# Universality of the specific heat of $^3$He-$^4$He mixtures at the λ transition*

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We present an analysis of specific-heat data of $^3$He-$^4$He mixtures at the λ transition in which a trial function with a correction term to the leading singularity is used. For mixtures up to 0.39 mole fraction of $^3$He in $^4$He we find a universal leading exponent $\alpha = \alpha' = -0.022$ and a universal leading amplitude ratio of $A/A' = 1.088$. These results are in agreement with theoretical expectations and other experimental results along the λ line as a function of pressure. The data at pure $^4$He and saturated vapor pressure appear to show a small deviation from universal behavior.

## I. INTRODUCTION

The behavior of a system at a critical point can be characterized by the asymptotic power-law dependence in some of its thermodynamic functions. The exponents which appear in these functions seem to obey homogeneity or scaling relations.[1] In addition to these one expects that physical systems which differ in nonessential ways should have universal values for these exponents,[2] as well as for some dimensionless parameters, or amplitude ratios.[3] The nonessential variables in the case of static properties seem to be the ones which do not affect the dimensionality of the system or the degrees of freedom of the order parameter. In the case of the λ transition in liquid helium, one has an opportunity to test some of the aspects of the universality hypothesis, since the transition occurs across a two-dimensional surface in $P$-$T$-$x$ space, i.e., pressure, temperature, and $^3$He mole fraction. It is expected, according to this hypothesis, that critical behavior, along a suitable path across this surface, would yield the same critical parameters. Almost all critical measurements to date have been made in the plane $x=0$, i.e., at the λ line as function of pressure, or on the surface of saturated vapor pressure, $P \cong 0.05$ bar, at the λ line as function of mole fraction.

Tests of universality along the λ line in the pressure plane have been done with various thermodynamic data.[4] The data on specific heat in particular, show some disagreement with universality at pressure $P \geq 15$ bar.[5] The most recent and most direct test of universality for specific-heat-like behavior have been made on $\beta_p$, the isobaric thermal expansion, at pressures between 5 and 30 bar.[6] $\beta_p$ is a thermodynamic quantity which has the same singularity at the transition as the specific heat at constant pressure $C_p$, hence can be analyzed with the same functional form, i.e.,

$$C_p = (A/\alpha)t^{-\alpha}(1 + Dt^y) + B \qquad (1)$$

for $T > T_\lambda$, where $t = |1 - T/T_\lambda|$, and as usual a set of prime parameters are used for $T < T_\lambda$. The presence in Eq. (1) of the $D$ term, i.e., the correction to scaling term, is necessary to retain the scaling requirement $\alpha = \alpha'$. Without this term the data on helium would not agree with scaling.

In the case of the λ line at saturated vapor pressure in the mole-fraction plane, an analysis of the specific heat $C_{px}$ has recently been presented by Gasparini and Moldover[7] (GM). In their paper, a thermodynamic analysis is first performed to calculate $C_{p\phi}$ where $\phi \equiv \mu_3 - \mu_4$ is the difference in the chemical potentials. This specific heat, unlike $C_{px}$ which is subject to a path renormalization, is expected to have a universal behavior along the λ line. In the analysis of GM, a simpler function than Eq. (1) was used in which $D = 0$, and no constraints on the remaining parameters were imposed. Their results showed that $C_{p\phi}$ is very much like $C_p$ for pure $^4$He and saturated vapor pressure. In particular, the data have the same asymmetry with the branch for $T > T_\lambda$ tending to be more singular ($\alpha > \alpha'$) than the branch for $T < T_\lambda$. This asymmetry persists as function of concentration, although at the higher concentrations the results become particularly sensitive to the choice of thermodynamic derivatives which enter in the calculation of $C_{p\phi}$. In this paper we report the results of an analysis in which the data are fitted to Eq. (1) and more conclusive answers are obtained to the question of universality.

## II. ANALYSIS AND RESULTS

The primary data of GM are very nearly $C_{px}$. In their paper they discuss how the conjugate specific heat $C_{p\phi}$ is calculated, and how the distance in temperature from $T_\lambda$ is converted from a $t$, measured along a path of constant $x$, to a $\theta$, the distance along a path of constant $\phi$. In both these calculations one uses thermodynamic information in the form of derivatives along paths parallel to the λ line. The precision with which these derivatives

are known affects the results. In order to fully investigate this effect we have used in the present work a procedure in which both $C_{p\phi}$ and $\theta$ are recalculated starting with different values of the thermodynamic derivatives. This gives one an important check on the extent to which the results are sensitive to the analysis. GM had investigated the effect of the derivatives on $C_{p\phi}$, which is indeed the most important one, but not on the calculation of $\theta$.

When using Eq. (1) to fit $C_{p\phi}$ one is allowed a total of ten variational parameters. This does not include $T_\lambda$ which is determined with sufficiently high precision from the primary data $C_{px}$. It is in practice impossible to obtain meaningful results if all ten parameters are least-squares adjusted to achieve an optimum fit. We have followed thus a procedure adopted by Mueller *et al.*[6] in the analysis of the thermal expansion data, and have imposed some constraints on the parameters in Eq. (1):

$$\alpha = \alpha' , \tag{2}$$

$$B = B' , \tag{3}$$

$$y = y' = 0.5 . \tag{4}$$

The first constraint is, of course, the scaling requirement. One demands that scaling be obeyed and asks if the resulting $\alpha$'s are independent of $\phi$.[8] Equation (3) reflects the fact that the $\alpha$'s resulting from this analysis are negative, hence this constraint is the condition that the specific heat be continuous. In this way $\alpha$, even though negative, still represents the leading singularity.[9] The value for the exponent $y$ is that which results in the analysis of second sound data,[10] and is the value used in the analysis of $\beta_p$. Theoretical calculations of this exponent give values in the range of 0.3 to 1.0.[11] We have in some instances allowed $y$ to vary in our analysis. In the case of the pure $^4$He data, a value of 0.46 was obtained with a very marginal improvement in the goodness of the fit. One should emphasize that imposing the constraints of Eqs. (2)–(4) is always subject to *a posteriori* verification that the data allow such constraints, i.e., that it can be fitted to Eq. (1) with random scatter after the remaining parameters are least square adjusted. The important result from our analysis is to check the universality predictions that the ratio $A/A'$, and the exponent $\alpha = \alpha'$ be independent of $\phi$. The ratio $D/D'$, for the correction to scaling is also of interest, although it is not clear that this should be a universal quantity.[12]

Our fitting routine follows the Marquardt algorithm[13] with each datum point being weighted in the manner prescribed by GM. The fitting routine, as well as the error calculation, are different from those used by GM. In particular, no approximations are used in the calculation of the standard derivations, such as the expansion of the trial function in powers of $\ln t$ as was done by GM. We have checked that this new routine gives the same results as GM, when used for the same data and trial function. We have also fitted the specific-heat data of Ahlers[14] at saturated vapor pressure to various functions, and have obtained his results. The only differences seem to be that our calculation of the standard deviation for the variational parameters gives results about 10% higher than those of Ahlers. We do not feel that this amounts to a significant difference.

After imposing the constraints, Eqs. (2)–(4), a total of six parameters are varied in Eq. (1) to fit $C_{p\phi}$. These are $\alpha$, $A/A'$, $D/D'$, $A'$, $D'$ and $B$. The range of data used extends to $t \simeq 0.003$ at $x = 0$, and a somewhat wider range at the highest mole fractions. In terms of the distance $\theta$ this represents very nearly a constant $\theta$ of $\lesssim 0.003$. This range of data is narrow enough so that no higher order terms are needed in Eq. (1), and also the assumptions in the thermodynamic analysis to calculate $C_{p\phi}$ and $\theta$ remain valid.

The results of our computer fits at the various mole fractions are shown as deviation plots in Fig. 1. These results are typically not as good as in the case where $D = 0$ and one allows $\alpha$ and $\alpha'$ to take independent values. Some small systematic deviations can be seen in Fig. 1 which would not be present in the latter case. These small deviations occur when the constraint $\alpha = \alpha'$ is imposed, thereby the two branches of the specific heat cannot choose their own best exponent. On the other hand, the deviations are small, and they do not warrant abandoning the constraint $\alpha = \alpha'$.

In Fig. 2 we plot the results for the parameters which are expected to be universal, $\alpha$ and $A/A'$. The error bars represent plus or minus one standard deviation. It can be seen from this figure that $\alpha$ and $A/A'$ are independent of $\phi$, or as plotted in this figure, the temperature at which lines of constant $\phi$ cross the $\lambda$ line. One can reasonably take the average values of $\alpha = -0.022$ and $A/A' = 1.088$.[15] These are weighted averages for all the results shown in this figure. They should be compared with the corresponding quantities obtained from the thermal expansion analysis along the $\lambda$ line in the pressure plane: $\alpha = -0.026 \pm 0.004$ and $A/A' = 1.112 \pm 0.022$.[6] The agreement is rather good. The numerical results of our analysis are listed in Table I. We note from this table that the data do not determine the ratio $D/D'$ very well. Thus, we cannot draw any conclusions on the universality of this ratio, but point out that within the rather large error bars, the results are consis-

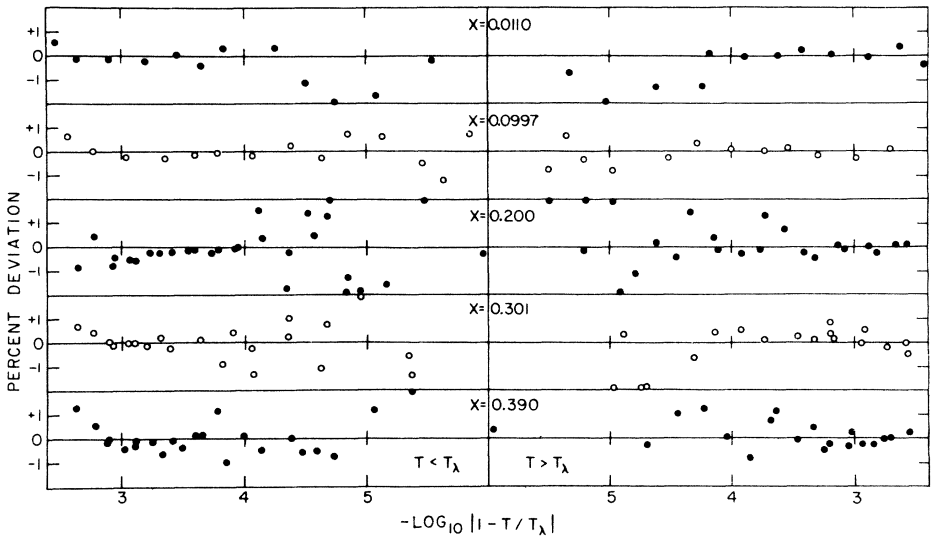


FIG. 1. Percent deviation of $C_{p\phi}$ from Eq. (1) when parameters are least-square adjusted, subject to the constraints of Eqs. (2)–(4).

tent with the value of $D/D' = 1.29 \pm 0.25$, as obtained in Ref. 6. We note that this value for $D/D'$ is obtained by doing a four-parameters fit after fixing $\alpha$ and $A/A'$ to the average values. We have not followed this procedure.

The small vertical bars next to some of the points in Fig. 2 represent the range of results obtained for those parameters when other choices of thermodynamic derivatives were made in the data analysis. Specifically, values in a range of 2% for $\partial x/\partial T|_\lambda$ and $\partial\phi/\partial T|_\lambda$, and 1 J/mole K$^2$ for $\partial s/\partial T|_\lambda$ were used. The combination of values within these bounds was chosen so as to have the maximum effect on the magnitude of $C_{p\phi}$. For instance at $x = 0.3$, $C_{p\phi}$ changes in this process by as much as 50%, the amplitudes $A$, $A'$ change by more than a factor of two, yet their ratio remains constant to within 1.5%. $\alpha$ itself varies in this process by 16%. This rather small sensitivity of the desired universal parameters in Eq. (1) to the thermodynamic derivatives is in marked contrast to the effect on $\alpha$ and $\alpha'$ when the constraint $\alpha = \alpha'$ is relaxed, e.g., see GM. We would also remark that while the results we report here use the $\lambda$ line derivatives tabulated by GM,[16] we have also used the values for these derivatives given by Ahlers.[4] These are identical to ours at low mole fraction, where they are matched to the values of GM, but differ somewhat at higher mole fractions. Again the results are insignificantly different from those of Fig. 2.

We can compare our experimental results for $\alpha$ and $A/A'$ with the theoretical results of the $\epsilon$-expansion calculation.[17] For a three dimensional system with two degrees of freedom in the order parameter, one obtains $\alpha = -0.02$ and $A/A' = 1.03$.[18] The agreement for $\alpha$ seems excellent. This could however be somewhat fortuitous, and one must keep in mind that this small exponent results from a subtraction of two large numbers in a nonconvergent series calculated to order $\epsilon^2$. The agreement with the amplitude ratio is reasonable, especially if one keeps in mind that the difference between experiment and theory is certainly substantially less than the difference in $A/A'$ for different universality classes.

Figure 2 represents a very nice support for universality. We also note that if the value of the parameters at $x = 0$ are omitted, and the remaining results averaged, one obtains $\alpha = -0.025$ and $A/A' = 1.096$ which are in even better agreement with the values from $\beta_p$ which also *do not* include data at $x = 0$, $P = 0.05$ bar. Looking at the results in this way the point at $x = 0$, $P = 0.05$ bar seems somewhat off from these average values. This is also true for the specific-heat data of Ahlers at this point.[14] We have fitted this data to Eq. (1), and obtained $\alpha = \alpha' = -0.016\,3 \pm 0.0017$ and $A/A'$

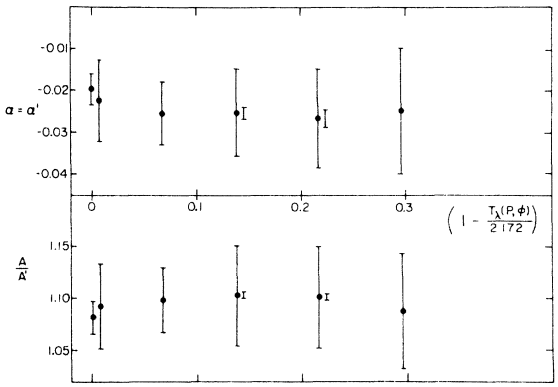


FIG. 2. Leading singularity exponent and amplitude ratio for $C_{p\phi}$ as function of $T_\lambda(P, \phi)$.

TABLE I. Parameters obtained in fitting $C_{p\Phi}$ to Eq. (1) subject to the constraints of Eqs. (2)–(4). All errors are one standard deviation.

| $x_\lambda$ | $\alpha$ | $A/A'$ | $D/D'$ |
|---|---|---|---|
| 0.0000 | −0.019 76 ± 0.0037 | 1.081 ± 0.016 | 6.8 ± 7.1 |
| 0.0000[a] | −0.016 26 ± 0.0017 | 1.068 ± 0.0073 | $2.6\times10^{8}\pm2.1\times10^{7}$ |
| 0.0110 | −0.022 42 ± 0.0095 | 1.092 ± 0.041 | 4.2 ± 7.3 |
| 0.0997 | −0.025 31 ± 0.0075 | 1.098 ± 0.031 | 1.9 ± 0.5 |
| 0.200 | −0.025 36 ± 0.011 | 1.102 ± 0.048 | −1.9 ± 2.1 |
| 0.301 | −0.026 74 ± 0.012 | 1.100 ± 0.049 | −3.5 ± 11 |
| 0.390 | −0.0250 ± 0.015 | 1.087 ± 0.055 | +1.9 ± 5 |
| $x_\lambda$ | $\alpha B$ | $A'$ | $D'$ |
| 0.0000 | −6.376 ± 0.190 | 6.161 ± 0.16 | −0.0121 ± 0.012 |
| 0.0000[a] | −6.115 ± 0.092 | 5.922 ± 0.076 | $2.1\times10^{-10}\pm2.4\times10^{-6}$ |
| 0.0110 | −6.757 ± 0.51 | 6.480 ± 0.43 | −0.0189 ± 0.032 |
| 0.0977 | −9.557 ± 0.61 | 9.206 ± 0.56 | −0.115 ± 0.047 |
| 0.200 | −9.527 ± 0.89 | 9.077 ± 0.76 | −0.0743 ± 0.077 |
| 0.301 | −9.124 ± 0.94 | 8.763 ± 0.87 | +0.0300 ± 0.083 |
| 0.390 | −6.323 ± 0.84 | 6.006 ± 0.72 | −0.0270 ± 0.064 |

[a]Data of G. Ahlers, Phys. Rev. A 3, 696 (1971).

= 1.068 ± 0.007 3.

We have attempted to check just how serious these deviations are by fitting all of the data at $x = 0$, $P = 0.05$ to Eq. (1), but with the additional constraints of $\alpha = \alpha' = -0.026$, $A/A' = 1.11$, and $D/D' = 1.11$. These seem to be representative values for these parameters along both λ lines away from this point. The only parameters varied in this case were $A'$, $D'$, and $B$.[19] In the lower part of Fig. 3 we show the deviation plot when these are least-square adjusted for a best fit. In this figure, we also show for comparison the results when the data is treated as discussed earlier for the mixtures. It is clear that the fit with the above constraints is not satisfactory, and most importantly that both independent sets of data give the

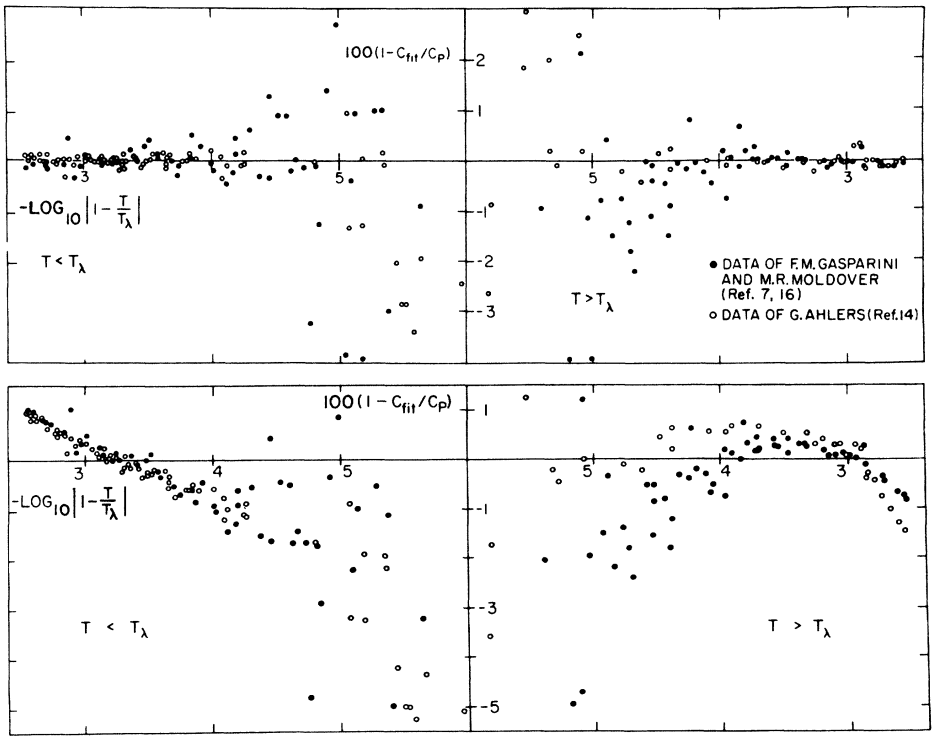


FIG. 3. Upper part: percent deviation of $C_p(x = 0, P = 0.05$ bar) when analyzed as data in Fig. 1. Lower part: percent deviation when the additional constraints $\alpha = \alpha' = 0.026$, $A/A' = 1.11$, and $D/D' = 1.11$ are imposed, and only $A'$, $D'$, and $B$ are least-square adjusted.

same systematic deviations. We have attempted to retain the average values of the universal parameters by adding another term to Eq. (1), a term linear in $T$. This helps to improve the fit far away from $T_\lambda$, but not in a very satisfactory way. This additional term also retains the deviations in the region close to $T_\lambda$. Of the various other attempts at fitting this data, relaxing the constraint $D/D' = 1.11$ and allowing it to be a free parameter while retaining $\alpha$ and $A/A'$ at their average, and presumably universal values, is the most effective way of obtaining a reasonable fit.

This procedure of testing a particular set of data against the average parameters would normally not really be a significant step. It is hardly necessary to point out that none of the data which enters in the average need give the average values themselves. All data should show deviations — although random — when tested against a function whose parameters are constrained to be the average ones. The situation here is somewhat different however, since data from two independent investigators is used, and all the data seem to deviate in the same systematic way. It seems unlikely that this would be a coincidence, on the other hand we do not know what significance to attach to it. This point on the phase diagram does not have, as far as phase transitions are concerned, any particular significance in comparison to any of the other points on the λ lines.

## III. SYNOPSIS

The data on the specific heat of helium along the λ line in the mole fraction plane is found consistent with scaling when a functional form with a higher order singularity is used. The resulting values of $\alpha$ and $A/A'$ are found to be universal along the λ line and in reasonable agreement with the results of the $\epsilon$-expansion calculation. In particular, however, values of $\alpha$ and $A/A'$ at $x = 0$, $P \cong 0.05$ seem to deviate slightly from the best values found by averaging the data away from this point. Both the data of Gasparini and Moldover, and of Ahlers show the same systematic deviations.

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[1]See, for instance, B. Widom, J. Chem. Phys. 43, 3898 (1965); and L. P. Kadanoff, Physics (N.Y.) 2, 263 (1966).

[2]A universal value for the exponent $\alpha$ of the specific heat was explicitly assumed by J. A. Lipa and M. J. Buckingham [Phys. Lett. A 26, 643 (1968)] and by M. E. Fisher [Phys. Rev. 176, 257 (1968)] in their discussion of path renormalization along a line of critical points. A more general discussion of the universality for the exponents has been given by R. B. Griffiths, Phys. Rev. Lett. 24, 1479 (1970). For a series-expansion calculation on the anisotropic Heisenberg model and the resulting universal exponents see D. Jasnow and M. Wortis, Phys. Rev. 176, 739 (1968). For a more recent discussion, see L. P. Kadanoff, in *Proceedings of the International School of Physics, "Enrico Fermi," Course LI*, edited by M. S. Green (Academic, New York, 1973).

[3]The first calculation of amplitude ratio was done by B. Widom, Ref. 1 in which he showed that $A/A' = 1$ for the case $\alpha = 0$. For universality of certain other dimensionless ratios see D. Stauffer, M. Ferer, and Michael Wortis, Phys. Rev. Lett. 29, 345 (1972). For the results of calculations of universal amplitude ratios for leading singularities by using the $\epsilon$ expansion see E. Brezin, J-C. LeGuillau, and J. Zinn-Justin, Phys. Lett. A 47, 285 (1974).

[4]For a recent review, see G. Ahlers, in *Physics of Liquid and Solid Helium*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1976).

[5]G. Ahlers, Phys. Rev. A 8, 530 (1973).

[6]K. H. Mueller, F. Pobell, and G. Ahlers, Phys. Rev. Lett. 34, 513 (1975); K. H. Mueller, G. Ahlers, and F. Pobell, Phys. Rev. B 14, 2096 (1976).

[7]F. M. Gasparini and M. R. Moldover, Phys. Rev. B 12, 93 (1975).

[8]Note that the pressure is slightly different for each set of data we analyze. These differences, a few Torr, are not significant and one can consider all the data at $P \cong 0$ bar.

[9]For a discussion of this point see M. Barmatz, P. C. Hohenberg, and A. Kornblit, Phys. Rev. B 12, 1947 (1975).

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[11]F. J. Wagner, Phys. Rev. B 5, 4529 (1972); E. Brezin, J. C. LeGuillau, and J. Zinn-Justin, Phys. Rev. D 8, 2418 (1973); J. Swift and M. R. Grover, Phys. Rev. A 9, 2579 (1974).

[12]D. S. Ritchie and D. D. Betts, Phys. Rev. B 11, 2559 (1975); D. D. Betts, *ibid.* 15, 2837 (1977).

[13]D. W. Marquardt, J. Soc. Ind. Appl. Math. 11, 431 (1963). See also discussion in *Data Reduction and Error Analysis for the Physics Sciences*, edited by P. R. Bevington (McGraw-Hill, New York, 1969).

[14]G. Ahlers, Phys. Rev. A 3, 696 (1971).

[15]It is not very meaningful in our case to assign error bars to these quantities in the usual way, since the deviation of the points from the average is much smaller than the individual error bars. This would result in unrealistically small standard deviations for the averages of $\alpha$ and $A/A'$. Reasonable errors for these results might be ±0.004 and ±0.02, respectively.

[16]For the calculation of these derivatives, see F. M. Gasparini, Ph.D. thesis (University of Minnesota, 1970) (unpublished).

[17]$\alpha$ is calculated by using the scaling relation $\alpha = 2 - 2\beta$

$-\gamma$, with $\gamma$ from K. G. Wilson, Phys. Rev. Lett. 28, 548 (1972), and $\beta$ from E. Brezin, D. J. Wallace, and K. G. Wilson, *ibid.* 29, 591 (1972).

[18]To obtain this value for $A/A'$ we have used expression 3.1′ in M. Barmatz *et al.* (Ref. 9). If one uses the expression as given by Brezin *et al.* in (Ref. 17) with $\alpha = 0.02$ one obtains $A/A' = 1.013$.

[19]Note that while both the data of Gasparini and Moldover, and of Ahlers were subject to the same constraints, the variational parameters were allowed to differ. It is expected that $A'$, $D'$ and $B$ be different since their magnitudes represent various possible errors in determining the absolute magnitude of the specific heat. We find that the two sets of data differ typically by about 0.3% in absolute magnitude.