the metastables of 5×10^{-20} cm^2 in reasonable agreement with Phelps' value of 3×10^{-20} cm^2 for the destruction of the 2^1S state. However, the validity of a comparison of data for liquid helium with that for helium gas at 300°K is doubtful.

The observations reported here were carried out for temperatures below T_λ. For the sake of completeness, previous data[5] (normalized at 2°K) are shown in Fig. 1 for temperatures above T_λ. The dotted line above T_λ is simply a smooth curve drawn through the experimental points with a sharp drop in intensity at T_λ.[5] Since this drop has been observed to disappear when a small overpressure is maintained, it may be related to the cessation of internal boiling at T_λ. The rise in intensity above T_λ is probably related to the 15% decrease in fluid density between T_λ and 4.2°K, and we hope that a refinement of the simple model proposed may account for it. The structure exhibited near 0.5°K is barely outside of the reproducibility of the data and may be instrumental in nature. In any case, we are unable to offer an interpretation.

As for the inhibition of scintillation below T_λ, the role of metastable atoms was suggested by Moss and one of us (F.L.H.)[1] in the first report of the anomalous scintillation behavior of He II. We believe that the data below T_λ show that the simple correlation between the destruction frequency and ρ_n has meaning and represents a reduced destruction rate of metastable atoms in He II. Superfluid liquid helium may be a uniquely suitable medium for the production and retention of high densities of metastable helium atoms and molecules.

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‡National Aeronautics and Space Administration, Graduate Trainee, 1966-1969.

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HEAT CAPACITY AT CONSTANT PRESSURE NEAR THE SUPERFLUID TRANSITION IN He^4

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We present high-precision data for C_p near T_λ and give three interpretations in terms of scaling predictions. We find no interpretation fully in agreement with the predicted symmetry of the transition and a divergent C_p.

Several measurements near the superfluid transition temperature T_λ of[1-5] He^4 have yielded quantitative confirmation for this critical point of theoretical predictions based upon "scaling."[6-10] It is the purpose of this communication to present measurements of the heat capacity at saturated vapor pressure C_s near T_λ. These results agree in detail with theoretical predictions[6-8] only if the heat capacity at constant pressure C_p is finite at T_λ. In order to confirm these observations measurements also were made of the heat capacity at constant volume C_V and of $(\partial P/\partial T)_V$ (P is the pressure) at a molar volume $V=26.81$ cm^3. From these quantities C_p can be calculated reliably. These results, although less precise, are consistent with the conclusions based on C_s.

The measurements were made in the apparatus used for studies of the thermal conductivity of He I near T_λ.[3] The temperature resolution was 10^{-7} °K which limited the precision of C_s for $|t|$

$\lesssim 10^{-4}\,^\circ\mathrm{K}$ ($t \equiv T_\lambda - T$). For this reason the data for $|t| < 10^{-4}\,^\circ\mathrm{K}$ contributed little to the final conclusions. For $|t| \geqslant 10^{-4}\,^\circ\mathrm{K}$ a precision of 0.1% was attained for C_s. All results were corrected for curvature and vaporization. Systematic errors in the measurements probably do not exceed 0.5%. The results agree well with previous measurements.[1] A full discussion will be given elsewhere.

The theoretical prediction of interest pertains to C_p.[10] However, $C_p - C_s < 10^{-3} C_p$ for $|t| \geqslant 10^{-4}$ °K, and it has the same functional form as C_p. This correction was not applied. As an alternative determination of C_p, the relation[11]

$$C_p \cong \left[C_v - \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial S}{\partial P}\right)_\lambda T\right] \times \left[1 - \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial P}\right)_\lambda\right]^{-1} \qquad (1)$$

was employed with the measured C_v and $(\partial P/\partial T)_v$. Direct determinations[12] of $(\partial T/\partial P)_v$ and $(\partial V/\partial P)_\lambda$, and the relation

$$(\partial P/\partial T)_v \cong (\partial S/\partial V)_\lambda - (\partial T/\partial V)_\lambda C_v T^{-1} \qquad (2)$$

for $(\partial S/\partial V)_\lambda$, were used. Equations (1) and (2) are rigorous as $t \to 0$, and Eq. (2) was found to be valid within error for $|t| \leqslant 5 \times 10^{-3}\,^\circ\mathrm{K}$. For $|t| \geqslant 10^{-4}\,^\circ\mathrm{K}$, $(C_p - C_v)/C_p \leqslant 0.044$ at 26.81 cm^3/mole.

For comparison with scaling predictions we write[13]

$$C_p = (A/\alpha)\{|\epsilon|^{-\alpha} - 1\} + B, \quad \epsilon \equiv 1 - T/T_\lambda, \qquad (3)$$

for $T > T_\lambda$. For $T < T_\lambda$ the same functional form pertains, but by convention the parameters are identified as A', B', and α'. In the limit as α vanishes, Eq. (3) becomes[13]

$$C_p = -A \ln|\epsilon| + B. \qquad (4)$$

In addition, terms of higher order than $|\epsilon|^{-\alpha}$ or $\epsilon^{-\alpha'}$ might be expected to contribute to C_p. Sufficiently near T_λ these can be neglected. The scaling assertions to be tested here are[6-8]

$$\alpha = \alpha' \qquad (5)$$

and

$$A = A' \text{ if } \alpha = \alpha' = 0. \qquad (6)$$

In addition, the divergence of C_p can be compared with the divergence of the coherence length for order-parameter fluctuations $\xi = \xi_0' \epsilon^{-\nu'}$ for $T < T_\lambda$ ($\xi = \xi_0 |\epsilon|^{-\nu}$ for $T > T_\lambda$) by the scaling relations[6-8]

$$3\nu' = 2 - \alpha', \quad 3\nu = 2 - \alpha. \qquad (7)$$

Before the data can be analyzed in terms of Eqs. (3) and (4), the effect of the gravitational field upon the transition[14] must be taken into account. The appropriate integrations yield

$$\langle C_p \rangle = (A/\alpha)\{[aH(1-\alpha)]^{-1}[|\epsilon_s - aH|^{1-\alpha} - |\epsilon_s|^{1-\alpha}] - 1\} + B \qquad (8)$$

if $\alpha \neq 0$, and

$$\langle C_p \rangle = -A\{\ln|\epsilon_s - aH| - 1 - [\epsilon_s/(aH)] \ln|(\epsilon_s - aH)/\epsilon_s|\} + B \qquad (9)$$

if $\alpha = 0$ for $T > T_\lambda$. For $T < T_\lambda$ the primed coefficients are to be substituted. The vertical length of the sample is $H = 1.59$ cm and $\epsilon_s \equiv 1 - T/T_{\lambda s}$, with $T_{\lambda s}$ the transition temperature at the top of the sample. At standard gravity, $a = 0.5861 \times 10^{-6}$ cm^{-1} at saturated vapor pressure,[14] and $a = 0.663 \times 10^{-6}$ cm^{-1} at 26.8 cm^3/mole. The angular brackets indicate the gravitational average.

A least-squares procedure was used[15] to analyze C_s, permitting A, B, and α (or A', B', and α') to vary. Only data for which $|\epsilon_s|$ was less than a certain value, say $\epsilon_{\max}$, were used. Resulting values of α and α' for several values of $\epsilon_{\max}$ are shown with their standard errors in Fig. 1.[16] For $\epsilon_{\max} \lesssim 3 \times 10^{-3}$, α and α' seem independent of $\epsilon_{\max}$. If in this temperature range higher order contributions to C_p are neglected, then [with C_p in J mole^{-1}(°K)$^{-1}$][17]

$$\alpha = 0.000 \pm 0.003, \quad \alpha' = -0.020 \pm 0.003; \qquad (10a)$$

$$A = 5.355 \pm 0.15, \quad A' = 6.081 \pm 0.15; \qquad (10b)$$

$$B = -7.773 \pm 0.5, \quad B' = 11.345 \pm 0.5. \qquad (10c)$$

It is apparent that α and α' do not satisfy the scaling prediction Eq. (5). Since $\alpha' \neq 0$, Eq. (6) does not apply. From Eq. (7) one obtains ν'

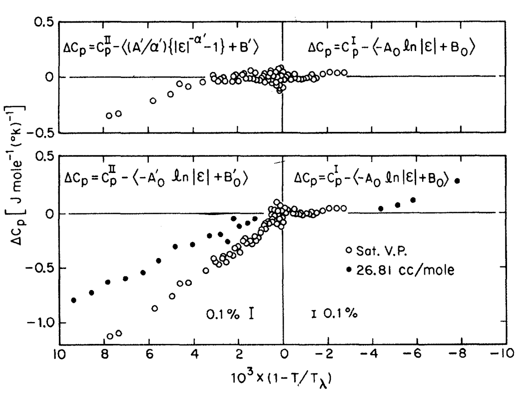

FIG. 1. α and α' as a function of the largest value of ϵ_s at which data were used. The numbers are the number of heat-capacity points used.

$=0.673\pm0.001$ and $\nu=0.666\pm0.001$. Direct measurements[2] of ρ_s and the asymptotic proportionality between ρ_s and ξ^{-1} yield $\nu'=0.666\pm0.006$, differing only by 1 standard error from the present results and Eq. (7). The thermal conductivity of He I[3] and dynamic scaling predictions[9,10] yield $2\nu-\frac{3}{2}\nu'=0.334\pm0.005$. The present work and Eq. (7) give 0.323 ± 0.003. In this case the difference is 1.4 times the sum of the standard errors and cannot be regarded as significant. Thus, the above analysis of the present data contradicts scaling only insofar as $\alpha\neq\alpha'$. We shall now examine an alternative interpretation.

Since according to scaling the divergent contribution to C_p is symmetric about T_λ if $\alpha=0$, we examine the difference $\Delta C=\langle C_p\rangle-\langle -A_0\ln|\epsilon_s|+B_0\rangle$. The subscripts on A and B indicate that $\alpha\equiv0$ is assumed. Values of ΔC, obtained with A_0 and B_0 in Eq. (10) and the measured values of $\langle C_s\rangle$, are shown as solid circles in Fig. 2. If there is a value of ϵ_{max} below which Eq. (9) adequately describes the He II measurements ($\alpha'=0$), then ΔC for $T<T_\lambda$ should be linear in $\log_{10}\epsilon_s$ for sufficiently small ϵ_s. It can be seen that $\alpha'=0$ is consistent with the data for $\epsilon_s\lesssim3\times10^{-4}$. However, $\alpha'=0$ implies that higher order terms begin to contribute appreciably for He II when $\epsilon_s\cong3\times10^{-4}$. For He I these terms are negligible for $|\epsilon_s|\lesssim3\times10^{-3}$ if $\alpha=0$. Thus, $\alpha=0$ and the scaling prediction $\alpha=\alpha'$ are consistent with the data but imply a severe asymmetry in higher order contributions. The scaling assertion $A_0=A_0'$ requires that ΔC for He II be constant when higher order contributions are negligible. Even for $\epsilon_{max}\leq3\times10^{-4}$, where $\alpha'=0$ is consistent with the data, the measured ΔC is temperature dependent. Thus, $A_0\neq A_0'$ in contradiction to Eq. (6). The data yield $A_0'\leq5.13$ for $\epsilon_{max}\leq5\times10^{-4}$, and $A_0=5.35\pm0.01$ for $\epsilon_{max}\leq3\times10^{-3}$. Thus,

$$A_0/A_0'\geq1.041 \text{ if } \alpha=\alpha'=0. \tag{11}$$

It does not seem likely that A_0/A_0' exceeds 1.06.[18]

Since the deviations from theory implied above are rather small (at most about 1% of C_s), one must be very concerned about possible unknown systematic errors which depend upon ϵ. One property of the apparatus which is singular near the transition is the He II film flow in the capillary.[3] However, the onset of superflow in the film was measured to occur at $\epsilon=2\times10^{-4}$ [19] (arrow labeled T_0 in Fig. 2). There is no observable singularity in C_s at this temperature. Nonetheless, concern over this possible source of systematic errors provided some of the motivation for measuring C_v. In this case the capillary was filled with liquid, and the heat transfer for $T<T_\lambda$ was larger by a factor of at least 14 and singular at $\epsilon=0$.[20] The derived data for C_p were not sufficiently precise to define α and α' with the accuracy required for the detection of deviations from Eq. (5). When it was assumed that $\alpha=0$, then $A_0=5.286$ and $B_0=-8.169$ were obtained. Values of ΔC calculated with these parameters are shown in Fig. 2 as open circles. It is evident that also for these measurements $A_0\neq A_0'$. If $\alpha'=0$, then again higher order contributions are not symmetric about T_λ.

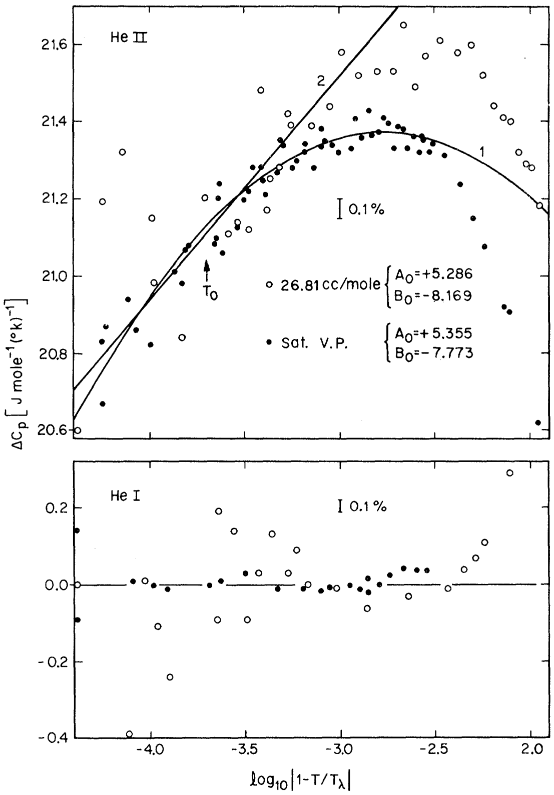

FIG. 2. The difference ΔC between the measured heat capacity and the function $\langle -A_0\ln|\epsilon|+B_0\rangle$ (A_0 and B_0 from He I). T_0 indicates the onset of superflow in the He II film in the capillary. The lines 1 and 2 correspond to Eqs. (10) and (11), respectively. The vertical bars indicate 0.1% of C_p.

The present data are not sufficiently precise to make a choice between the above interpretations [Eqs. (10) and (11)]. This is demonstrated in Fig. 2 by the lines labeled 1 and 2 which correspond to Eqs. (10) and (11), respectively. For $4\times10^{-5}\leq\epsilon_s\leq6\times10^{-4}$, the two functions differ by at most 0.15% of C_p. In order to show the temperature dependence of higher order contribu-

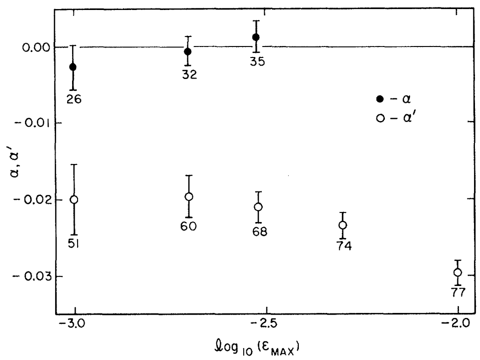

FIG. 3. Deviations of C_p from the best fit as a function of ϵ. Top: $\alpha=0$, $\alpha'=-0.02$. Bottom: $\alpha=0$, $\alpha'=0$.

tions implied by Eqs. (10) and (11), the deviations from the asymptotic expressions are shown in Fig. 3 as a function of ϵ.[21] One sees that the deviations are regular at T_λ if $\alpha'=-0.02$. If $\alpha'=0$ however, then higher order contributions appear to be singular at T_λ for both experimental paths. In this latter case, the higher order contributions can be approximated by $D'\epsilon$ for He II.

Since it is possible to change the derived exponent α' by invoking contributions to C_p in He II of the form $D'\epsilon$, a third interpretation of the data was obtained by also permitting contributions of the form $D\epsilon$ for He I. Then $\alpha \cong -0.005 \pm 0.005$ and $\alpha' \cong -0.015 \pm 0.007$. These results reasonably permit the specific values

$$\alpha' = \alpha = -0.009; \tag{12a}$$

$$A' = 5.504, \quad A = 5.820; \tag{12b}$$

$$B' = 13.85, \quad B = -9.90; \tag{12c}$$

$$D' \cong D \cong -120. \tag{12d}$$

These parameters satisfy the scaling prediction $\alpha=\alpha'$ [Eq. (5)]. Since $\alpha \neq 0$, Eq. (6) does not apply. Further, we note that $D'=D$ indicates that higher order contributions, although appreciable in the temperature range of interest, are regular at T_λ. The derived exponents $\nu'=0.670$ and $2\nu-\frac{3}{2}\nu'=0.335$ are in very good agreement with the more direct determinations (0.666 ± 0.006[2] and 0.334 ± 0.005[3]). This interpretation appears to be fully in agreement with scaling predictions. However, it implies that C_p although singular at T_λ does not diverge at T_λ.[22]

In this paper data for C_p have been presented which permit several interpretations. If higher order contributions to C_p are neglected for $|\epsilon_s| \lesssim 3\times10^{-3}$, then the data imply $\alpha'<0$ and $\alpha=0$. If higher order terms for He II are considered for $\epsilon_s \gtrsim 3\times10^{-4}$, then the data permit $\alpha=\alpha'=0$, but imply a severe asymmetry in the higher order contributions and a measurable asymmetry in the divergent contribution ($A_0 \neq A_0'$). If higher order contributions whose temperature dependence is ϵ are assumed to exist both for He I and He II, then $\alpha=\alpha'<0$, and higher order contributions are regular at T_λ. The last interpretation, although in agreement with scaling, implies that C_p is finite at T_λ.[22]

I am grateful to P. C. Hohenberg for many stimulating discussions of critical-point theories and to J. F. Macre for assistance in the data processing.

Note added in proof.—It has been pointed out to the author by M. E. Fisher that the prediction Eq. (6) and the conclusions to be drawn from the result (11), depend sensitively on the assumption, made in Refs. 6-8, of a simple power-law behavior for the scaling functions. This goes beyond a natural "minimal scaling hypothesis" which may be expressed, for example, by rewriting Eq. (9) of Ref. 8 in the form $H(M,T)=\eta(M)h[t/\tau(M)]$ and allowing the functions $\eta(M)$ and $\tau(M)$ to be more general than powers. Specifically, if $\tau(M)=|M|^{1/\beta}$ and $\eta(M)=\mathrm{sgn}\{M\}|M|^{\delta}\ln(1/|M|)$ and $h''(0)=0$ with $\beta(1+\delta)=2$, one finds a pure logarithmic divergence in the specific heat ($\alpha=\alpha'=0$) but with, in general, unequal amplitudes, i.e., $A\neq A'$.

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[11]Numerical estimates show that the approximation in Eq. (1) introduces negligible errors [G. Ahlers, Phys. Rev. 182, 352 (1969)].

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[14]G. Ahlers, Phys. Rev. 171, 275 (1968).

[15]Weights inversely proportional to the square of the random probable error of each point were used.

[16]All quoted uncertainties are standard errors exclusive of possible systematic errors.

[17]A value for α' of -0.002 ± 0.008 was quoted previously (Ref. 19 of Ahlers, Ref. 14) on the basis of preliminary measurements for a very tall sample. Additional measurements and more accurate vaporization corrections have modified this value to -0.012, and reconsideration of possible systematic errors in the temperature scale, the vaporization correction, and the gravitational inhomogeneity (height on the sample) have increased the probable error to ±0.012.

[18]Values of A_0 and A_0' also have been deduced from thermal-expansion measurements by Elwell and Meyer [Phys. Rev. 164, 245 (1967)]. They find $A_0/A_0' = 0.9 \pm 0.2$

[19]G. Ahlers, to be published.

[20]G. Ahlers, Phys. Rev. Letters 22, 54 (1969).

[21]Information regarding higher order contributions should be regarded as qualitative since these terms are sensitive to possible nonsingular systematic errors in the temperature scale.

[22]Fisher [Phys. Rev. 176, 257 (1968)] predicted that certain "hidden" variables in the real system may result in a finite C_p at T_λ even though C_p diverges for the corresponding "ideal" system. Also, in finite systems, departures from ideal limiting behavior should be noticeable at $|\epsilon| \cong N^{-1/3} \cong 10^{-8}$ [M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967)]. At $|\epsilon| = 10^{-8}$, Eqs. (10) and (12) for He I predict heat capacities which differ by only 2.2%.

SIZE EFFECTS IN QUASIPARTICLE LIFETIMES AND PHONON GENERATION IN SUPERCONDUCTORS

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In thin films and granular superconductors, the quantization of the phonon wave vector delimits the phonons which can be emitted in a recombination process. We predict jumps in lifetimes for injected quasiparticles and the disappearance of some emitted phonons at characteristic values of Δ/kT.

In a previous paper[1] we discussed the effects of real phonons on the measurement of quasiparticle recombination times in superconductors. In this Letter we discuss another effect which affects the recombination time. Experimental studies[2] of the recombination time have utilized multiple tunnel junctions by injecting quasiparticles at one junction and detecting them at another. In all cases thin films have been used in the measurements. In addition to experiments to determine the recombination time, the recombination process has been used to generate phonons with energy $\sim 2\Delta(T)$. As we show below the results in both types of experiments can depend strongly upon the thickness of the film in which the recombination takes place.

In the recombination experiments, a quasiparticle is injected into a superconductor, and pairs with a thermally excited quasiparticle by emitting a phonon of energy $\hbar\omega \geqslant 2\Delta(T)$, where $\Delta(T)$ is the temperature-dependent gap parameter. The transition probability for this process is directly proportional to the phonon density of states at $2\Delta(T)$. For a small cubical grain with side d, the smallest phonon wave vector is $q_{\min} = \pi/d$. The phonon density of states is thus zero for energies less than $\hbar\omega_{\min} = \hbar c_t \pi/d$, where c_t is the transverse speed of sound. If quasiparticles were injected into such a grain they could not recombine if $2\Delta(T) < \hbar c_t \pi/d$. We define at $T=0$ a critical size $d_0 = \hbar c_t \pi/2\Delta(0)$, which in Al is ~175 Å.

For thin films a similar effect exists. When the film thickness d is less than d_0 [or at finite T, $2\Delta(T) < \hbar c_t \pi/d$] only phonons with wave vectors in the plane of the film can be emitted in the recombination process. This limitation results in an anomalously long recombination time. In addition, for the phonon generation experiments in the geometry used by Eisenmenger and Dayem[3] no phonons would emerge from the film. Since Eisenmenger and Dayem worked with 1000-Å films for which d_0 is ~45Å, their results are unaffected by a size correction. Levine and Hsieh,[2] however, used Al films 300 Å thick, and the effects of small size should be observable in their work.

In thin films the phonon density of states suffers discontinuities at characteristic energies. This can be seen most readily from the expression for the phonon density of states

$$g(E) = \sum_{\lambda, q_x, q_y, q_z} \delta(E - \hbar c_\lambda [q_x^2 + q_y^2 + q_z^2]^{1/2}), \quad (1)$$

where λ is the polarization index, and for a cubic