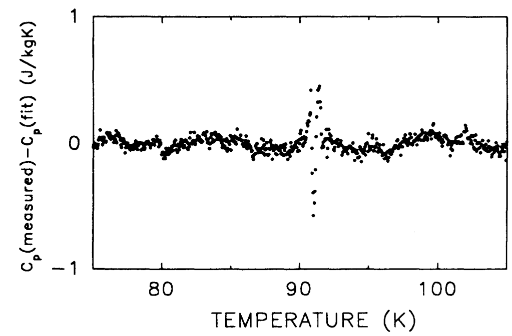

FIG. 4. Residuals for $(n,d)=(2,3)$.

The insensitivity to $\bar{u}/\lambda$ introduces considerable uncertainty into our estimates of q_c and ξ_0, but does not affect the conclusions that follow.

Table II gives s^2 for the possible choices of $(n,3)$. The error bars reflect the insensitivity of the fit to the ratio $\bar{u}/\lambda$. The best fit was obtained for $n=2$ for which the result is plotted together with the experimental data[12] in Fig. 3. Figure 4 shows the residuals for $n=2$, $d=3$. Clearly, the crossover model for $n=2$ provides a satisfactory fit to the data over the range $5\times10^{-3}\leq|\bar{t}|\leq0.15$. All data points are included in the calculated s^2; more than half the value in Table II is contributed by points in the rounding regime $|\bar{t}|<5\times10^{-3}$.

V. DISCUSSION

In the previous section, we showed that the choice (2,3) produces the best fit to the heat-capacity data. What can be said about the crossover between mean-field and critical behavior? The crossover behavior can be extracted most easily from Eq. (8) for $\bar{t}>0$, where $\psi=0$ and

$$\kappa/\Lambda=(\sqrt{\bar{t}}/\lambda)Y^{(1-1/2\nu)/\omega}\,. \qquad (11)$$

Following Ref. 9, we introduce a scale factor c_q to relate the dimensionless κ and Λ to the physical coherence length $\xi(T)=c_q/\kappa$ and cutoff wave vector $q_c=\Lambda/c_q$. In the mean-field limit $Y\to1$, then, we find $\xi(T)=(\lambda/q_c)t^{-1/2}$. Consequently, defining $\xi_0^{\rm mf}$ to be the amplitude of the coherence length in the mean-field regime, we find that $\xi_0^{\rm mf}q_c=\lambda\geq30$, from Table II. In other words, the coherence length is no less than five times the cutoff wavelength, which must be on the order of the lattice constant.

In the limit of asymptotic critical behavior, on the other hand, both κ and Y tend to zero, so that we can approximate $Y\simeq(\kappa/\bar{u}\Lambda)^{\omega}$ from Eq. (6). Substituting that result into Eq. (11) and rearranging terms, we obtain $\xi(T)=\xi_0^{\rm crit}\bar{t}^{-\nu}$, with $\xi_0^{\rm crit}=\xi_0^{\rm mf}(\bar{u}\lambda)^{2\nu-1}$. Because $\bar{u}\lambda\simeq1$ in our fit, the mean-field and critical values of ξ_0 are equal within experimental uncertainty. The magnitude of ξ_0 can best be determined in the mean-field limit. Setting $Y=1$ in Eq. (5), we can readily show the underlying heat-capacity step to be $\Delta C=3A_0\rho/u^*\bar{u}\lambda T_c\simeq39$ mJ/cm^3 K, a value close to that reported earlier[15] using a

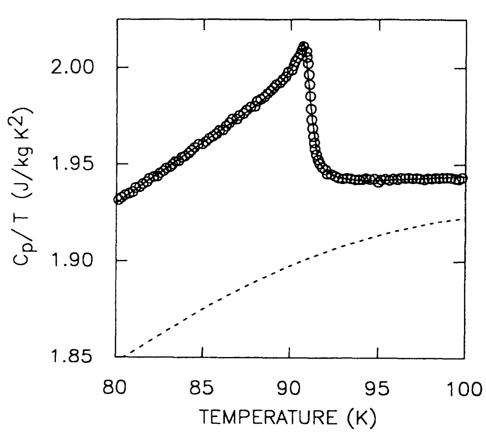

FIG. 3. Result of the cross-over analysis (solid line) plotted through the data points. The dashed line indicates the smooth, polynomial background. For clarity, only 25% of the data points used in the fit are shown.

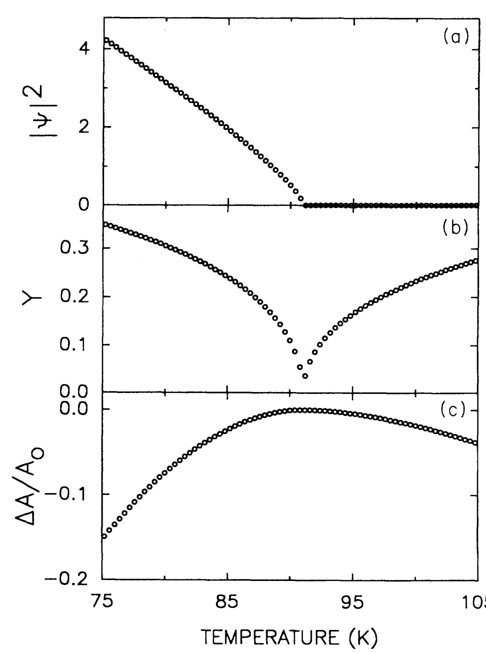

FIG. 5. Calculated behavior, for the $n=2$ fit, of (a) the gap function $|\psi|^2$, (b) the crossover function $Y(T)$, and (c) the critical part of the free energy $\Delta A(T)$.

logarithmic representation of the critical behavior. We assume that the mean-field coherence length corresponds to the BCS solution, and use[16]

$$\Delta C \xi_0 = (1.76 k_B / \pi) \hbar v_F g(E_F) \ . \quad (12)$$

For $v_F \simeq 2\times 10^7$ cm/s and $g(E_F)\simeq 3$ states/eV Cu,[17] we estimate that $\xi_0 \simeq 12$ Å and that the cutoff wave vector $q_c = \lambda/\xi_0^{\mathrm{mf}} \geq 2.5$ Å^{-1}, both reasonable values.

The CAS formalism matches both mean-field results and critical behavior in the limit $Y\rightarrow 1$ and $Y\rightarrow 0$, respectively. However, as seen in Fig. 5, Y does not approached either limit within the experimentally accessible range. Indeed, even as $\bar{t}\rightarrow 1$ ($T=2T_c$), Y only approaches the value 0.5. We somewhat arbitrarily take as our crossover criterion the value of $\bar{t}_x$ for which $Y(\bar{t}_x)=Y(1)/2=0.25$, which gives $\bar{t}_x \simeq 0.1$. The deviations from the Gaussian fit shown in Fig. 1 correspond to $\bar{t}=0.04$ and $Y=0.17$. Clearly, our initial assertion that the experimental data are entirely in the crossover region between mean-field and XY-like critical behavior is adequately supported by this analysis. Finally, we include in Fig. 5 the calculated variation in the order parameter and the critical part of the free energy. The change of curvature in ΔA near T_c is apparent on this scale, but not the vertical approach of $|\psi|^2$ toward zero.

The CAS approach to crossover phenomena provides the experimentalist with a useful tool for analyzing data when ξ_0 is mesoscopic. It is particularly valuable here, where the critical region has not yet been reached,[18] and yet the corrections to mean-field theory appear to be inadequate. Further, it supports our assertion[12] that the application of a magnetic field, which is known to enhance fluctuations, moves the experimentally accessible range fully into the critical regime. While the analysis presented here is involved, it has the distinct advantage of being asymptotically correct both near and far from T_c, giving us confidence that these data are in the crossover region, and that they belong to the $n=2$, $d=3$ universality class.

ACKNOWLEDGMENTS

We are grateful to Z.Y. Chen for several helpful communications. This work was supported in part by NSF Grant No. DMR-8920538 through the University of Illinois Materials Research Laboratory.

[1] D. R. Tilley and J. Tilley, *Superfluidity and Superconductivity* (Hilger, Bristol, 1986), p. 327; P. Pfeuty and G. Toulouse, *Introduction to the Renormalization Group and to Critical Phenomena* (Wiley, London, 1977), p. 32.

[2] V. L. Ginzburg, Fiz. Tverd. Tela. **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1960)].

[3] A. Junod, in *Physical Properties of High Temperature Superconductors II,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Chap. 2.

[4] R. J. Cava *et al.*, Phys. Rev. Lett. **58**, 1676 (1987); M. B. Salamon and J. Bardeen, Phys. Rev. Lett. **59**, 2615 (1987).

[5] S. E. Inderhees *et al.* Phys. Rev. Lett. **60**, 1178 (1988).

[6] T. A. Friedmann, J. P. Rice, J. Giapintzakis, and D. M. Ginsberg, Phys. Rev. B **39**, 4258 (1989).

[7] K. Kanoda *et al.*, J. Phys. Soc. Jpn. **57**, 1554 (1988).

[8] D. S. Fisher, M. P. A. Fisher, and D. A. Huse, Phys. Rev. B **43**, 130 (1991).

[9] Z. Y. Chen, P. C. Albright, and J. V. Sengers, Phys. Rev. A **41**, 3161 (1990).

[10] Z. Y. Chen, A. Abbaci, S. Tang, and J. V. Sengers, Phys. Rev. A **42**, 4470 (1990).

[11] Z. Y. Chen, Phys. Rev. B **41**, 9516 (1990).

[12] S. E. Inderhees *et al.*, Phys. Rev. Lett. **66**, 232 (1991).

[13] S-K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1976), p. 92.

[14] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), p. 162.

[15] S. E. Inderhees, M. B. Salamon, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B (to be published); S. E. Inderhees, Ph.D. thesis, University of Illinois, 1990.

[16] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), Chap. 2.

[17] B. Batlogg, Physica B **169**, 7 (1991).

[18] D. Wohlleben, E. Braun, W. Schnelle, J. Harnischmacher, S. Ruppel, and R. Dömel, in *Proceedings of the International Conference on Superconductivity,* edited by S. K. Joshi, C. N. R. Rao, and S. V. Subramanyam (World Scientific, Singapore, 1990), p. 194.