Properties of He³ at Pressures Greater than the Minimum in the Melting Curve*

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Measurements of the specific heat and velocity of sound in He³ as functions of pressure and temperature have been obtained for temperatures from 0.02 to 0.3°K and pressures greater than the minimum in the melting curve. These measurements indicate that only two phases, liquid and α solid, exist in this region of the phase diagram. The melting curve was measured to 0.03°K. The thermodynamic consistency of the data is discussed in terms of a two-phase model. The data are compared with predictions which assume the solid entropy to be $R \ln 2$, and qualitative agreement is obtained. Additional evidence from magnetic measurements is given in support of the two-phase description.

I. INTRODUCTION

IN our preliminary survey of the properties of He³ at low temperatures and at moderate pressures we measured, among other quantities, the specific heat,[1] the propagation of ultrasound,[2] and the magnetic susceptibility and diffusion coefficient[3] when the pressure on the He³ cell before magnetic cooling was greater than the minimum, P_{min}, in the melting curve. Under these conditions it is known that during cooling a plug forms in the filling line when the melting curve is reached. In these experiments, and evidently in others also,[4] the plug could slip on further cooling and lead to nonreproducibility in the final molar volume for a given initial pressure.

The specific heat results in this region of pressure were taken in such a small range of temperature that they served only to indicate the magnitude of the specific heat but not its temperature dependence. The specific heat was less than that of the liquid at pressures slightly less than P_{min}.

The results on the propagation of 15 Mc/sec ultrasound were as follows: For initial pressures somewhat higher than P_{min}, we observed at low temperatures velocities of the order of 400 to 410 m/sec characteristic of the liquid as if its properties were linearly extrapolated with the change of starting pressure. We were also able to observe the propagation of sound in the solid and found velocities averaging around 475 m/sec, without a strong pressure dependence. Above a certain region of initial pressure we found that below 0.1°K sound propagated with a velocity of between 500 and 510 m/sec, the attenuation being less at lower temperatures. In one case we were able to follow the development of a set of double-echoes, one characteristic of 475 m/sec and the other of 510 m/sec, and the size of the echoes

corresponding to the high-velocity component increased with decreasing temperature while the others decreased.

Shortly after the sound measurements we measured the nuclear susceptibility and self-diffusion coefficient in the same region. We found that the diffusion coefficient was too small to be measured by our apparatus and that the susceptibility increased rapidly with increasing starting pressure toward the Curie law value for the solid. These observations of low-diffusion coefficient and high susceptibility coupled with the sound measurements which indicated larger (stiffer) elastic constants than those usually observed for the solid led us to suggest that we might be dealing with a different type of solid, rather than liquid, in the region of temperatures less than about 0.1°K but in an unknown region of pressure.

All of the above experiments suffered from the experimental defect that because of the plug in the filling line we could not measure the pressure. Since coupled with this problem we had a problem of plug slippage which did not allow the final molar volumes to be reproduced, all of the previous results had only qualitative significance. In the work which is discussed in this paper the problem of pressure measurement was overcome by the use of strain gauges, and a higher accuracy of the temperature scale and of temperature differences was achieved than in the previous work. Propagation of sound, specific heat, and the magnetic properties have been systematically studied as functions of temperature and pressure for pressures greater than P_{min} and temperatures less than T_{min}.

The most important qualitative result of the new work is that we were never able to reproduce the high velocity (greater than 500 m/sec) sound propagation which had been readily reproduced in the first experiments. Since the supposition that we might be dealing with a new type of solid in this region was largely based on the observation of this high-velocity component, the basis for assuming the existence of a new type of solid disappeared with this experiment.

In the meantime, Fairbank[5] proposed that the susceptibility, sound, and specific heat results could equally well be interpreted in terms of a two-phase mixture of liquid and solid together with a plug-slippage phenome-

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[1] A. C. Anderson, G. L. Salinger, W. A. Steyert, and J. C. Wheatley, Phys. Rev. Letters **7**, 295 (1961).

[2] W. R. Abel, A. C. Anderson, and J. C. Wheatley, Phys. Rev. Letters **7**, 299 (1961).

[3] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. Letters **7**, 366 (1961).

[4] A. L. Thomson and H. Meyer, Bull. Am. Phys. Soc. **7**, 76 (1962); A. L. Thomson, H. Meyer, and E. D. Adams, Phys. Rev. **128**, 509 (1962).

[5] H. A. Fairbank, Phys. Rev. Letters **8**, 49 (1962).

non. Indeed, all the specific heat results described in this paper can be qualitatively explained on this two-phase picture assuming that the liquid behavior can be extrapolated from the known properties of the liquid at pressures just less than P_{min} using thermodynamics and reasonable assumptions regarding the expansion coefficient. It has not been possible to observe a self-diffusion coefficient for the liquid in this region characteristic of the values observed for pressures just less than P_{min}. Moreover, the wide discrepancy in liquid and solid relaxation times and susceptibilities makes observation of a liquid fraction difficult, but we have made observations which will be discussed here which indicate that in the region of the phase diagram where the susceptibility was increasing rapidly toward the Curie law value that we had a mixture containing two components with two different relaxation times, the longer presumably being the liquid.

The principal motive for postulating a different type of solid-like behavior in this region came from the initial sound propagation results. Although we do not have any certain explanation for the anomalous sound velocity results we obtained, this does not seem to impede a general interpretation of the thermodynamic properties of the He³ in this region in terms of reasonable and smoothly changing properties of solid and liquid. In particular, the liquid properties have been observed to change smoothly and continuously down to 0.021°K and 33.3 atm.

II. APPARATUS AND TECHNIQUE

A. Specific-Heat Measurements

The construction of the demagnetization cryostat and He³ sample cell have been described in a previous paper.[6] Only the strain gauges used to detect the pressure on the He³ sample will be elaborated upon here.

The positions of the strain gauges in the sample cell are shown in Fig. 1. Each gauge consisted of a coil of 87 cm of 0.0006-in.-diam Evanohm wire[7] molded into the wall of the cell. The active coil was embedded in the inner surface of the cell and centered on the cavity. A passive coil, used to compensate for changes in temperature, was located at the upper end of the cell and centered over the plug. Leads of 0.003-in.-diam Manganin wire were soldered to the Evanohm by dipping the joints into molten silver-solder covered with a molten layer of Handy[8] flux. The leads were connected to a three wire transmission line. The two active leads of the transmission line were glued together to form a bifilar pair to insure equal temperature, and thus resistance, changes in each lead.

The difference in resistance between the two strain gauges was measured to about 0.02Ω on a Rubicon Mueller bridge. The bridge was electrically and thermally shielded and operated at $33\frac{1}{3}$ cps. The output was
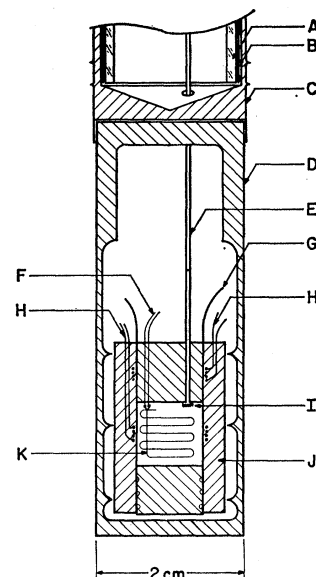

FIG. 1. Specific heat cell. A—Pyrex support tube, B—coil foil, C—nylon cylinder, D—nylon yoke of rectangular cross section (3 mm depth), E—1/64 in. 70-30 cupro-nickel filling tube, F—heater leads, G—pure copper cooling wires, H—leads to strain gauges, I—cotton filter plug, J—Epibond 100a, and K—cavity for powdered CMN and He³.

fed to a narrow band amplifier and a phase-sensitive detector.

The gauges were initially calibrated at temperatures greater than the melting temperature using a dead weight tester accurate to 0.1%. The temperature independence of the gauges was tested down to a temperature of 0.06°K at 416 psi. The calibration was checked following each run at pressures less than the minimum in the melting curve. Erratic measurements were noted when portions of the two active wires in the transmission line consisted of superconducting material, either niobium wire or lead-coated Manganin wire. No difficulties were experienced when the active wires were made entirely of Manganin.

B. Acoustic and Magnetic Measurements

The demagnetization cryostats used for the acoustic and magnetic measurements were those used in previous experiments,[2,9] but with the addition of strain gauges to measure the pressure on the He³ samples. In order to make use of the existing equipment, the gauges were located immediately above the chromium potassium alum refrigerator. Although in this case the gauges were separated from the He³ cell, measurements of the melting curve agree with those made with the specific heat apparatus in which the gauges were located in the He³ cell. Thus, it is believed that pressures measured by the remote gauges were representative of pressures in the He³ cell.

The construction of the gauges was similar to that used for the specific heat cell as described above. A

[6] A. C. Anderson, W. Reese, and J. C. Wheatley (to be published).

[7] Wilber B. Driver Company, 1875 McCarter Highway, Newark 4, New Jersey.

[8] Handy and Harman, Inc., 850 Third Avenue, New York 22, New York.

[9] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. 127, 671 (1962).

scale drawing is shown in Fig. 2. The copper cooling wires made direct thermal contact with the chromium potassium alum refrigerator. A pair of such gauges was used, with only the active gauge being coupled to the He³ capillary tube.

The velocity of sound was measured by a pulse technique using a single transducer operated at 15 Mc/sec.[2] The X-cut quartz transducer was backed with a roughened layer of Epibond 100a [10] in order to mechanically reduce the Q of the crystal. Pulses were generated by an Arenberg[11] PG-650-C oscillator and detected using an Arenberg PA-620 preamplifier and WA-600 amplifier. The rf signal was displayed on a Tektronix type 551 oscilloscope with type-L plug-in unit, utilizing the 5-X sweep magnifier of the 551. Time markers from a Tektronix time mark generator were superimposed on the signal, the two traces being photographed for purposes of analysis. Each picture was multiply exposed for five sweeps to increase the signal-to-noise ratio. The time separation of from five to twenty echoes was measured to determine the time of transit.

The electronics and technique used in the measurement of the magnetic properties of He³ have been described elsewhere.[9]

III. RESULTS

In this series of experiments we have measured the velocity of sound in the solid and liquid at pressures near the melting pressure, the solid-liquid phase boundary, and the heat capacity of one- and two-phase samples. When this information is combined with information about the specific heat, entropy, and expansion coefficient of liquid He³ found at lower pressures from a previous paper,[6] a rather complete qualitative picture of the thermodynamic properties of He³ along the melting curve emerges. Thermodynamic inconsistencies between the various sets of data make the picture less quantita-
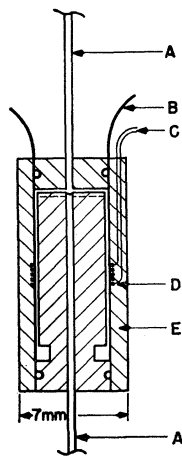

FIG. 2. Strain gauge. A—1/64-in. cupro-nickel tube, B—pure copper cooling wires, C—leads to strain sensing wire, D—strain sensing wire, E—Epibond 100a.

[10] Furane Plastics, Inc., 4516 Brazil Street, Los Angeles 39, California.
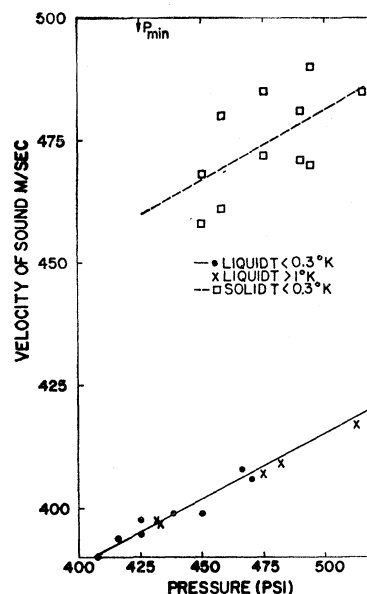[11] Arenberg Ultrasonic Laboratory, Inc., 94 Green Street, Jamaica Plain 30, Massachusetts.

FIG. 3. The velocity of longitudinal sound in liquid and solid He³ as functions of pressure. The liquid points for temperatures greater than 1°K are for comparison only. The lines are linear functions fit by least squares to the data and, in the case of the solid, are intended only as a guide to the eye.

tive than might be desired. In addition to the above data, information about the magnetic properties was obtained.

A. Sound Velocity

The results of measurements of the sound velocity are given in Fig. 3. No difference in behavior was noted between samples with a He⁴ to He³ ratio of 7×10^{-3} and those with a ratio of 5×10^{-5}. Although the accuracy to which the sound velocity could be measured was about 0.5%, considerably larger scatter (about 5%) is displayed by the measurements of the solid. A similar phenomenon has been noted in measurements at higher temperatures by Vignos and Fairbank[12] who attribute it to possible variations in the number and orientation of crystals in the sample. In the present case, in all of the runs where there was a difference in velocity between those observed while cooling and those observed while warming, the possibility of recrystallization at the low-temperature side of the melting curve existed, so this explanation might be applicable. Additionally, in our measurements the pressures were determined with a strain gauge external to the sound cell as described in Sec. II, so it is possible that the scatter could be due to differences in pressure which developed in the sound cell and were not detected by the strain gauges.

The region in which the velocity of sound in the solid was measured does not overlap the results of Vignos and Fairbank. However, our results seem to join smoothly with theirs. The liquid velocities join smoothly with those previously reported[2] for pressures below the minimum of the melting curve and also agree very well with measurements in the liquid at temperatures greater than the melting temperature.[2]

[12] J. Vignos and H. A. Fairbank, in Proceedings of the Eighth International Congress on Low Temperature Physics (to be published).

Considerable effort was devoted to the search to observe sound with an anomalously high velocity as reported in reference 2. Fairbank[5] has suggested that the anomalously high velocity could be explained by slippage of the He³ plug in the filling capillary during the cooling cycle, thus resulting in a higher pressure on the sample than expected. However, in the present experiment, measurements were made at higher pressures than it would have been possible to obtain from the initial conditions of reference 2 even with maximum slippage. These measurements did not reveal a velocity as high as the 500 m/sec velocity reported in reference 2.

Thus, it is necessary to consider alternative explanations. An explanation which seems plausible could be based on the assumption that the α phase of solid He³ is acoustically anisotropic. Support for this assumption can be drawn from the observed scatter in the solid velocities in the present experiment and in the experiment of Vignos and Fairbank.[12] Additionally, the compressibility of solid He³ as deduced from the present sound velocity measurements assuming isotropy and using the Cauchy relations is approximately 20% larger than the values deduced by Heltemes and Swenson[13] from thermodynamic measurements. If one accepts this explanation, one must relegate to chance the occurrence of conditions suitable for the observation of high-velocity sound previously and the non-occurrence of such conditions in the present experiment.
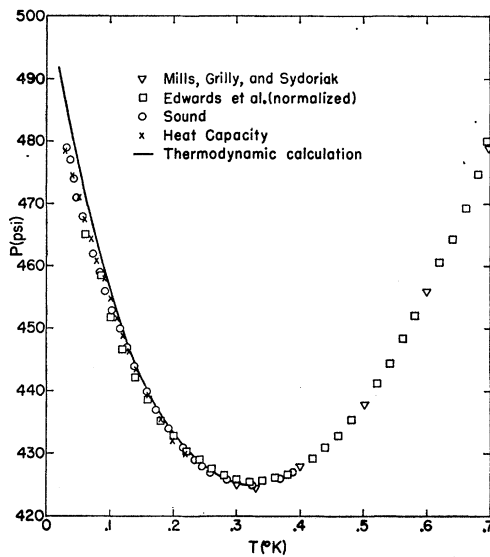

FIG. 4. The melting curve for pure He³. The points from the present experiment are the smoothed results of measurements made during the sound experiment and the heat capacity measurements. The points labeled Mills, Grilly and Sydoriak are from reference 15 while those labeled Edwards *et al.* are smoothed values taken from reference 16 and normalized as discussed in the text. The solid curve is the result of a thermodynamic calculation which assumes the solid entropy to be $R \ln 2$.

[13] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

B. Melting Curve

The smoothed results of the measurements of the melting curve are given in Fig. 4. The smoothed points represent a total of about 200 raw data points. The raw data from both the specific heat and the sound experiments had comparable accuracy, between ± 2 and ± 3 psi, and represented measurements from runs in which either sound velocity or heat capacity was also being measured so that one could have confidence that two phases were present. As can be seen, no maximum, such as that predicted by Bernardes and Primakoff,[14] is observed down to the lowest temperature of the measurements, about 0.03°K. This is consistent with a large entropy of the solid to very low temperatures as is discussed in Sec. IV.

The smoothed results were fit by least squares to the polynomial

$$P_{melt} = 425.0 + 485.8(0.3191 - T)^2$$
$$+ 546.5(0.3191 - T)^3 \text{ psi},$$
$$0.03°K \leq T \leq 0.40°K. \quad (1a)$$

The raw data fit this relation with a rms deviation of 2.9 psi. The shape of the curve near the minimum as well as the minimum pressure as determined in this experiment compare very favorably with the result given by Mills, Grilly, and Sydoriak.[15]

$$P_{melt} = 425.0 + 473.3(T - 0.330)^2 \text{ psi},$$
$$0.3 \leq T \leq 0.5°K. \quad (1b)$$

A comparison of all the determinations of the location of the minimum in the melting curve is given in Table I. All of the determinations agree with each other within

TABLE I. A summary of various determinations of the location of the minimum of the melting curve for pure He³.

Work	P_{min} (psi)	T_{min} (°K)	Method
Mills, Grilly, and Sydoriak[a]	425.0±0.3	0.330±0.005	Spring loading for $P > P_{min}$
Edwards, Baum, Brewer, Daunt, and McWilliams[b]	430.7±1.5	0.32	Strain gauge
Lee, Fairbank, and Walker[c]	427.8±1.5	0.32 ±0.01	Observation of density
Anderson, Salinger, Steyert, and Wheatley[d]	425.5±1.5	...	Melting of plug
Current work	425.5±1.0	0.319±0.005	Strain gauge and observation of compressional cooling

[a] See reference 15.
[b] See reference 16.
[c] See reference 17.
[d] See reference 1.

[14] N. Bernardes and H. Primakoff, Phys. Rev. **119**, 968 (1960).
[15] R. L. Mills, E. R. Grilly, and S. G. Sydoriak, Ann. Phys. (N. Y.) **12**, 41 (1961).

TABLE II. A summary of the thermodynamic properties of He^3 along the melting curve based on a self-consistent thermodynamic calculation which assumes the solid entropy to be $R\ln2$.

T (°K)	P_{melt} (psi)	V_l (cm³/mole)	β_l (10^{-4} psi^{-1})	α_l (10^{-3} °K^{-1})	ΔV_m (cm³/mole)	$-(dP/dT)_m$ (psi/°K)
0.32	425.00	25.990	3.84	−7.00	1.200	0
0.30	425.21	25.991	3.82	−7.30	1.200	20.61
0.28	425.84	25.988	3.82	−7.57	1.204	41.99
0.26	426.92	25.982	3.82	−7.79	1.209	64.75
0.24	428.47	25.971	3.81	−8.01	1.214	89.20
0.22	430.52	25.956	3.80	−8.18	1.222	115.4
0.20	433.12	25.934	3.79	−8.30	1.229	143.9
0.18	436.18	25.906	3.77	−8.38	1.233	175.3
0.16	440.19	25.875	3.74	−8.36	1.243	208.8
0.14	444.75	25.833	3.72	−8.26	1.251	245.6
0.12	450.07	25.787	3.70	−8.03	1.260	285.8
0.10	456.22	25.733	3.67	−7.69	1.265	330.7
0.08	463.29	25.672	3.63	−7.13	1.274	379.0
0.06	471.43	25.600	3.59	−6.14	1.274	435.5
0.04	480.74	25.517	3.54	−4.67	1.271	500.3
0.02	491.51	25.422	3.48	−2.64	1.262	577.7

the quoted error limits except for those of Edwards *et al.*[16] However, if one normalizes the pressure coordinates given by Edwards *et al.* by lowering them by 4 psi so as to cause them to agree with the result of Mills, Grilly, and Sydoriak[15] at high temperatures, as has been done in Fig. 4, their results agree quite well with ours at lower temperatures, although their results have slightly less curvature than do ours. The success of such a simple normalization procedure in reconciling the results quite possibly indicates a systematic error in the measurements of pressure by Edwards *et al.*

A second method of determining the pressure of the minimum of the melting curve was also employed in this series of experiments. This method was to suddenly increase the pressure on the He^3 from various starting pressures by 10 psi while the sample was below 0.28°K. Under these conditions, if the initial pressure was less than the minimum but the final pressure was greater than the minimum, the pressure on the He^3 cell would be rapidly increased to P_{min} and a plug would form quickly in the filling line. Cooling of the sample would accompany this pressure change as the liquid was compressed. The absence of any cooling indicated that the initial pressure was greater than the minimum. Such a determination led to $425.2 \leq P_{min} \leq 426.2$ psi. Combining our two results, we take as the best value, $P_{min} = 425.5 \pm 1.0$ psi, as determined in our laboratory.

C. Specific Heat

A few of the results of the specific heat measurements on samples containing less than 0.004% He^4 are shown in Fig. 5. The points plotted are averages of all the points taken in each interval of 0.005°K, the number of points ranging from one to five. The data were taken on a single warming run because nonreproducibilities in

[16] D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, in *Helium Three*, edited by J. G. Daunt, (Ohio State University Press, Columbus, 1960), p. 126.

[17] D. M. Lee, H. A. Fairbank, and E. J. Walker, Phys. Rev. 121, 1258 (1961).

the process of plug formation and the possibility of plug slippage during a run made it questionable that upon cooling again the sample would be at the same density as before. As this work was performed using the same apparatus and techniques as a previous experiment[6] on the specific heat of liquid He^3 and using the same calibrations for the volume and temperature scale, the individual points should be of comparable accuracy to the data taken in the previous experiment, i.e., a possible 1% random error together with a maximum systematic error of 3%. However, because of much longer thermal relaxation times encountered in run E, the determinations of the temperature change accompanying a given heat input were less precise than before, necessitating a more generous allowance for possible random errors.

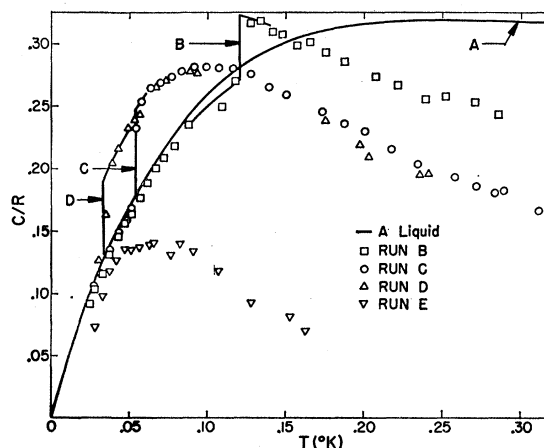In selecting the data to be presented, we have dis-

FIG. 5. Typical results of the specific heat of He^3 at pressures above the minimum in the melting curve. Curve A is the specific heat of the liquid along the melting curve based on the specific heat and expansion coefficient results of reference 6 and the thermodynamic calculation of the melting curve discussed in Sec. IV. The solid curve for runs $B-D$ at the discontinuities are only intended as guides to the eye. The points are averages of all the points taken in 0.005°K intervals.

criminated against runs in which no discontinuity in the specific heat occurs, such as run E, in favor of runs in which such a discontinuity, which is characteristic of the onset of two-phase behavior, occurs. This discrimination was practiced for two related reasons: (1) the molar volume which characterizes a given run, if the run proceeds at constant density, is then that of the liquid at the melting curve at the temperature of the discontinuity and can be considered known; and (2) the properties of the specific heat curve are then, under the same assumption of constant density, uniquely defined by the properties of the liquid and solid phases. On the other hand, in those runs where there is no characteristic discontinuity, the molar volume is undetermined, injecting an additional variable into the analysis and hence making the findings of such an analysis less meaningful. The appropriate molar volume data used for reducing the heat capacity data to specific heats were taken to be those calculated in Sec. IV, the results of this calculation being found in Table II. For runs with no discontinuity, such as run E, the molar volume was chosen by fitting the data to an expression for the heat capacity of a two-phase mixture at the highest temperature, where the latent heat contribution was least.

Curve A, which is included for the purpose of comparison, represents the specific heat of the liquid phase along the melting curve and has been calculated from the specific heat and expansion coefficient of liquid He³ at 423.4 psi[6] together with the melting curve given by the thermodynamic calculation of Sec. IV of this paper.

Runs B, C, and D represent all of the runs which were taken over an appreciable temperature range and in which the discontinuity signifying the onset of two-phase behavior also occurred. Such discontinuities were also observed in runs covering much more restricted temperature ranges, the lowest temperature of such an observation being 0.021°K. The magnitudes of these discontinuities will be discussed in Sec. IV.

Run E is included to demonstrate that the experimental conditions were such that anomalously low as well as anomalously high-specific heat curves could be produced. Additionally, run E demonstrates the unreliability of the process of plug formation in that the initial conditions which were used to produce run E were also used to produce run B.

At the minimum of the melting curve the solid and liquid phases have the same molar entropy, and thus this same condition must apply to any two-phase mixture at the temperature and pressure of the minimum of the melting curve. Hence, one test of our specific heat data for runs B, C, and D is the value of the entropy obtained from these curves at 0.32°K. As the same temperature scale and volume calibration were used in a previous experiment which found that the entropy of the liquid at the pressure and the temperature of the melting curve minimum was $R \ln 2$,[6] the entropy values deduced from runs B, C, and D should equal $R \ln 2$ with,

at worst, a random error of 2%. The entropy at 0.32°K found from run B is 4.6% less, that from run C is 6.1% less, and that from run D is 4.1% less than $R \ln 2$. This discrepancy is outside the allowable limits of error and, since the specific heat data at pressures below the minimum were taken under well-controlled and reproducible conditions while the present data were not, brings the present data into question.

One possible explanation of this discrepancy could be that slippage of additional material into the cell occurred. Addition of extra material would cause a more than proportionate increase in the molar fraction of solid and thus, as the solid specific heat is less than that of the liquid over the entire range investigated, would produce a reduction in the measured specific heat and hence entropy.

Some measurements of poor quality ($\pm 25\%$) were made of the specific heat of solid samples at low densities. These results were carried to about 0.015°K, and, while they were in no way definitive, were consistent with the small values of the exchange integral for solid He³ deduced from the higher temperature measurements by Edwards, McWilliams, and Daunt.[18] For example, our measurements indicate that the specific heat at a molar volume corresponding to a filling pressure of 643 psi was about $0.018R$ at 0.02°K and decreased with increasing temperatures less rapidly than $1/T^2$, the indicated temperature dependence being between $T^{-1.6}$ and $T^{-0.8}$. Because of this temperature dependence, because of the possibility of a contribution of unknown magnitude from an isotopic ordering process,[19] and because of the very poor quality of the data we hesitate to assign a value to the exchange integral. However, our results are definitely not in agreement with the values of the exchange integral deduced from nuclear magnetic resonance measurements by Reich[20] and by Garwin and Landesman.[21] Our results are consistent, however, with the fact that the curvature of the melting curve is still increasing at the lowest temperatures of our measurements, 0.03°K.

D. Magnetic Properties

Measurements of the magnetic properties (susceptibility, transverse and longitudinal relaxation times, and spin diffusion coefficient) were made to test the previous observation of anomalous behavior.[3] In this case, in contrast to the anomalous sound velocity results, the observations were qualitatively the same as before. However, additional studies were made which indicated the anomalous properties could be explained in terms of a two-phase liquid-solid mixture.

[18] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Letters 1, 218 (1962).
[19] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Rev. Letters 9, 195 (1962).
[20] H. Reich, Phys. Rev. 129, 630 (1963).
[21] R. L. Garwin and A. M. Landesman, Proceedings of the Eighth International Congress on Low Temperature Physics (to be published).

The properties of the solid relevant to this discussion are that the longitudinal relaxation time, T_1, is about 300 msec and the susceptibility obeys the Curie law, $\chi = C/T$. On the other hand, the liquid displays a much longer T_1, about 20 sec, and a molar susceptibility at low temperatures which is roughly given by C/T^*, where $T^* = 0.17°K$. Hence, at low temperatures the susceptibility of the solid is roughly $(0.17°K/T)$ larger than that of the liquid and, upon changing the field, the magnetization of the solid will respond much more quickly than that of the liquid. Thus, at low temperatures, unless the fraction of solid is very small, the magnetic behavior of a two-phase mixture will be dominated by that of the solid.

The additional studies made were as follows: First, the magnetization was initially destroyed, then about 2 sec later a $\pi - \pi/2 - \pi$ pulse sequence was applied. Under these conditions the solid should be fully magnetized and the liquid very weakly magnetized. When the interval between the first π pulse and the $\pi/2$ pulse is equal to $T_{1s} \ln 2$ (the subscript s refers to the solid), no signal should follow the $\pi/2$ pulse and hence no echo should occur after the final π pulse. This study yielded $T_{1s} = 320 \pm 16$ msec. By allowing the interval between the destruction of the magnetization and the initiation of the $\pi - \pi/2 - \pi$ pulse sequence to lengthen so as to allow the liquid to become fully magnetized, a small echo, presumably due to the liquid, would occur where previously no signal was observed.

Second, the sample was magnetized in a field H^* about four times the resonance field so as to enhance the signal. If at $t=0$ the field is rapidly reduced to the resonance field, H_0, the magnetization at time t will be given by

$$M(t) = x\chi_s[H_0 + (H^* - H_0)e^{-t/T_{1s}}]$$
$$+ (1-x)\chi_l[H_0 + (H^* - H_0)e^{-t/T_{1l}}], \quad (2)$$

where the subscript l refers to liquid, s to solid, x is the molar fraction of solid in the mixture, and χ is the molar susceptibility. If $T_{1s} \ll t$, which should be the case for times of the order of a few seconds, the solid magnetization should have completely decayed to its final value, while, if t is not too much greater than T_{1l}, the liquid magnetization will be considerably enhanced and will decay to its final value with a time constant T_{1l}. The measurements made were to study the decay of magnetization using a $\pi/2 - \pi$ pulse sequence after having turned off the enhancing field H^*. Upon varying the time t through times greater than 2 sec, a simple exponential sufficed to fit the data. The time constant for the exponential varied between 4 and 10 sec, chiefly seeming to depend upon the fraction of solid present. Although this time was less than T_1 for the single-phase liquid, it can be identified as T_1 for the liquid fraction of the sample.

As in the case of the previous measurements of reference 3, no clear measurements could be obtained for the self-diffusion coefficient of either the two-phase

mixture or the liquid fraction thereof. A special technique was employed to try to sort out any possible contribution due to the liquid fraction. This technique was to first make a series of measurements of the normalized echo heights when only the solid was allowed to magnetize in the field H_0 and subtracting from this the results of an identical series of measurements where the magnetization of the liquid and solid was first enhanced and then initiating the measuring sequence, $(\pi/2 - \pi - \pi)$, 2 sec after turning off H^*. The results of these measurements were not conclusive, but were sufficient to show that the diffusion coefficient for the liquid fraction was at least a factor of 5 less than in the pure liquid at the same temperature and a pressure just below the minimum of the melting curve, which could be taken to indicate that the liquid was confined to rather small regions.

IV. DISCUSSION

Thermodynamics enables one to calculate some of the quantities which we have measured, namely the melting curve and the specific heat of two-phase mixtures, given a complete knowledge of the entropy, S, and the molar volume, V, for both phases. We have, from a previous experiment,[6] the entropy and the thermal expansion coefficient of the liquid at 423.4 psi, just below the minimum in the melting curve. Hence, given an initial value for the molar volume at this pressure, we know the molar volumes at all temperatures. In this experiment we have measured the sound velocity and hence the isentropic compressibility which is a very good approximation to the isothermal compressibility, β_l. Hence, we can take

$$\beta_l = 1/c_l^2 \rho_l, \quad (3)$$

where c_l is the velocity of sound in the liquid which is given in Fig. 3, and ρ_l is the liquid density. Taking as an initial condition the lowest temperature value of the liquid molar volume given by Mills, Grilly, and Sydoriak,[15] using the values for β_l and α_l (the thermal expansion coefficient) found as above, one can generate the liquid molar volume at any given temperature and pressure.

The liquid entropy at 423.4 psi, which is given by[6]

$$S_l/R = 4.439T - 11.076T^2, \quad T < 0.05°K, \quad (4a)$$

$$S_l/R = 0.02086 + 0.0103 \ln(T/0.05)$$
$$+ 3.845T - 7.893T^2 + 7.033T^3,$$
$$0.05°K \le T \le 0.32°K, \quad (4b)$$

can be extended above the minimum in the melting curve by extrapolating the values of the expansion coefficient above P_{min} and using the Maxwell relation

$$(\partial S/\partial P)_T = -V\alpha. \quad (5)$$

The situation with respect to the solid is much less clear. However, the specific heat data obtained for the solid by Heltemas and Swenson[13] indicate that, to an

excellent approximation, only the spin entropy $R \ln 2$ is left in the solid at temperatures as high as $0.3°K$. The results of the specific-heat measurements of Edwards, McWilliams, and Daunt[18] down to $0.1°K$, the fact that the magnetic susceptibility of the solid seems to obey Curie's law at a temperature of about $0.03°K$ at low densities[3] and, to a limited extent, our measurements of only a small solid heat capacity to $0.015°K$, indicate that the solid entropy is probably nearly equal to $R \ln 2$ along the melting curve to quite low temperatures. Evidence that the proper value of the entropy is the expected $R \ln 2$ is provided by the fact that the entropy of the liquid at the pressure of the minimum of the melting curve is equal to $R \ln 2$ at $0.321°K$,[6] in very good agreement with the measured temperature of the minimum in the melting curve.

Thus, we shall assume that the solid entropy is $R \ln 2$ over the entire region of interest, recognizing that this assumption will become invalid at sufficiently high as well as sufficiently low temperatures. Under this assumption, we can take both the solid expansion coefficient and specific heat to be zero. At higher temperatures the value of the expansion coefficient could be obtained from the work of Heltemas and Swenson[18]; however, we shall not do this as the correction which it would produce would be small and the determination is an indirect one. Under these assumptions the solid molar volume will be a function of pressure only. One can then use the determinations of molar volume as functions of temperature along the melting curve and the determination of the melting curve by Mills, Grilly, and Sydoriak[15] to give the solid molar volume as a function of pressure.

Thus, one has a set of values for the appropriate state functions for both phases. The melting curve can then be calculated in a self-consistent manner as follows. Starting from an initial point, which we took to be $P = 425.0 \text{ psi}$, $T = 0.32°K$, $(dp/dT)_m = 0$ (the subscript m refers to the melting curve), one can extend the values through a temperature interval, which we took to be $0.01°K$, by assuming a new value for $(dP/dT)_m$ and P_{melt}. Then one can calculate the liquid molar volume using

$$\frac{1}{V_l} \frac{dV_l}{dT} = \alpha_l - \beta_l \left(\frac{dP}{dT}\right)_m, \qquad (6)$$

and the liquid entropy using Eqs. (4) and (5). The solid molar volume, of course, is obtained from the pressure. Clapeyron's equation,

$$\left(\frac{dP}{dT}\right)_m = \frac{S_l - S_s}{V_l - V_s} = \frac{S_l - R \ln 2}{\Delta V_m}, \qquad (7)$$

is used to determine the slope of the melting curve at this point. Having determined this, one can check to see if ones initial estimates were correct. If not, one can use the new estimates and repeat the entire procedure until all the values are self-consistent. These values are then used as the initial values for the next step which is taken in the same manner. These calculations are summarized in Table II. The melting curve so calculated is compared with the strain gauge measurements in Fig. 4 and is seen to give higher pressures at low temperature than do the strain gauge measurements. The discrepancy increases gradually with decreasing temperature, reaching almost 7 psi at $0.03°K$.

Using the above assumption concerning the solid entropy, one finds the specific heat of a constant density two-phase system is given by

$$\frac{C}{R} = (1-x) \left\{ \frac{C_{pl}}{R} + \frac{V_l T}{R} \left(\frac{dP}{dT}\right)_m \left[\beta_l \left(\frac{dP}{dT}\right)_m - 2\alpha_l \right] \right\} + x \frac{TV_s}{R} \beta_s \left(\frac{dP}{dT}\right)_m^2, \qquad (8)$$

where C_{pl} is the specific heat of the liquid at constant pressure evaluated at the pressure of the melting curve and x, the molar fraction of solid, is given by

$$x(T) = [V_l(T) - V_0] / \Delta V_m(T), \qquad (9)$$

where V_0 is the molar volume of the mixture and ΔV_m is the difference in molar volumes between the liquid and the solid along the melting line. This expression, using the values of the thermodynamic quantities determined above augmented with a value of β_s evaluated using the solid molar volume data of Mills, Grilly, and Sydoriak[15] together with the assumption that at the lowest temperatures $\alpha_s = 0$, will be compared with some of the specific heat data presently.

The most pronounced feature of the two-phase specific heat curve is the discontinuity, ΔC, which occurs when the sample passes from single-phase to two-phase behavior. This quantity is related to the slope of the melting curve at this point [taking account of the difference between the specific heat at constant volume which is that measured prior to the advent of two phase behavior and the specific heat at constant pressure which enters into Eq. (8)] through the relation

$$\left(\frac{dP}{dT}\right)_m = \frac{\alpha_l}{\beta_l} - \left(\frac{\Delta C}{V_l \beta_l T}\right)^{1/2}. \qquad (10)$$

Actually, one can derive this expression independently of any assumptions about the solid [see Eq. (12)], so the slope of the melting curve so derived should be rigorously correct, if the specific heat measurements are correct.

In Fig. 6 we compare the derivative of the melting curve obtained from the strain gauge measurements with that obtained from the specific heat discontinuities through Eq. (10) and with that obtained in the thermodynamic calculation based on the assumption that the solid entropy was $R \ln 2$. As can be seen, the values ob-
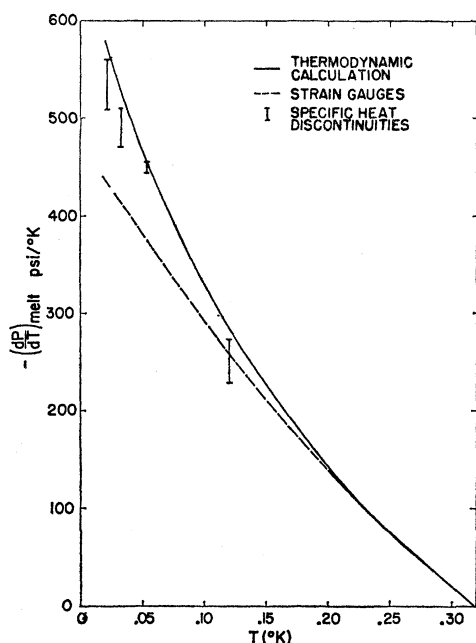
FIG. 6. The temperature derivative of the melting curve of pure He[3] as determined from the strain gauge measurements, from the thermodynamic calculation assuming the entropy of the solid is $R \ln 2$, and from the discontinuities in the specific heat curves.

tained from the specific heat discontinuities agree much better with the thermodynamic calculations than they do with the strain gauge measurements. This indicates that our heat-capacity measurements are not thermodynamically consistent with the strain gauge measurements.

The thermodynamic inconsistency between the strain gauge measurements and the heat-capacity measurements can be shown in another way. Expressing the solid entropy in terms of the slope of the melting curve through Clapeyron's equation, one finds that the entropy of the two-phase mixture is given by

$$S = xS_s + (1-x)S_l = S_l - (V_l - V_0)\left(\frac{dP}{dT}\right)_m. \quad (11)$$

Passing from the entropy to the specific heat yields

$$\frac{C}{R} = \frac{C_{pl}}{R} + \frac{TV_l}{R}\left(\frac{dP}{dT}\right)_m\left[\beta_l\left(\frac{dP}{dT}\right)_m - 2\alpha_l\right]$$

$$-\frac{T(V_l - V_0)}{R}\left(\frac{d^2P}{dT^2}\right)_m. \quad (12)$$

In case the solid entropy is $R \ln 2$, this equation can be reduced to Eq. (8). If one inserts the values of the first and second derivatives of the melting curve as determined by the strain gauge measurements together with values of V_l, C_{pl}, and β_l (α_l is taken to be independent of pressure) obtained by using the strain gauge

melting curve, one can obtain a second calculated specific heat curve which differs from the previous curve, since the strain gauge melting curve is not identical to the thermodynamically calculated one.

Figure 7 shows a comparison of the specific heat data for run C with the two calculations of the specific heat of a constant density two-phase mixture, the first using Eqs. (8) and (9) and the results of the thermodynamic calculation based on the assumption that the solid entropy is $R \ln 2$ and the second using the strain gauge melting curve and Eq. (12). The data do not agree with either calculation, although they seem to agree a bit more closely with the calculation based on the assumption of $R \ln 2$ for the solid entropy than they do with the calculation based on the strain gauge data. The fact that the data fall lower than either of the two calculations is a reflection that both calculations lead to an entropy of the mixture of $R \ln 2$ at $0.32°K$ while the specific heat data do not. The comparison between run C and the two calculations which are supposed to simulate run C is quite representative of the kind of qualitative, but not quantitative, agreement obtained in trying to simulate the other runs. As we have mentioned, part of the quantitative disagreement may stem from the fact that the runs may not have proceeded at constant density, but that, as the pressure within the cell is lowered, additional material may have entered the cell. This would have the effect of reducing V_0 in Eq. (12) and hence of decreasing the specific heat below the expected value.

In spite of the lack of precise thermodynamic consistency between the various sets of data, certain deductions can be made. The most significant conclusion is that the data can at least be qualitatively accepted by
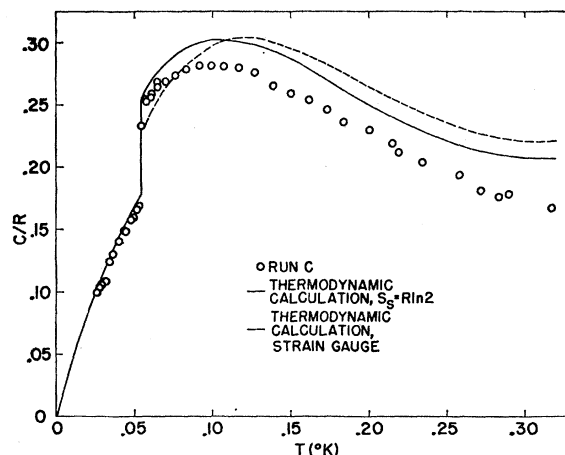

FIG. 7. A comparison of the two calculations of the specific heat of a constant density, solid-liquid mixture with the data from run C. The solid line is the calculation based on the assumption that the solid entropy is $R \ln 2$ while the broken line is that calculated using Eq. (12) and employing the melting curve given by the strain gauge measurements. In both calculations, the molar volume has been chosen so that the specific heat discontinuity will occur at $0.054°K$.

a model of two phases whose properties can be reasonably related to that of the liquid and the solid. Thus, there is no evidence to support the introduction of a region of anomalous behavior. This is consistent with results obtained in other laboratories,[22,23] but which did not extend to as low a temperature as the present measurements. In addition, the data are reasonably consistent with the assumption that the solid entropy is $R \ln 2$. The best evidence for this statement is as follows. Although the specific heat data are not entirely correct because they lead to entropy values at the minimum different from that of the liquid, this fact can possibly be attributed to the run not occurring at constant density. Such a phenomenon should affect only slightly the discontinuity in the specific heat which occurs when

two-phase behavior begins. Since these discontinuities agree better with the calculation based on the assumption that the solid entropy is $R \ln 2$ than with the strain gauge data, this lends support to the idea that the entropy is large and the strain gauge data are in error to the extent of about 20% in the slope at the low-temperature end. In view of the rather poor precision of the strain gauge measurements, it might be attractive to assume that this error could be attributed to such a source. However, the size of the discrepancy (about 7 psi at 0.03°K) is enough to make this explanation rather unlikely.

ACKNOWLEDGMENTS

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[23] H. Weinstock, F. P. Lipschultz, D. M. Lee, and C. F. Kellers, Proceedings of the Eighth International Congress on Low Temperature Physics (to be published).