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Properties of He^4 Near the γ Phase*

GUENTER AHLERS†
Inorganic Materials Research Division, Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

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The heat capacity of solid He^4 was measured at several constant volumes in the vicinity of the γ phase. The heat capacity of the α phase near the melting line was found to decrease exceptionally rapidly with decreasing molar volume, and the heat capacity of the γ phase was found to increase with decreasing molar volume. The unusual behavior of the γ phase is consistent with the existence of anomalous thermal excitations in this phase. The thermal expansion coefficient and the compressibility of the γ phase were estimated. Their temperature dependences are consistent with the volume dependence of the heat capacity. The triple-point temperatures and the λ temperature at the solid-liquid boundary were found to be 1.462, 1.773, and 1.763°K, respectively.

I. INTRODUCTION

THE properties of solid He^4 near the melting line and the λ transition in the liquid became of special interest in recent years. Goldstein, by means of thermodynamic correlations between the thermal properties of the solid and the liquid, predicted that the solid should exhibit unusual properties near the melting line and in particular that the thermal expansion coefficient should become negative.[1] He suggested that these anomalous properties imply the existence of thermal excitations other than the expected vibrational modes of the crystal and that these anomalous thermal excitations may be similar to those responsible for the anomalous properties of the liquid.

Soon after Goldstein's suggestions Vignos and Fairbanks observed a new solid phase, now called the γ phase, in He^4 in the immediate vicinity of the intersection of the λ-transition line with the melting line.[2] This phase has a body-centered cubic crystal structure.[3] A possible relation between the existence of this phase, the predicted anomalous properties of the solid, and the observed anomalous properties of the liquid immediately suggests itself.

Grilly and Mills recently determined the *PVT* relations for the transitions from the hexagonal close-packed α phase and the γ phase to the liquid, and for the transition from the α to the γ phase.[4] Their work permitted an indirect determination of the thermal expansion coefficient of the solids along the solid-liquid equilibrium line if reasonable values for the compressibilities of the solids were assumed. In agreement with Goldstein's predictions the thermal expansion coefficient was found to be negative for the α phase and the low-temperature region of the γ phase. In the γ phase, the thermal expansion coefficient appears to have a maximum. Unfortunately, the results of Grilly and Mills cannot be considered as conclusive because they are based on an assumed value of the compressibility for the solid equal to 0.8 times the compressibility of the liquid.

A detailed knowledge of the thermal properties of solid He^4 in this interesting region would shed some further light on the nature of the possible anomalous behavior. The comparison between the properties of the body-centered cubic phases of He^3 and He^4 is also of great interest. The heat capacity of He^4 was therefore measured at several closely spaced constant volumes at temperatures above 1.3°K. Some gross features of the results, and particularly the comparison with measurements on He^3 by Heltemes and Swenson,[5] were already presented elsewhere.[6] Since this publication, more accurate calibration of the thermometer used in this work made it possible to deduce many more detailed properties particularly of the γ phase, and these results together with a description of the experiments are presented here.

II. EXPERIMENTAL

A. Apparatus, Procedures, and Errors

The apparatus used in these measurements was described elsewhere.[7] It consisted of a cryostat containing a beryllium-copper cell, and a pressure generating system. The cell was suspended by means of a 0.5-mm-i.d. stainless-steel capillary. This capillary was in thermal contact with the liquid helium bath. In the present work the sample was admitted through the capillary directly from a cylinder containing helium gas at a pressure of about 1100 psi. The delivery pressure of the cylinder could be regulated. The gas in the cylinder had been previously purified by passing it over silica gel at 78°K.

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* This research was supported by the U. S. Atomic Energy Commission.

† Present address: Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey.

[1] L. Goldstein, Phys. Rev. **122**, 726 (1961).

[2] J. H. Vignos and H. A. Fairbanks, Phys. Rev. Letters **6**, 265 (1961).

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[4] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **18**, 250 (1962).

[5] E. C. Heltemes and C. A. Swenson, Phys. Rev. Letters **7**, 363 (1961).

[6] G. Ahlers, Phys. Rev. Letters **10**, 439 (1963).

[7] G. Ahlers and W. H. Orttung, Phys. Rev. **133**, A1642 (1964).

The volume of the sample cell at low temperatures was measured with an accuracy of 0.3% by filling it completely with liquid normal hydrogen at a known temperature and at a pressure barely in excess of its vapor pressure. The amount of hydrogen required was measured by expanding the liquid into large vessels of known volume and temperature. The molar volume measurements for normal hydrogen by Scott and Brickwedde[8] were then used to determine the cell volume. The volume was found to be 8.26 cc.

The sample was usually introduced into the cell at 4.2°K, at the desired density. The data by Megaw[9] on the molar volume of the fluid at 4.2°K as a function of pressure and those by Grilly and Mills[4] on the molar volume of the solid along the melting line were used to estimate the required pressure. After introducing the sample, the cell was thermally isolated by opening a mechanical-heat switch. The 0.5-mm core of sample in the capillary was then frozen by cooling the bath to 1.2°K. This solid plug was relied upon to support any pressure gradients across the capillary which developed when the sample itself was cooled to 1.2°K. In order to prevent movement of the plug, it was found necessary to reduce the external pressure as the sample cooled. Any plug movement, if it had occurred, would have been immediately noticeable because of the large thermal effects associated with it. The procedure used here to confine the sample to the cell sets an upper limit for the molar volume at which measurements are possible. At volumes larger than 20.98 cc/M there is no freezing in the capillary, and the sample cannot be kept at constant volume. The measurements are thus limited to the lower third of the volume range over which the γ phase exists.

The molar volume of the sample was determined by observing the temperature of the discontinuity in the heat capacity associated with the beginning of melting. This temperature could be determined with an accuracy of 1×10^{-3} °K, and with a precision of 0.2×10^{-3} °K. The accuracy of the molar-volume determination is thus limited by the accuracy with which the molar volume of the solid in equilibrium with the liquid is known. The data of Grilly and Mills were used for this purpose, and their accuracy was of the order of 0.02 cc/M or 0.1%. It is estimated that differences in molar volumes of different samples could be determined with an accuracy of 0.004 cc/M.

The amount of sample was determined from the cell volume and the molar volume of the sample. Due to the combined errors in the cell volume and in the molar volumes a systematic error of 0.4% in the heat capacities is thus possible.

The heat capacity of the empty cell was measured with an accuracy of 3%. It was at most 7% of the total heat capacity, and thus may have caused an additional systematic error of at most 0.2% in the sample heat capacity. It is thus estimated that systematic errors in the sample heat capacity do not exceed 0.6%.

The scatter in the heat-capacity measurements is of the order of ±0.5% for the measurements in the single-phase regions. In the α-γ two-phase region the scatter is at times as large as ±5% because of slow establishment of equilibrium between the two phases. Most of the scatter in the single-phase regions is due to the small temperature increments which were used in the heat-capacity measurements. The γ phase at constant volume exists over a temperature range of only about 0.03°K, and temperature increments of $(1 \text{ or } 2)\times10^{-3}$ °K were used because it was desired to obtain several heat-capacity points in this phase. Thermal equilibrium was attained within about one minute after heat inputs in the single-phase regions. All electrical and time measurements were made with an accuracy of 0.1%.

B. The Temperature Scale

A series-II germanium thermometer purchased from the Honeywell Company was used as the working thermometer. It was calibrated against the vapor pressure of He^4. The 1958 He^4 scale of temperatures[10] was used. The calibration was carried out with the thermometer mounted on the sample cell and in thermal contact with a vapor-pressure bulb for temperatures above 2.2°K, and in a separate apparatus for temperatures between 1.29 and 4.2°K. In the overlapping temperature range the two calibrations agree within 1×10^{-3} °K. The first calibration is described in detail elsewhere.[11] During the second calibration the vapor-pressure measurements were made by means of a vapor-pressure bulb with a vacuum-jacketed line above 2.2°K, and by measuring the bath vapor pressure below 2.2°K. Thermal equilibrium was established by mechanical-heat links as well as by exchange gas. It is believed that the working temperature scale differs from the 1958 He^4 temperature scale by no more than 1×10^{-3} °K.

Whereas in heat-capacity measurements small errors in the temperature scale are relatively unimportant, such errors are very important in the determination of the triple-point temperatures, and the temperatures at the phase boundaries. It is thus worthwhile to consider independent evidence for the correctness of the temperature scale.

The thermometer used in this work was also used to determine the heat capacity of copper above 2°K.[11] It was found that the heat capacity of copper could be represented by

$$C=0.704T+0.0478T^3 \text{ mJ/M °K} \qquad (1)$$

for $T\leq5$°K, with a precision of ±0.2%. The coefficients

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[10] H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur. Std. (U. S.) Monograph No. 10 (1960).

[11] G. Ahlers, J. Chem. Phys. (to be published).

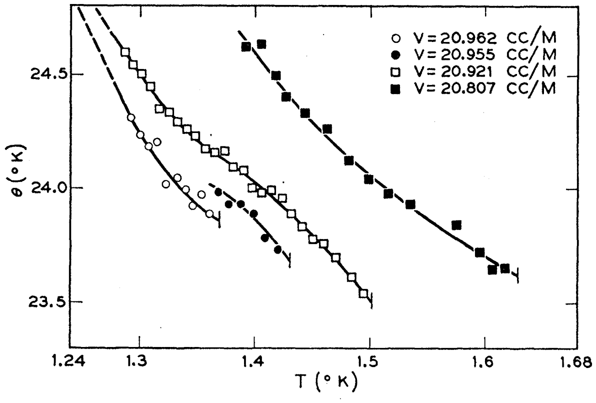

FIG. 1. The Debye theta of the α phase of He^4. The vertical bars at the end of the lines indicate the phase boundaries.

in Eq. (1) are in good agreement with other work.[11] Absence of systematic deviations from Eq. (1) in excess of 0.2% is further evidence for the reliability of the temperature scale above 2°K.

During the second calibration, the susceptibility of $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$ in thermal contact with the germanium thermometer was also determined between 1.29 and 4.2°K. It was found that over the entire temperature range the mutual inductance M of a set of coils surrounding the salt could, within the precision of the measurements, be represented by

$$M=A+BT^{-1}, \tag{2}$$

where T is the vapor-pressure temperature, and A and B are constants. The precision of the inductance measurements was such that errors of 2×10^{-3} °K at 1.3°K and 6×10^{-3} °K at 4°K could have been noticed. It is felt that the combined results of the copper heat-capacity measurements and the susceptibility measurements indicate that the working temperature scale differs from the 1958 He^4 temperature scale by less than 2×10^{-3} °K.

The thermometer resistance versus temperature data were fitted to the equation

$$T_c=\frac{\log R}{[A+B\log R+C\log(1+DR^E)]^2} \tag{3}$$

and a difference table of $\Delta=T/T_c$ versus T_c was constructed. The temperatures T_c were calculated from thermometer resistances R, and then corrected by multiplying by Δ. Values of Δ for each T_c were calculated by quadratic interpolation in the table. All calculations were done with an IBM-7094 computer. The computer was also used to calculate heat capacities, Debye thetas, and related quantities.

In the present work the α-γ-liquid triple-point temperatures were redetermined. These temperatures had been determined by Grilly and Mills[4] during their work on the PVT properties along the solid-liquid equilibrium lines. The present results differ considerably from those of Grilly and Mills. A reason for some of this difference may be a difference in the temperature scales. Since it was desired to use the PVT data for molar volume determinations, it seemed desirable to adjust the Grilly and Mills temperature scale in such a fashion that the triple-point temperatures coincide with the values determined here. A temperature increment

$$\Delta T=0.079-0.0375T_{\mathrm{GM}} \tag{4}$$

was thus added to all Grilly and Mills temperatures before the PVT data were used for the molar volume determinations. Whereas this procedure is somewhat arbitrary, it appears to be the only reasonable method of obtaining consistency between the old and new data. It may have resulted in a systematic error in the molar volume determinations, but should have had relatively little effect on differences in molar volumes.

III. RESULTS

A. Heat-Capacity Measurements

The heat capacity of solid He^4 was measured at seven molar volumes. Five of the volumes were in the immediate vicinity of the γ phase, and for three of the volumes successful measurements of the heat capacity of the γ phase were obtained. The various transition temperatures, the discontinuities in the heat capacities at the transitions, and the deduced molar volumes are given in Table I.

1. The Heat Capacity of the α Phase

Most of the measurements on the α phase at volumes larger than 20.8 cc/M are presented in Fig. 1. Some smoothed values of Debye thetas over the entire volume range are given in Table II.

TABLE I. The transition temperatures, heat-capacity discontinuities, and molar volumes for the heat-capacity measurements. For each transition the top number is the transition temperature in °K, and the bottom number is the heat-capacity discontinuity in J/M °K.

	Transitions				
Sample	$\alpha\to\alpha+$liq	$\alpha\to\alpha+\gamma$	$\alpha+\gamma\to\gamma$	$\gamma\to\gamma+$liq	V[cc/M]
1	1.3687	···	1.6641	1.7106	20.962
	0.072	···	1.49	3.08	
2	1.4301	···	1.6741	···	20.955
	0.12	···	1.6	···	
3	1.4608	···	1.6968	1.7310	20.940
	···	1.02[a]	1.68	5.10	
4	···	1.5009	1.7279	1.7503	20.921
	···	1.10	1.72	5.73	
5	···	1.6280	···	···	20.807
	···	1.85	···	···	
6	2.1594	···	···	···	19.886
	14.0	···	···	···	
7	2.1918	···	···	···	19.816
	14.4	···	···	···	

[a] The heat capacity of the α phase was extrapolated to the lower triple point.

It was pointed out elsewhere[6] that to a first approximation the Debye theta decreases linearly with increasing temperature over the temperature range studied here. On the basis of the present more reliable temperature scale it is now clear that there are small but definite deviations from this linear temperature dependence, and indeed from the temperature dependence expected from the lattice vibrations of a simple solid. Particularly at temperatures near the melting line there is an excessive decrease in the Debye theta with increasing temperature. Such a phenomenon was observed in argon and krypton, and in these solids it was attributed to vacancy formation.[12]

The volume dependence of the heat capacity is shown in Fig. 2 in terms of the Grüneisen γ,

$$-\gamma=\frac{V}{\theta}\left(\frac{\partial\theta}{\partial V}\right)_T, \tag{5}$$

as a function of the temperature at several molar volumes. The volumes quoted in Fig. 2 are the averages of the volumes for those heat-capacity measurements which were used to calculate γ. At the largest volumes γ assumes rather large values, and exhibits a strong temperature dependence. This large rate of change of the heat capacity with volume indicates an anomalous behavior for the ratio of the thermal expansion coefficient α to the isothermal compressibility K, for

$$\left[\frac{\partial}{\partial T}\left(\frac{\alpha}{K}\right)\right]_V=\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_V. \tag{6}$$

An unusually large rate of change of α/K with temperature at volumes near the melting line is thus indicated. The calculation of actual values of α/K requires a knowledge of the entropy at several volumes. The heat-capacity measurements do not extend to sufficiently low temperatures for this purpose. Such low-temperature measurements in the immediate vicinity of the melting line would be extremely interesting; for if α/K is indeed negative, then according to Eq. (5) γ must become negative over some temperature range because α must approach zero at low enough temperatures. Extrapolation of the present measurements at 20.962 and 20.921 cc/M indicates that this temperature range may have its upper limit in the vicinity of 1°K.

TABLE II. Smoothed values of the Debye theta for the α phase of He⁴.

T[°K]	V[cc/M] 20.962	20.955	20.921	20.807	19.886	19.816
1.30	24.24	···	24.50	···	···	29.36
1.33	24.03	···	24.31	···	28.95	29.24
1.37	23.86	23.98	24.13	···	28.77	29.08
1.40	···	23.86	24.02	24.59	28.64	28.95
1.43	···	23.68	23.89	24.40	28.51	28.82
1.46	···	···	23.74	24.23	28.39	28.69
1.50	···	···	23.51	24.05	28.22	28.53
1.55	···	···	···	23.86	28.02	28.34
1.60	···	···	···	23.70	27.83	28.15
1.70	···	···	···	···	27.49	27.78
1.80	···	···	···	···	27.16	27.44
1.90	···	···	···	···	26.79	27.08
2.00	···	···	···	···	26.41	26.68
2.10	···	···	···	···	26.01	26.28

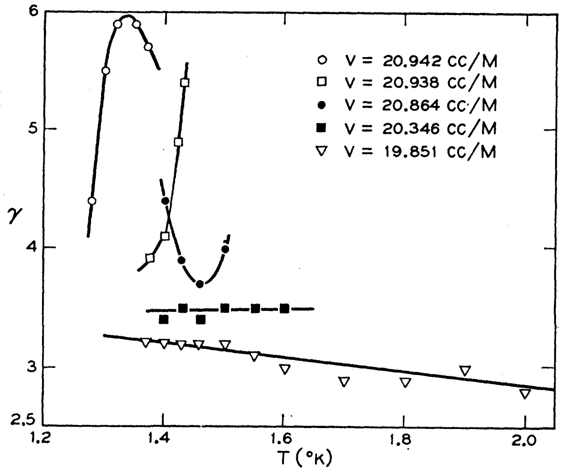

FIG. 2. The Grüneisen gamma of the α phase of He⁴.

At smaller volumes γ becomes well behaved over the temperature range studied here, indicating perhaps that the extremely anomalous behavior of the thermal expansion coefficient does not extend too far into the solid region. At 19.851 cc/M, γ exhibits only a slight temperature dependence, and at high temperatures approaches a value consistent with those reported by others.[5,13]

2. *The Heat Capacity of the γ Phase*

Considerable experimental difficulties were encountered during the heat-capacity measurements of the γ phase. In the α-γ two-phase region, thermal equilibrium was attained only very slowly after heat inputs, and therefore rather large temperature increments had to be used to make measurements possible in a reasonable length of time. On the other hand, if too large a temperature increment was used very near the γ phase, then there was a tendency to miss this phase completely because of the narrow temperature range over which this phase exists. Nonetheless, satisfactory measurements were made at three volumes, and the results are presented in Fig. 3.

Little can be said about the temperature dependence of the heat capacity in the γ phase because of the small temperature range which can be studied. The heat

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[12] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1462 (1961).

[13] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

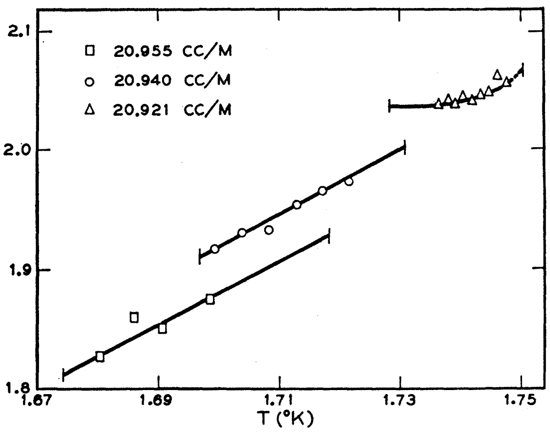

FIG. 3. The heat capacity of the γ phase of He^4.

capacity does, however, increase with increasing temperature at a rate which results in an almost temperature-independent Debye theta. In view of the fact that the relative temperature T/θ is about 0.1, this is consistent with the behavior of other solids.[11,12]

The volume dependence of the heat capacity is most unusual. The heat capacity increases with decreasing volume. It thus appears that there exist thermal excitations which become more accessible as the volume is decreased. If one assumes that the frequency spectrum of the lattice vibrations has a volume dependence similar to that for other solids, then it is necessary to postulate the existence of anomalous thermal excitations for the γ phase, such as was suggested by Goldstein for solid He^4 in general.[1] These anomalous excitations must have a negative volume dependence, and in this respect they are similar to those responsible for the λ anomaly in the liquid. There appears to be no other direct experimental evidence for a negative volume dependence of the heat capacity of a simple solid. As mentioned earlier, such behavior must be expected for α-He^4 at sufficiently low temperatures if the thermal expansion is negative in the vicinity of 1.3°K. Such behavior has also been observed in liquid He^4 below the λ temperature.[14] In liquid He^4 this is consistent with values of α and K as determined by Grilly and Mills[4] and Eq. (6). The possibility of a thermodynamically similar situation in solid parahydrogen was pointed out elsewhere.[11]

B. The Fixed Points

During the course of the heat-capacity measurements several determinations of the two triple-point temperatures and of the temperature for the intersection of the λ line in the liquid with the solid-liquid equilibrium line were made. The triple points were easily observed because they manifest themselves in the form of an apparently infinite heat capacity. The upper triple point could be determined with a precision greater than the accuracy of the temperature scale. At the lower triple point the heat effects are rather small because of the small heat of melting, and equilibrium between the three phases is slow. In this case it was estimated that the determinations may be as much as 5×10^{-3} °K high. The λ temperature at the solid-liquid equilibrium line was determined by measuring the heat capacity with very small temperature increments in the γ-liquid two-phase region. The results of the fixed point determinations are summarized in Table III, and the heat capacity across the λ temperature is shown in Fig. 4.

TABLE III. Triple-point temperatures and the λ temperature in °K at the solid-liquid equilibrium line for He^4.

Source	Upper T.P.	Lower T.P.	λ Point
Vignos and Fairbanks (Ref. 2)	1.778 ±0.003	1.449±0.003	1.765 ±0.003
Grilly and Mills (Ref. 4)	1.760 ±0.004	1.437±0.006	1.760 ±0.001
Swenson[a]	···	···	1.764 ±0.003
This work	1.7730±0.001	1.462[b]	1.7625±0.001
	1.7731±0.001	1.463[b]	1.7631±0.001
	1.7731±0.001	1.464[b]	
		1.465[b]	

[a] C. A. Swenson, Phys. Rev. 89, 538 (1953); based on 1949 Cambridge vapor pressure scale.
[b] Errors are estimated to be +0.001, −0.005°K.

The upper triple-point temperature as determined here lies between the two previously determined values.[2,4] However, the lower triple point was found at a considerably higher temperature than those quoted by others.[2,4] It is possible that these differences are in part due to differences in the temperature scales; however, it is disturbing that these differences are so large. The λ temperature is definitely 0.010°K lower than the upper triple point, as can be seen from Fig. 4. It was possible to obtain several heat-capacity points in the liquid I-γ region. It is thus clearly established that the

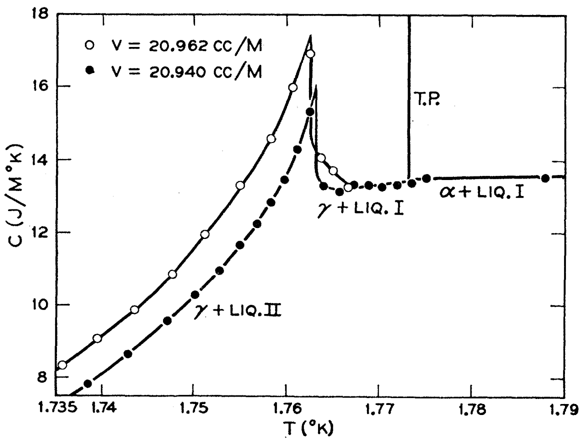

FIG. 4. The heat capacity of He^4 in the solid-liquid two-phase region in the vicinity of the λ temperature.

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[14] O. V. Lounasmaa and E. Kojo, Ann. Acad. Sci. Fennicae Ser. A VI, No. 36 (1959).

λ line meets the solid-liquid equilibrium line in the γ-phase region, and that it does not touch the α phase.

C. The *PVT* Properties of the γ Phase

Grilly and Mills[4] determined the volumes of the α and γ phases in equilibrium with liquid, and the volume change for the transition from the α phase to the γ phase. But there has been no determination of the volume of the γ phase in equilibrium with the α phase. During some of the present heat-capacity measurements the temperatures for the transitions from the α-γ two-phase region to the γ phase and from the γ phase to the γ-liquid two-phase region were determined. The latter was used to establish the sample volume, and the former yielded a point on the lower boundary of the γ phase in a V-T diagram. The data of Grilly and Mills together with three new points on the lower boundary of the γ phase are shown in Fig. 5. In order to achieve consistency between the old and new data, the temperatures for the points by Grilly and Mills were adjusted so that their triple points agree with the present triple-point determinations. The present data extend only to a maximum volume of 20.962 cc/M. The lower boundary of the γ phase was therefore extrapolated to the lower triple point in two reasonable but arbitrary ways. The true lower boundary of the γ phase can be expected to lie between these two extrapolations.

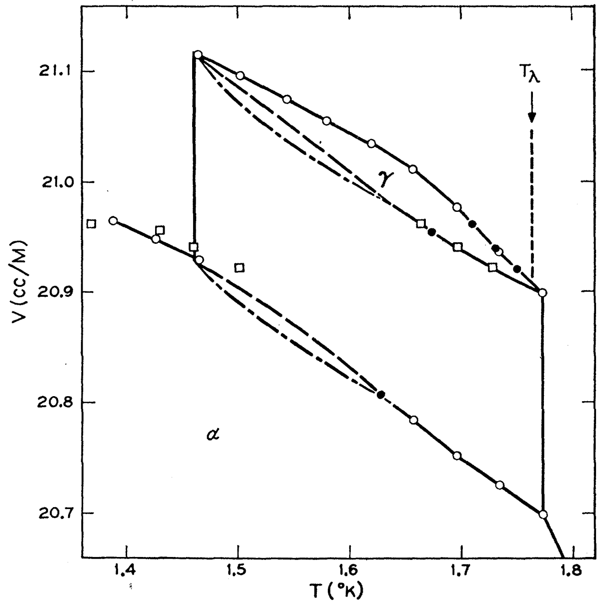

FIG. 5. The volume at the boundaries of the α and γ phases of He^4 as a function of temperature. The open circles are the measurements of Grilly and Mills,[4] the solid circles were used to establish the molar volumes in this work, and the open squares are new points.

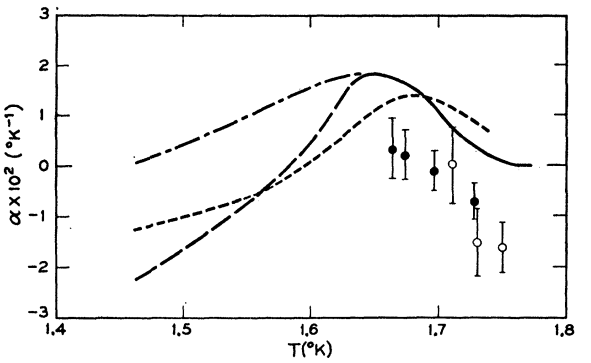

FIG. 6. The estimated thermal expansion coefficient α for the γ phase of He^4. The solid line represents the average value over the existence range of the phase, and the two dashed extensions represent the averages over the phase for the two extrapolations of the lower phase boundary in Fig. 5. The open and solid circles are the values calculated from the heat capacity discontinuities at the upper and lower phase boundaries respectively. The dashed curve is the one obtained by Grilly and Mills.[4]

A knowledge of the *PVT* relations along both boundaries of the γ phase makes the calculation of the *average* thermal expansion and isothermal compressibility for the phase possible. The results of this calculation are shown in Figs. 6 and 7 for both extrapolations of the phase boundary. The thermal expansion coefficient is in qualitative agreement with the results deduced by Grilly and Mills.[4]

The thermal expansion and compressibility *at the phase boundary* can be calculated from the discontinuity in the heat capacity at that boundary, provided certain *PVT* properties along the boundary are known. The necessary thermodynamic relations are[15]

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{dV}{dT}+\frac{T}{\Delta C_V}\left(\frac{dV}{dT}\right)^2\frac{dP}{dT}, \tag{7}$$

$$\left(\frac{\partial V}{\partial P}\right)_T=-\frac{T(dV/dT)^2}{\Delta C_V}, \tag{8}$$

where the total derivatives are to be taken along the

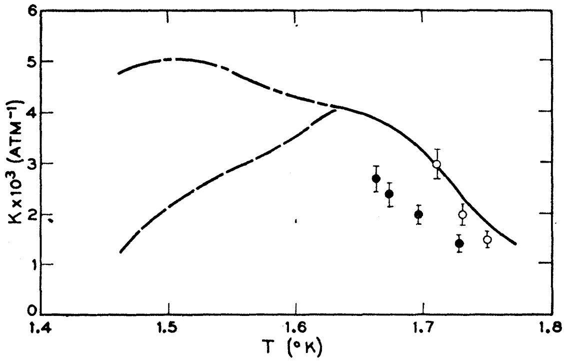

FIG. 7. The isothermal compressibility K of the γ phase of He^4. The lines and points represent the same values for K as those defined in Fig. 6 for the thermal expansion coefficient.

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[15] O. V. Lounasmaa, J. Chem. Phys. 33, 443 (1960).

phase boundary. The present results for ΔC_V and the data of Grilly and Mills yield the points in Figs. 6 and 7. In general, these results are somewhat lower than the average values over the phase. However, both α and K when calculated from Eqs. (7) and (8) are very sensitive to systematic errors in dV/dT. For this reason it is not certain that the difference between the values at the phase boundary and the average values over the phase are real.

It is interesting to note that above 1.65°K, both α and K decrease with increasing temperature. However, α decreases more rapidly than K, and thus the temperature dependence of α/K is qualitatively consistent with the volume dependence of the heat capacity [Eq. (6)].

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Phenomenological Model for the Electronic Thermal Conductivity of Superconductors

ASHOK KUMAR GUPTA AND G. S. VERMA
Department of Physics, Allahabad University, Allahabad, India

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A phenomenological model is proposed within the framework of BCS theory and the Boltzmann equation approach for the electronic thermal conductivity of superconductors limited by phonon scattering. Values of the parameters of the model are determined from comparison with the experimental data. In the case of weak coupling of electrons and lattice vibrations, it is found that τ_s, the time a quasiparticle takes to relax to the equilibrium flow of supercurrent, is comparable with τ_n in the normal state. In the case of strong electron-phonon interaction, it is found that τ_s is 10^{14} times τ_n at the reduced temperature $t=0.80$.

I. INTRODUCTION

RECENTLY Tewordt[1,2] has obtained theoretical expressions for the lifetime of a quasiparticle in a superconductor at finite temperatures and has applied successfully the results[2,3] to the problem of intrinsic electronic thermal conductivity of tin and indium, where the electron-phonon interaction is weak. But the problem of very large slopes (~5 or 6) of K_s/K_n versus T/T_c curves for mercury and lead, the two typical cases of strong electron-phonon interaction, remains still unsolved.

It has been argued[3] that the large limiting slopes of K_s/K_n measured for lead and mercury cannot be explained completely within the scope of the BCS model and a modification of the theory is strongly needed to include the strong-coupling cases. In the absence of such a theory it seems desirable to propose a phenomenological model and obtain some information regarding the behavior of the quasiparticles from the experimental data on transport properties. The proposed phenomenological model is within the framework of the BCS theory and conventional Boltzmann equation approach.

Recently doubts have been expressed regarding the applicability of the quasiparticle picture and the Boltzmann equation approach to the transport problems of

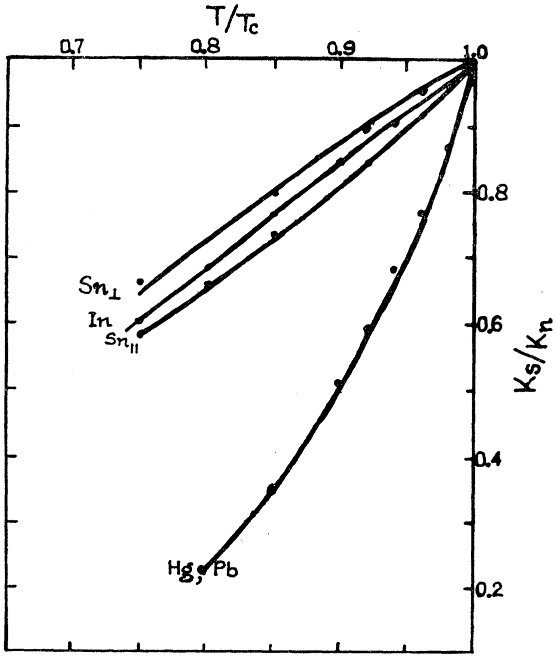

FIG. 1. Theoretical curves for the ratio of the thermal conductivity in the superconducting state K_s to that in the normal state K_n versus the reduced temperature T/T_c. Solid lines represent the theoretical results while the experimental points are shown as black dots. The curve designated by Hg,Pb is calculated by taking the ratio $2\,\epsilon_0(0)/kT$ equal to 4.1, while all other curves are with the value of the ratio equal to 3.52.

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[2] L. Tewordt, Phys. Rev. **128**, 12 (1962).
[3] L. Tewordt, Phys. Rev. **129**, 657 (1963).