Specific heat of normal and superfluid ³He on the melting curve*

W. P. Halperin,[†] C. N. Archie, F. B. Rasmussen,[‡] T. A. Alvesalo, and R. C. Richardson

Laboratory of Atomic and Solid State Physics, and Materials Science Center, Cornell University, Ithaca, New York 14853 (Received 14 July 1975)

A method has been developed for determining the specific heat of liquid ³He on the melting curve as a function of temperature and magnetic field. This approach depends on the accurate measurement of pressure and volume responses to heat pulses applied to the 3 He in a Pomeranchuk cell. Analysis of a number of different experiments at a particular melting pressure yields both the specific heat of the liquid and its temperature. The thermodynamic determination of the temperature has been separately discussed in another publication. Measurements were performed between 1.1 and 23 mK in magnetic fields up to 8.8 kOe. From the normal-fluid specific-heat data the low-temperature value of the effective mass at the melting curve was found to be $m^*/m = 5.5 \pm 0.2$. This is substantially smaller than that reported by Wheatley. Specific-heat discontinuities at the A, A_1 , A_2 , and B superfluid transitions have been measured. These give values for certain combinations of the coefficients of the fourth-order invariants in a Ginzburg-Landau expansion. Comparison was made with the predictions of spin-fluctuation theories. It was found that these alone cannot account for the behavior of ³He at melting pressures. The entropy difference between the A and B phases was calculated from the specific-heat data and compared with that calculated from (i) measurement of the latent heat at the $B \rightarrow A$ transition, and (ii) measurement of the suppression of the B transition by magnetic field, B phase susceptibility data, and a magnetic Clausius-Clapeyron equation. The different methods give a consistent picture in which the thermal differences between A and B phases are quite small. The A-phase specific heat at $T/T_c \sim 0.5$ appears to have a weaker dependence on temperature than that expected for the limiting lowtemperature behavior of the Anderson-Brinkman-Morel state.

I. INTRODUCTION

The superfluid transition in liquid ³He was first observed¹ through the effect of its specificheat discontinuity on the cooling rate of ³He in a Pomeranchuk cell. Although it was not understood at the time, this effect was later correctly identified by Vvendenskii.² Measurement of the specific heat by Webb $et al.^3$ at a number of liquid densities showed that this transition was of second order with a specific-heat jump. In particular, at the pressure 33.4 bar they observed a discontinuity in the specific heat 1.8 times that of the normal Fermi liquid. Qualitative agreement on the melting curve was found by Anufriev et al.⁴ This suggested an analogy with superconducting transitions giving support to the idea that the liquid-³He ordered phases might be of the BCS type. In the weak-coupling theory of BCS the specific-heat jump of an isotropic superfluid is expected to be $\Delta c/c_n = 1.43$; anisotropy in the energy gap function would reduce this value. Larger specific-heat jumps, as observed for example in Nb and Hg, have been attributed to strong-coupling effects, a jargon that has been carried over to the case of liquid ³He. Dundon et al.⁵ used nuclear demagnetization refrigeration to measure the ³He specific heat at lower temperatures than had been previously reported; however, they found structure and hysteresis in their work which has not yet been explained.

In this article we report measurements of the

specific heat of liquid ³He as a function of temperature in various magnetic fields. These were performed at melting curve densities in the four known fluid phases: the normal Fermi liquid (NFL); and the A_1 , A, and B superfluids. Magnetic fields up to 8.8 kOe were used to: (i) produce the field splitting of the A transition into two separate transitions A_1 and A_2 , and (ii) suppress the onset of the B phase and thus extend the temperature range available for measurements in the A phase. T_{A_1} and T_{A_2} ($T_{A_1} > T_{A_2}$) are the temperatures of phase transitions to different equal spin pairing states with the paired spins aligned along and opposed to the applied magnetic field. The splitting $T_{A_1} - T_{A_2}$ has been measured⁶ to be 6.4*H* μ KkOe⁻¹, which in 8.8 kOe gave a 56- μ K region in which A₁-phase specific-heat measurements were obtained. The liquid specific heats were determined with pulse techniques which are unique to measurements performed along the melting curve. In this work we have found a new value of the ³He effective mass at melting pressures and determined five specific-heat discontinuities which fix various combinations of the coefficients of the fourthorder invariants in a general Ginzburg-Landau expansion. These coefficients are a quantitative measure of the strong-coupling effects in ³He.

II. EXPERIMENTAL METHOD

The experimental arrangement was essentially that of our previously reported work⁷ in which a

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thermodynamic method was employed to establish the ³He melting curve P-T relation. A compression cell of adjustable volume, nominally 4.3 cm³, was used to produce ³He temperatures down to 1.1 mK. The pressure and volume of the ³He could be independently measured with 0.01 and 1% accuracies, respectively. Calibrated heat pulses delivered to the ³He through a copper heater wire were known to an accuracy of 0.3%. In this work we have added a superconducting solenoid capable of producing 10 kOe with a homogeneity of 10⁻³ across the cell. Consequently, the measured variables in our experimental cell are heat, volume, pressure, and magnetic field.

Let us briefly discuss the compression cell methods by which the liquid specific heat may be determined in any fixed magnetic field. Consider the effect of adding an amount of heat ΔQ to an equilibrium mixture of liquid and solid ³He selfcooled by adiabatic compression to a pressure *P* and temperature *T*. Following a heat pulse the response in pressure ΔP , temperature ΔT , volume ΔV , and the change in moles of liquid by conversion to/from solid, Δn_i , are related by

$$\Delta Q = \Delta T (n_1 c_1 + n_s c_s) + \Delta n_1 (s_1 - s_s) T, \qquad (1)$$

$$\Delta V = \Delta n_1 \left(v_1 - v_s \right) - \Delta P \left(k_1 V_1 + k_s V_s \right). \tag{2}$$

These equations provide the basis for description of all our thermal experiments on the ³He melting curve. The quantities s, v, n, k, and V are molar entropy, molar volume, number of moles, compressibility, and volume, of liquid or solid as indicated by the subscripts l and s. At 20 mK in zero field, we found from measurement of volume and pressure that $v_1 - v_s = 1.314 \pm 0.013$ cm³ mole⁻¹ and $k_s \simeq k_l = a - bP$, where $a = 9.17 \times 10^{-3}$ bar⁻¹ and $b = 1.27 \times 10^{-4}$ bar⁻² with an accuracy of 1.5%. Since the compressibilities are independent of temperature, the molar volume difference between the liquid and solid phases remains essentially constant below 20 mK: between 20 and 1.1 mK the melting pressure changes by 0.731 bar from which we calculate, neglecting expansion coefficients, that the molar volume difference changes by less than 0.4% in this interval. The molar amounts of liquid and solid are determined (to an accuracy of 1.5%) from the absolute volume measurements, where the molar volume of the liquid at 20 mK is taken⁸ to be 25.621 cm³ mole⁻¹.

In separating the thermal properties of the liquid component in the cell from the solid fraction and the container itself, we took advantage of the fortuitous distribution of time constants in this system. After a heat pulse ΔQ , the response ΔT , as indicated by the pressure change ΔP , shows two distinct characteristic relaxation times

differing by a factor of 30 at 20 mK and more than 3000 at 2 mK. The shorter time (~1 sec) was identified with the liquid component n_1c_1 in Eq. (1) and corresponds to equilibrium establishing within the liquid and at the liquid-solid interface. The longer time corresponds to thermal equilibration in the solid. The time constant of the container appeared to be of the order of $\frac{1}{2}$ h. These observations are discussed in detail elsewhere.9,10 We determined the liquid heat capacity in the pulse method by inserting into Eqs. (1) and (2) measured initial responses in pressure and volume, ΔP and ΔV ; then in solving for c_1 we could omit the term $\Delta T n_s c_s$ in Eq. (1). Using the Clausius-Clapeyron equation for the melting curve slope, $(dP/dT)_{MC} = (s_s - s_l)/(v_s - v_l)$, this result can be expressed

$$c_{l} = n_{l}^{-1} \left(\frac{dP}{dT} \right)_{MC} \left[\frac{\Delta Q}{\Delta P} - T \left(\frac{dP}{dT} \right)_{MC} \left(k_{l} V_{l} + k_{s} V_{s} + \frac{\Delta V}{\Delta P} \right) \right].$$
(3)

This analysis effectively assumes that all of the heat in the pulse goes first to the liquid, where pressure and temperature equilibrium establishes rapidly, and then subsequently leaks into the solid. The melting curve slope $(dP/dT)_{\rm MC}$ and the temperature *T* at each melting pressure and field



FIG. 1. Schematic shows the main features of the experimental arrangement used to take liquid specific-heat data and/or regulate the ³He pressure. Two ac capacitance bridges (reference signals are not shown) determine pressure and volume of the ³He through the measured displacement of two flexible diaphragms. The liquid ⁴He in the lower 5 cm³ volume shown at cryogenic temperatures was pressurized by heating of a resistance wire inside this volume. This method of ⁴He pressurization was used to control the ³He pressure at a preset value of the ³He pressure gauge. The error signal from the gauge, combined with an appropriate dc bias was amplified and then applied to the ⁴He heater.

were obtained from measurements of the latent heat of solidification of ³He, following the method developed by Halperin *et al.*¹¹

We also obtained the liquid heat capacity using another technique that is closely related to the latent heat measurements. In this approach, use is made of a device that regulates to a constant value the ³He pressure, and hence the temperature. A schematic of the experimental arrangement is shown in Fig. 1. When the ³He pressure was abruptly shifted from one regulated value to another by an amount ΔP , a volume change ΔV was measured that is related to the liquid specific heat by setting $\Delta Q = 0$ in Eq. (3) above:

$$c_{l} = -n_{l}^{-1}T\left(\frac{dP}{dT}\right)_{\rm MC}^{2}\left(k_{l}V_{l} + k_{s}V_{s} + \frac{\Delta V}{\Delta P}\right).$$
(4)

This method employs pulses of heat or cool from pulsed melting or solidification of ³He, and can be contrasted with that of Eq. (3) where electrically generated heat pulses are used. These techniques produced specific-heat results in excellent agreement and of equivalent precision over the entire range of measurement between 23 and 1.1 mK. Their accuracy of 4% is determined by the combined accuracies in the measurement of heat (0.3%), volume (1.5%), and pressure (0.01%). The results were independent of effects from solid ³He other than a decrease in precision for solid fractions greater than ~30%. In Fig. 2 we show



FIG. 2. Chart recorder tracings of volume and pressure gauge outputs are shown during measurement of the liquid specific heat by heat pulse and pulsed compression techniques.

representative chart tracings of the outputs of the pressure and volume gauges during a heat pulse and during a compression pulse experiment. In the latter the ³He pressure was not regulated in order to more clearly display the relative changes in volume and pressure. This data was taken at 6 mK in the normal Fermi liquid. At lower temperatures, in the superfluid phases, the amount of heat ΔQ was adjusted between 1 and 10 ergs such that temperature and pressure excursions, ΔT and ΔP , were of order 20 μ K and 0.8 mbar, respectively.

In each magnetic field the pressure, volume, and heater resistance calibrations were repeated revealing that the only field-dependent effect was that of the magnetoresistance in the copper heater wire.

III. RESULTS AND DISCUSSION

A. Normal Fermi liquid

The results in the normal Fermi liquid, 2.75 < T < 23 mK, indicate that at melting pressure the specific heat is essentially linear in temperature. We found that the empirical relation $c_1/R = aT - bT^2$ fits the data best where a = 4.33K⁻¹, b = 11.0 K⁻², and R is the gas constant. Consequently, at 34.34 bar we deduced the effective mass in the liquid, $m^*/m = 5.5 \pm 0.2$, and the corresponding Fermi liquid parameter, $F_1^s = 13.5 \pm 0.7$. This is in substantial disagreement with the 10% higher values reported by Wheatley¹² who used an extrapolation to low temperatures



FIG. 3. Normal Fermi liquid specific heat c_l divided by the gas constant R and the temperature T is shown after adjustment to the constant pressure 27.36 bar. The results of the current work are the open circles. As described in the text when allowance is made for the differences between the CMN magnetic temperature scale and ours the data of Anderson *et al.* (1963), and the data of Abel *et al.* (1966) can be compared with that of this work and are shown as solid and open triangles, respectively.

of specific-heat data of Abel et al.¹³ Although the latter work is reported in the form $\Delta Q / \Delta T^*_{CMN}$, where T_{CMN}^* is the magnetic temperature of cerium magnesium nitrate, a comparison with our own work can be made if we assume a relation between T^*_{CMN} and the melting curve temperature scale: $T_{CMN}^* = T - a - b/T$. Measurement of the melting curve, $P - P_A$ vs T_{CMN}^* by Johnson et al.¹⁴ combined with the melting curve temperature scale $P - P_A$ vs T, yields $b = 1.46 \text{ mK}^2$. This quantity can be presumed to be the same for each salt thermometer according to Wheatley.¹² On the other hand a must be estimated, and can be taken to be $a \simeq 0.2$ mK as suggested by Abel *et al.*¹³ With the above prescription, the specific-heat results of Abel $et \ al.$ ¹³ are recalculated and plotted as open triangles in Fig. 3. Our data is given by the open circles when adjusted to the constant pressure 27.36 bar using the relation

$$\left(\frac{\partial c_1}{\partial P}\right)_T = v_1 T \left[-\alpha^2 - \left(\frac{\partial \alpha}{\partial T}\right)_P\right].$$

The expansion coefficient α is given by Anderson $et \ al.^{15}$ to be $\alpha = -0.12 \ TK^{-2}$. The earlier hightemperature work of Anderson $et \ al.,^{15}$ similarily adjusted to the pressure 27.36 bar, is shown by the solid triangles. Even after allowance for differences between T^*_{CMN} and T scales there appears to be a 7% discrepancy between the measurements of Abel $et \ al.^{13}$ and ours. This could be accounted for in the thermometry comparison should a have the unlikely value of 1 mK. We note that the $T-T^*_{CMN}$ relation that we have used does not alter the conclusion of Anderson $et \ al.^{16}$ that the specific heat of dilute mixtures of ³He in ⁴He



FIG. 4. Specific-heat data in the superfluid phases obtained in zero magnetic field is plotted vs the reduced temperature, where the *B* transition occurs at T/T_c = 0.791.

is proportional to the temperature and that the diffusion coefficient is proportional to T^{-2} .

B. Superfluid phases

Specific-heat data obtained in zero magnetic field in the A and B phases was obtained with the heat-pulse method and Eq. (3). These are shown in Fig. 4. The jump in specific heat at the Atransition was first quantitatively interpreted by Vvedenskii² using pressurization data of Osheroff et al.¹ and was later measured in a liquid ³He-CMN mixture by Webb et al.³ We have found in four different experiments the specific-heat jump at the A transition, $\Delta c_A/c_{NFL} = 1.98$, 2.02, 1.99, and 2.00; the solid fraction in the cell was 17, 23, 32, and 33% respectively. We have averaged these to obtain $\Delta c_{\rm A}/c_{\rm NFL}$ = 2.00 ± 0.08. This is in reasonable agreement with the results of Webb et al.³ when allowance is made for the different values they have used for $c_{\rm NFL}$ as discussed in Sec. III A.

The temperature of the transition, whose inherent width was less than 1 μ K, was obtained both from pressurization traces and analysis of pulses that produced temperature excursions which bridged the transition itself. The latter was deemed a more precise method by which the transition temperature could be identified with a resolution of 0.03%.

At the *B* transition a smaller jump in specific heat $(c_B - c_A)/c_A = 0.091$ was observed. This is clearly displayed in Fig. 5 in which the major temperature dependence is removed by plotting $c_1(T_c/T)^3 vs T/T_c$. The straight lines in this figure represent least-squares fits to the zero field data. The open circles are the *B*-phase measurements. The *A*-phase data points in zero field are equivalent to the solid circles obtained in 3 kOe.



FIG. 5. Specific-heat data in the superfluid phases is plotted following multiplication by $(T_c/T)^3$ in order to remove most of the temperature dependence. The various lines are described in the text. The solid circles are A-phase data taken in 3-kOe field. The open circles are B-phase measurements in zero magnetic field. The open squares are B-phase measurements in 3 kOe.

In a 3-kOe field, decompression and compression pulse data were interpreted via Eq. (4) and plotted in Fig. 5 as solid circles for the A phase and open squares for the B phase. Supercooling of the $A \rightarrow B$ transition permitted A -phase measurements to be performed to a temperature $T/T_c = 0.49$. The transition on warming in this field occurred at T/T_c = 0.59. Since the field dependence of specific heat is given by $\partial c_1 / \partial H = T \partial^2 M / \partial T^2$ we expect $\partial c_1 / \partial H = 0$ in the A and NFL phases where the magnetization is known to be "precisely" temperature independent.¹⁷ This is confirmed in the Aphase by the data shown in Fig. 5. Using the Bphase susceptibility data obtained at the melting curve by Corruccini and Osheroff¹⁸ and the relation above, we calculate that the B-phase specific heat should increase less than 1% as the field is increased to 3 kOe. This would not be observable in the present work. From Fig. 5 we conclude that the A and B phases have very similar thermal properties that are essentially field independent other than that of the $A \rightarrow B$ transition temperature itself. Paulson et al.¹⁹ have inferred a similar result in lower pressure ³He, using static magnetization measurements and the profound effect of small magnetic fields on the A - B phase diagram.

Some interesting results can be deduced from the specific-heat data keeping in mind the third law of thermodynamics which requires that the entropy of the various phases at T = 0, be zero. First we use the normal fluid measurements extrapolated to T = 0 to determine that the entropy of the normal liquid at T_c is 984 erg mole⁻¹ mK⁻¹. Since the A transition is of second order this therefore must be the entropy of the superfluid at T_c . Then, in any particular magnetic field the entropy of the superfluid can be separately evaluated from the specific-heat data in those phases and compared with the above result. This procedure depends on an extrapolation of the specific-heat data to absolute zero temperature. Consequently the entropy comparison can be viewed either, as an internal consistency check of the specific-heat measurements in normal and superfluid phases, or as an indication of the validity of the extrapolation which, in fact, gives information about the low-temperature specific heat in a temperature region not currently accessible. When this procedure was applied to the zero magnetic field data it was found that the entropy at T_c deduced from the superfluid specific heat was only 2.6% less than that of the normal liquid. The *B*-phase specific heat was extrapolated to T = 0by just extending the straight line in Fig. 5. The entropy in the superfluid at T_c was calculated from $\int_{0}^{T_{c}} c_{I} T^{-1} dT$ plus a small 0.7% contribution

from the latent heat at the $A \rightarrow B$ transition. The most generally accepted candidate for the microscopic state of the *B* phase, the Balian-Werthamer state,²⁰ should have a specific heat at low temperatures that decreases as $\exp - \Delta(\vec{k})/k_BT$, where $\Delta(\vec{k})$ is an isotropic energy gap. This behavior has not been observed in the available temperature range of our measurements and should it occur at lower temperatures would give an entropy at T_c that would tend to slightly increase the 2.6% difference that we calculated above.

In sufficiently large fields such that the *B* phase is not stable, this entropy calculation can be performed on specific-heat data obtained entirely in the A phase. (As mentioned previously the Aphase specific heat can be expected to be field independent.) Since the A phase is thought to be the Anderson-Brinkman-Morel state it is useful to bear in mind that the expected²¹ low-temperature specific heat of this state is proportional to T^3 . We have found that the superfluid specific heat at T_c is just three times that of the normal fluid. If the A phase were to have a pure T^3 specific heat with this same jump then it would have precisely the correct entropy at T_c . Our 3-kOe data of Fig. 5 show that there is a somewhat steeper temperature dependence than T^3 near T_c which therefore must be compensated for by a weaker dependence than T^3 at lower temperatures; in fact near $T/T_c = 0.5$ the A -phase data indicate this sort of behavior. This result is not that expected for the Anderson-Brinkman-Morel state where only single particle excitations were considered significant. Possible effects of collective excitations or "mixing in" of higher-order



FIG. 6. Specific-heat data taken in 8.8-kOe field are shown in the vicinity of T_c where measurements in the A_1 phase could be obtained, $(T_{A_2} < T < T_{A_1})$. The solid lines above A_1 and below A_2 in temperature are fits to zero field data in the normal and A phases, respectively.

TABLE I. Coefficients $\beta_1, \beta_2, ..., \beta_5$, of the fourth-order terms in a Ginzburg-Landau expansion are determined in certain combinations by measurements of the specific-heat discontinuities. The notation β_{ijk} is used for the sum $\beta_i + \beta_j + \beta_k$. The corresponding weak coupling prediction for these sums is given, as is the calculation of the spin-fluctuation parameter δ from the data.

| | Expt. | Gives β sum | eta sum equals | Weak-coupling prediction | ô |
|-----------------------------|----------------|-----------------------------|-------------------|-----------------------------|-----------------|
| $\Delta c_{A}/_{\rm NFL}$ | $2.00 \pm 4\%$ | β_{245} | 1.20 ± 0.05 | 2 | 0.76 ± 0.05 |
| $\Delta c_{A1}/c_{\rm NFL}$ | $0.74\pm4\%$ | β_{24} | 3.30 ± 0.13 | 4 | 2.00 ± 0.37 |
| $\Delta c_B/c_{\rm NFL}$ | $1.90 \pm 4\%$ | $3\beta_{12} + \beta_{345}$ | 3.75 ± 0.15 | 5 | 1.25 ± 0.15 |

partial waves in the order parameter have been discussed by Leggett.²²

Some success has been reported²³ in accounting for the specific heat of strong-coupling superconductors by phenomenologically scaling the BCS energy gap by a constant factor. When this factor is taken to be $(\Delta c_B / \Delta c_{BCS})^{1/2}$ the procedure yields the curved line in Fig. 5. In the case of ³He this approach does not appear to be very fruitful. $\Delta c_B (1.87 \times 10^3 \text{ erg mK}^{-1} \text{ mole}^{-1})$ is the difference at T_c between the normal liquid specific heat and that of the superfluid *B* phase extrapolated to T_c . The extrapolation was performed according to a thermodynamic procedure that is described later in this paper.

In a nonzero magnetic field the A-transition specific-heat jump Δc_A becomes two separate jumps Δc_{A_1} and Δc_{A_2} at the transition temperatures T_{A_1} and T_{A_2} . Defining $T_c = 2.75$ mK, which is the temperature of the zero field transition T_A , it can be shown using Ehrenfest equations that

$$(T_c - T_{A_2})/(T_c - T_{A_1}) = -T_{A_2} \Delta c_{A_1}/T_{A_1} \Delta c_{A_2}.$$
 (5)

In Fig. 6 we plot specific-heat points obtained in 8.8 kOe with heat pulses and Eq. (3). The solid lines below A_2 and above A_1 in temperature represent fits to the zero-field measurements in the A and NFL phases. The slope of the line drawn through the data in the A_1 phase is that of the weak-coupling BCS prediction. The specific-heat jumps at A_1 and A_2 are indicated in the figure by dashed vertical lines and are insensitive to that particular choice of slope. [The temperature interval corresponding to the A_1 phase was not large enough in our experiments to allow the temperature dependence of the specific heat in this phase to be determined. The choice of the weak coupling slope therefore is intended as an instructive comparison. Judging from the magnitude of the jump at T_{A_1} , $\Delta c_{A_1}/c_{\rm NFL}$ = 0.74, versus the weak-coupling value of 0.60, we expect that the actual slope is slightly steeper ($\sim 20\%$) than

that indicated in Fig. 6. This would not significantly affect the values we have taken for the specific-heat discontinuities at T_{A_1} and T_{A_2} .] We found in 8.8 kOe that $\Delta c_{A_1} = 741 \text{ erg mk}^{-1} \text{ mole}^{-1} \text{ and } \Delta c_{A_2} = 1.22 \times 10^3 \text{ erg mk}^{-1} \text{ mole}^{-1}$. The scale of the temperature axis in Fig. 6 was found by solving Eq. (5) for $T_{\rm A1}/T_{\rm c}$ and making use of the measurement $T_{\rm A1}-T_{\rm A2}$ $= (dP/dT)_{MC}^{-1}(P_{A_1} - P_{A_2}) = 56 \,\mu \text{K}.$ We find the result $T_{A_1}/T_c = 1.014 \pm 0.001$. Alternatively, although less accurately, we can determine absolute temperatures from the zero-field temperature scale⁷ assuming that the normal fluid specific heat is field independent. This gives $T_{A_1}/T_c = 1.029 \pm 0.02$. A similar procedure applied to the A-phase specific heat yields $T_{A_1}/T_c = 1.018 \pm 0.01$. We note that in magnetic fields where $\mu H \ll \epsilon_F$ (μ is the magnetic moment of the ³He atom and ϵ_F is the Fermi energy), the expression in Eq. (5) is field independent and is the ratio of the phase line slopes dT/dH separating NFL and A_1 phases on the one hand, and A_1 and A phases on the other. Our value for this quantity is -1.75 ± 0.07 as compared with that of Osheroff and Anderson⁶ who found -1.67 ± 0.05 .

Ginzburg-Landau theory for p-wave pairing²⁴ predicts the three discontinuities Δc_{A_1} at T_{A_1} , and Δc_A and Δc_B at T_c , in terms of different combinations of five coefficients of the fourth-order invariants. These are coefficients of the fourthorder terms in a series expansion of the free energy of the superfluid as a function of the order parameter. Although phenomenological in origin, once these parameters are specified they give a complete thermodynamic characterization of the liquid near T_c . Our results give the experimental values listed in Table I. The corresponding weak coupling BCS predictions are shown for comparison. The "naive" spin-fluctuation model,²⁵ which assumes that strong-coupling effects present in ³He can be described by a single adjustable parameter δ , also makes predictions for these discontinuities. Listed in the table are values of δ determined separately from each specific-heat



FIG. 7. Entropy differences between the A and B phases have been determined from specific-heat data, solid curve; latent-heat data, open squares; and the measurement of suppression of the B transition by magnetic field, dashed line.

jump. Clearly the simple model cannot account for the deviations from weak-coupling predictions. Although the *B*-phase specific heat is not available near T_c , the jump Δc_B can be found by smoothly extrapolating the line of *B*-phase specific heats to T_c , as indicated by the dashed curve in Fig. 5, but subject to the rather stringent condition that

$$T_B(s_A - s_B) = T_B \int_{T_c}^{T_B} (c_A - c_B) T^{-1} dT = l_{AB},$$

where l_{AB} is the latent heat measured in zero magnetic field at the *B* transition where $T/T_c = 0.791$.

- *Support for this work was obtained from the Research Corporation, the NSF through Grant No. DMR75-15933, and the Material Science Center of Cornell University; Grant No. GH 33637 MSC Report No. 2472.
- [†]Present address, Department of Physics, Northwestern University, Evanston, Ill. 60201.
- [‡]Present address, Physics Laboratory 1, H. C. Oersted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark.
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Using a previously reported method²⁶ we obtained $l_{AB} = 15.4 \pm 0.6$ erg mole⁻¹.

In Fig. 7 we show the entropy difference $s_A - s_B$ obtained in different ways. The curved line is deduced from the specific-heat measurements using the expression above. The open squares are found from latent heat measurements in 0- and 3-kOe fields. In addition $s_A - s_B$ can be calculated from the magnetic Clausius-Clapeyron equation

$$\left(\frac{dT}{dH}\right)_{AB} = - \frac{(\chi_A - \chi_B)H}{s_A - s_B}.$$

The phase line slope can be found from measurements of the suppression of the *B* transition on the melting curve,²⁷ and since $\chi_A = \chi_{NFL}$ then the susceptibility difference $\chi_A - \chi_B$ can be determined from the *B*-phase susceptibility measurements of Corruccini and Osheroff.¹⁸ These results for the entropy difference are plotted as the dashed curve in Fig. 7. The maximum in $s_A - s_B$ at low temperatures indicates that the *A*- and *B*phase specific heats cross near $T/T_c = 0.5$ consistent with our direct measurements.

ACKNOWLEDGMENTS

We gratefully acknowledge communications from R. B. Kummer and R. M. Mueller, and from D. D. Osheroff of their unpublished data. We thank D. M. Lee and J. D. Reppy for help and encouragement. Discussions with N. D. Mermin, V. Ambegaokar, D. Rainer, R. Combescot, H. Smith, and C. Gould have been greatly appreciated.

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