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Measurement of $(\partial P/\partial T)_V$ and Related Properties in Solidified Gases. I. Solid He^4†

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A very sensitive strain gauge that is able to detect pressure changes of 2×10^{-5} bar inside a small container filled with solidified helium is described. Measurements of the variation of pressure with temperature along several isochores, both in the hcp and in the bcc phase of He^4, are reported. From these data, the equation of state at $T=0$ °K is obtained, leading to the compressibility coefficient k_T and the change in internal energy as a function of volume. The temperature variation of k_T is then obtained at several molar volumes and compared with results from other experiments. The quantity $(\partial P/\partial T)_V$ is tabulated and its temperature variation is discussed. Combination of $(\partial P/\partial T)_V$ data with those of others for the specific heat gives values of the Grüneisen coefficient, which is shown to be volume- and temperature-dependent.

I. INTRODUCTION

THIS paper describes a method for measuring with a strain gauge the pressure in a solidified gas as a function of temperature at constant volume. A study of solid He^4, both hcp and bcc phases, by this method is then presented. A similar study of solid H_2 and D_2 for various ortho concentrations has been carried out[1] and will be described in future papers. The temperature variation of the pressure, $P(T)$, for several isochores in solid He^4 is used to obtain the equation of state at $T=0$°K and the variation of the compressibility with temperature. The behavior of $(\partial P/\partial T)_V$ is briefly discussed in the light of recent evidence[2] for low optical modes in the dispersion spectrum. Combination of $(\partial P/\partial T)_V$ with specific-heat data[3,4] gives the Grüneisen "constant" γ. In a short, previous publication[5] it was shown that there is both a volume and temperature dependence of γ in this solid. This has been confirmed by the specific-heat data of Ahlers,[6] who has considerably extended the range of molar volumes over which the variation of γ was studied. Sample and Swenson[7] have also found such a behavior for solid He^3.

II. EXPERIMENTAL APPARATUS

In recent years, several versions of strain gauges for low-temperature experiments have been reported.[8–13] We wish to describe a strain gauge that has been designed to give a maximum of sensitivity and stability for measuring very small pressure changes in a reproducible way. Independently, another version based on the same idea has been developed by Adams and coworkers.[14] These authors have investigated solid He^3 and the melting curve of He^3 and He^4.

The basic requirement of the method is to measure the small pressure changes caused by temperature variations in a constant volume of solidified gas. The device adopted is a capacity strain gauge which has a sensitivity of about 2×10^{-5} bar (1 bar = 0.98692 atm). The main advantage of the capacity gauge over the resistive-type[8,9,13] gauge is that essentially no electric power is dissipated in the sample of solidified gas during the measurements.

The principle of measurement consists of forming a solid sample in the strain gauge and of measuring the pressure as a function of temperature. The cryostat has a main He^4 bath at 4.2°K. Liquid He^4 from this bath is introduced into a 50-cm^3 pot by means of a needle valve. This pot allows covering the range between 1.0 and 4.2°K. A liquid-He^3 container, thermally attached to the strain gauge, is used to operate in the temperature range down to 0.35°K.

Strain Gauge

The strain gauge is shown schematically in Fig. 1. The sample is contained in an annular space of about 0.4 cm^3. The inner wall belongs to a copper block in good thermal contact with a He^3 pot and the thermometers. The outer wall is a section of stainless-steel

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tubing with 0.5-mm wall thickness and 12.7-mm o.d. The strain on this membrane changes with the pressure in the sample container. Another stainless-steel tube is concentric with the membrane and is held in place by several small Mylar shims. The two cylinders form a capacitor with a spacing of about 0.025 mm. This capacitance C is part of a simple oscillator powered by a General Electric BD-5 tunnel diode. The inductance L is situated below the sample cavity and the tunnel diode, and associated circuitry are thermally grounded to the copper block. The frequency of the oscillator is transmitted via the coaxial cable to the top of the cryostat where it is amplified and measured by a Hewlett-Packard electronic counter. It can be shown that the relation between the pressure P acting on the membrane and the frequency is given by

$$P=\frac{1}{K}\left[1+\left\{\frac{C(0)+C_s}{C(0)}\left(\frac{\nu_0^2}{\nu_p^2}-1\right)-1\right\}^{-1}\right], \qquad (1)$$

where C_s is the stray capacitance in the tank circuit, $C(0)$ is the capacitance of the cylindrical sample container at zero pressure, and ν_p and ν_0 are the frequencies of the tank circuit with the sample at the pressure P and without the sample, respectively. The frequency ν_0 is slightly temperature-dependent and is determined at the beginning of each experiment. The constant K represents the elasticity of the stainless-steel membrane.

To use Eq. (1) for the determination of P from the frequency measurements, the constants $C(0)$, C_s, and K must be obtained. The capacitances can be calculated to sufficient accuracy by geometrical means and K is determined from calibration of ν_p versus P using liquid He^4 at 4.2°K up to 120 bar. The pressure gauge is a helicoid Ashcroft test gauge calibrated with a dead-weight tester to ± 0.05 bar. The pressure readings from the gauge for the cell calibration are then considered accurate to about 0.1 bar.

The measurement of P when the annular cell space is filled with solid He^4 assumes that the solid is plastic enough so as to behave like a fluid. This assumption is very likely to be justified in solid He, certainly at the low pressures where the present experiments are being carried out. The stability of the frequency for any of the solid samples at a given temperature, and its reproducibility after cycling, seems to indicate that any small inhomogeneity in pressure throughout the cell is rapidly annealed out.

Since in actual fact the sample volume changes slightly with pressure, it is necessary to estimate the correction to be made for obtaining $(\partial P/\partial T)_V$. Using the condition that during the measurement the number of atoms is kept constant, one finds

$$\left(\frac{\partial P}{\partial T}\right)_V=\left(1+\frac{1}{V}\frac{dV}{dP}k_T^{-1}\right)\frac{dP}{dT}, \qquad (2)$$

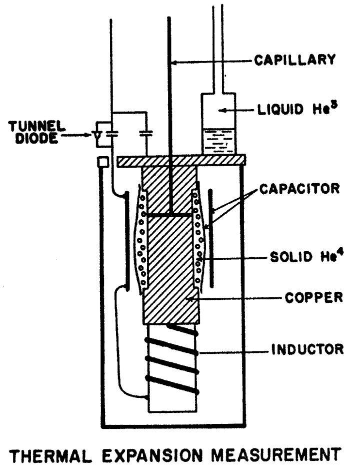

FIG. 1. Schematic presentation of the capacity strain gauge.

where dV is the variation of the sample volume for a change of pressure dP and is determined by the elasticity of the membrane, and k_T is the compressibility coefficient of the sample. For He^4 over the range $P=30$–100 bar, the quantity $(1/V)(dV/dP)k_T^{-1}$ is about 0.01. For solid H_2 at $P=30$ bar, the correction term is about 0.07. Some hysteresis was noted in the ν_P-versus-P calibration curve after first assembling the device, but it became very small after cycling the pressure from zero to about 100 bar several times. The hysteresis was then less than $\pm 0.1\%$ of the maximum working pressure.

The precision of the pressure-change measurements is limited by the stability of the oscillator. The frequency being about 15 MHz, the frequency drift is less than 1 Hz/h. Long-term changes over periods of days including all normal handling of the apparatus are of the order of several hundred cycles. These long-term effects are not important since they occur during liquid He^4 transfers into the Dewar and not during data recording. The pressure gauge had a sensitivity of 5 kHz/bar, which permitted a resolution of 2×10^{-5} bar when making measurements over 10-sec periods. The stability of both the electronic counter and the tunnel diode oscillator was such that this resolution could be used.

Thermometry

Two carbon resistors (Allen Bradley 20- and 62-Ω nominal resistance) covering different ranges of temperature above 0.4°K were used. Their resistance was measured with an ac Wheatstone bridge and calibrated, using, respectively, the 1962 and 1958 vapor-pressure temperature scale of He^3 and He^4. Below 0.7°K, the temperature scale was extrapolated by a magnetic-susceptibility thermometer, to be described below. The carbon-resistor calibration data could be fitted to an equation

$$T^{-1}=\sum_{i=-2}^{i=+2} a_i Z^i,$$

where

$$Z=\ln[R-R_{\text{leads}}]-R_0.$$

Here, R_{leads} is the electrical resistance of the wires to the resistor and R_0 is a constant. For each pair of R_{leads} and R_0, the five constants a_i were determined by the least-squares method. For the 62-Ω resistor, a standard deviation of 0.002°K (for $1.10<T<4.2$°K) or better was considered satisfactory; a standard deviation of 0.001°K (for $0.5<T<1.5$°K) could usually be achieved with the 20-Ω resistor.

The susceptibility thermometer that was developed offered sufficient advantages over the carbon resistors so that it was used as the thermometer between 4 and 0.35°K for experiments on solid H_2 and D_2. The principle is again a resonant LC tank circuit, powered by a tunnel diode, where the inductance is wrapped around an ellipsoidal crystal of chromium methylammonium alum. The frequency, which is about 300 kHz, changes with the susceptibility, and is recorded by a Hewlett-Packard electronic counter. It can be shown that the frequency will be given by

$$\nu'(T)=\nu'(T^{-1}=0)[1+C''/(T^*-\Delta)]^{-2}, \qquad (3)$$

where C'' is a calibration constant which is proportional to the Curie constant and the filling factor, T^* is the magnetic temperature, and Δ is the demagnetization constant. The magnetic temperature T^* was related to the absolute temperature by calibrating the chrome alum against cerium magnesium nitrate. The sensitivity of this thermometer, $d\nu'/dT^{-1}$, is constant in T and has a value of about -4 kHz °K. Since experience has shown that the frequency is reproducible to within 1 Hz, this gives an uncertainty of 3×10^{-4}°K at 1°K. For greater sensitivity, higher frequencies could be used, but this was found unnecessary for the He^4 or the H_2 and D_2 problems.

III. EXPERIMENTAL PROCEDURE

After cooling the apparatus to liquid-He temperatures and calibration of the carbon-resistance thermometers, the frequency ν_0 was measured as a function of temperature. Then the frequency ν_P was measured as a function of applied pressure of liquid He^4 at different temperatures below 4.2°K. To obtain a solid sample of the desired molar volume, a liquid sample was first formed under pressure, about 0.03°K above the melting curve. The temperature was then lowered slowly by pumping on the He^4 pot, which was in thermal contact with the capillary. Therefore, it could be assumed that it was the capillary that froze first. When the melting curve was reached, dP/dT suddenly became very large. Once the capillary had blocked, the sample cell was cooled rapidly to the melting temperature T_m where it filled completely with solid. The sample was then warmed a few millidegrees above the melting temperature T_m and allowed to stay at this temperature until no pressure change with time was noticeable. This annealing procedure could take up to 2 h. Finally, one or two cycles of cooling slowly 0.2°K below the melting temperature and warming back to the melting curve were made. The cycling was adequate when the warming and cooling values for dP/dT agreed to $\pm3\%$. The values of T_m and of the melting pressure P_m were then recorded.

After the solid was formed, the pressure in the He^4 gas line to the density cell was usually kept at a somewhat higher value than in the sample and was frequently checked. The solid plug in the capillary was about 15 cm long. The capillary i.d. of 0.15 mm together with the inserted 0.125-mm stainless-steel wire prevented any slippage of the plug in our experiments. This point had been carefully considered in the designing of the cryostat. The amount of the sample in the cell thus was held constant, as shown by the reproducibility of the data.

The cumulative experience with this method of sample preparation indicates that effective annealing away of strains in the solid can only occur in the presence of a small amount of liquid. Other experiments[15] have also indicated that an annealing procedure can play a large part in the measured properties of the solid; therefore great care was taken on this point. The molar volume was determined, after annealing, from this melting temperature T_m using the V-T_m data by Grilly and Mills,[16] with the small temperature correction between 1.4 and 1.8°K as taken by Ahlers.[17] For the measurements in the bcc phase, use was made of Fig. 2 in Ref. 3 for the determination of V.

The method of taking data then consisted in cooling the solid sample at rates from 2 to 5m°K/min to the lowest temperatures and warming it at the same rate to the melting curve. During this time, the frequency of the sample tank circuit and another set of numbers corresponding to the thermometer resistance were recorded directly on IBM data processing cards by means of an automatic system designed for the IBM 526 keypunch.[18] Several computer programs were written that included the strain-gauge and carbon-resistor calibrations to produce the P-versus-T lists from the data originally recorded on cards. The final step in the data-reduction process was to calculate the derivative dP/dT from the lists of approximately

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[15] See, for instance, J. P. Frank, Phys. Letters **11**, 208 (1964); L. P. Mezhov-Deglin, Zh. Eksperim. i Teor. Fiz. **49**, 66 (1965) [English transl.: Soviet Phys.—JETP **22**, 47 (1966)].

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[18] The reader interested in the details of this equipment is referred to the J. F. Jarvis, Ph.D. thesis, Duke University, 1967 (unpublished).

evenly spaced values of $P(T)$. The most obvious means of obtaining the derivatives is to plot the data and obtain the slopes by graphical techniques. However, for the quantity of data produced in this experiment, this method was too time consuming. Two numerical differentiation methods were used where fitting was done to a linear or a quadratic equation in T over a limited temperature range. In the first version, a fixed number of points that spanned 30–100 m°K were fitted with a linear equation in T and the derivative was calculated at the average temperature of the points to be used for the fit. This process was repeated to give derivative values every 50 to 100 m°K. From the resulting smoothed curve, a table of derivative values at specified temperatures was made. The second and most used numerical method was to make a fit to all points in the interval $(T_0-\delta T)$ to $(T_0+\delta T)$, with the derivative being evaluated at one temperature T_0. For the hcp He^4, δT was typically 25 m°K, and a quadratic expression was used. The resulting values of dP/dT for each T_0 were then averaged to produce a final list of derivatives that encompassed all the $P(T)$ data for a given density. The graphical differentiation technique and both numerical differentiation techniques showed no systematic differences when compared. The numerical methods used in this portion of the data reduction are preferred to the graphical techniques since the accuracy is considerably better and the amount of effort involved in obtaining the $dP(T)/dT$ list is much smaller. Both these advantages are a direct consequence of having the ability to record automatically large quantities of data. The relative accuracy of dP/dT is, of course, highly dependent on its magnitude. The largest errors occurred close to the melting temperature, where the problems of hysteresis gave dP/dT to $\pm 3\%$. At temperatures below about 0.8°K, when dv_p/dT became comparable to dv_0/dT, the scatter was again larger. Over most of the temperature range covered, the reproducibility of the $P(T)$ curves, both warming and cooling, made it possible to measure dP/dT to within ± 0.001 bar $°K^{-1}$ over a temperature interval of 0.05°K. The absolute accuracy is limited by the calibration uncertainty of the density cell.

IV. RESULTS AND DISCUSSION

hcp Phase

The quantity dP/dT, corrected to $(\partial P/\partial T)_V$, has been measured as a function of temperature at eight molar volumes ranging from 17.77 to 20.72 cm³/mole. Table I gives the ratio $(\partial P/\partial T)_V$ for the various samples. Isochores at lower molar volumes were not taken because it was feared that the gauge would not deform elastically at pressures higher than 120 atm, which is the initial pressure necessary to form a sample of $V=18.22$ cm³/mole by the blocked-capillary method. The 17.77-cm³/mole sample was formed at constant pressure by using a heater in the fill capillary to prevent a plug from forming. The $(\partial P/\partial T)_V$ data, scaled by a factor of T^{-3} are plotted in Fig. 2 for the various molar volumes. Such a plot is more useful and sensitive than a presentation of $(\partial P/\partial T)_V$, since it reveals the existence of a region in which this ratio is proportional to T^3. From the scatter of the experimental data, it was concluded that $(\partial P/\partial T)_V$ could be measured with a precision almost comparable with that of specific heats.

TABLE I. The ratio $(\partial P/\partial T)_V$ (in bar $°K^{-1}$) in the hcp phase of He^4 for various molar volumes as a function of temperature.

T (°K) \ V (cm³/mole)	17.77	18.22	18.80	19.41	19.93	19.97	20.40	20.72
0.50	0.0056	0.0069	0.0083	0.010	0.012	0.012	0.015	0.017
0.60	0.0097	0.012	0.014	0.018	0.021	0.022	0.026	0.030
0.70	0.016	0.019	0.023	0.028	0.034	0.034	0.041	0.048
0.80	0.023	0.028	0.034	0.042	0.051	0.052	0.062	0.072
0.90	0.033	0.040	0.048	0.060	0.073	0.074	0.090	0.104
1.00	0.045	0.055	0.067	0.083	0.102	0.104	0.126	0.146
1.10	0.060	0.074	0.090	0.111	0.139	0.141	0.173	0.202
1.20	0.078	0.096	0.118	0.147	0.185	0.188	0.233	0.276
1.30	0.099	0.122	0.152	0.192	0.244	0.248	0.309	0.372
1.40	0.124	0.154	0.194	0.248	0.317	0.324	0.406	0.493
1.50	0.155	0.193	0.245	0.318	0.409	0.418	0.530	0.648
1.60	0.191	0.239	0.306	0.402	0.521	0.532	0.681	0.738
1.70	0.233	0.295	0.380	0.505	0.656	0.672	0.860	1.07
1.80	0.284	0.359	0.467	0.626	0.820	0.839	1.08	
1.90	0.345	0.435	0.570	0.765	0.993	1.04	1.33	
2.00	0.415	0.522	0.688	0.927	1.22	1.27		
2.10	0.494	0.623	0.824	1.11	1.50	1.54		
2.20	0.584	0.738	0.980	1.33				
2.30	0.684	0.866	1.15	1.57				
2.40	0.797	1.01	1.35	1.85				
2.50	0.921	1.17	1.57					
2.60	1.06	1.36	1.81					
2.70	1.21	1.56	2.08					
2.80	1.38	1.78	2.38					
2.90	1.56	2.02						
3.00	1.76	2.28						
3.10	1.97	2.56						
3.20	2.21							
3.30	2.46							
3.40	2.75							
3.50	3.06							

Several other thermodynamic properties can now be obtained fairly directly from the thermodynamic relations

$$(\partial P/\partial T)_V=\alpha_p/k_T, \tag{4}$$

where

$$\alpha_p\equiv(1/V)(\partial V/\partial T)_P$$

and

$$(\partial\alpha_p/\partial P)_T=-(\partial k_T/\partial T)_P. \tag{5}$$

The compressibility coefficient $k_T(T=0)$ was obtained after forming the extrapolated $P(V)$ curve at $T=0°K$. These values of $k_T(T=0)$ were then used to calculate the first approximation of α_p from Eq. (4), and then $(\partial\alpha_p/\partial P)_V$. These values of $k_T(T)$, obtained by integrating Eq. (5), were in turn used to get new values of α_p and the iteration procedure was repeated. After three trials, the values converged and are presented in Table II. For a Debye solid, it can be shown[3] that the quantity $[k_T^{-1}(T=0)-k_T^{-1}(T)]V/RT$ is a function of T/Θ_0 only, and Edwards and Pandorf[3] used this representation to tabulate their values derived from specific-

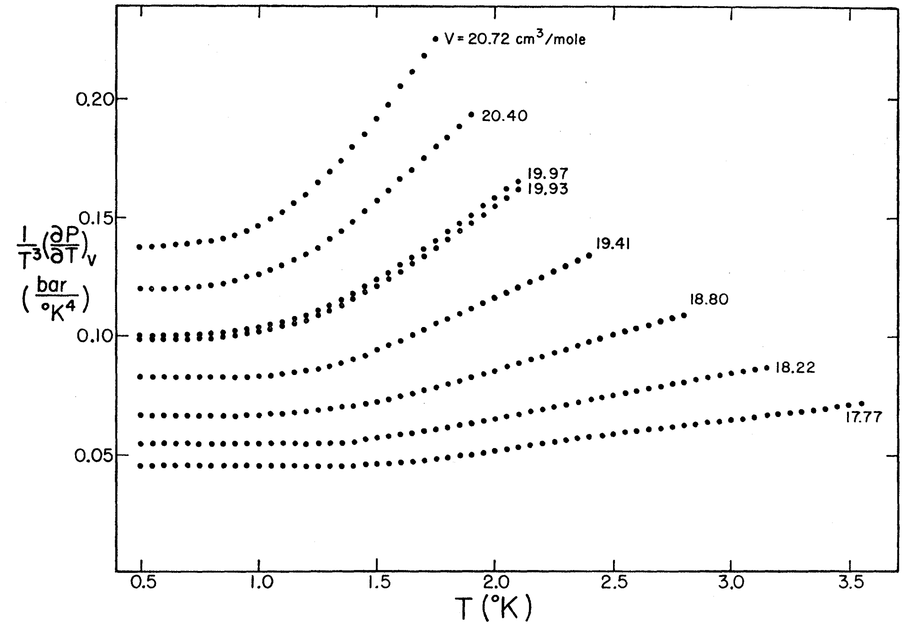

FIG. 2. Plot of $(1/T^3)(\partial P/\partial T)_V$ versus temperature for the different molar volumes in the hcp phase.

heat data. In Fig. 3, our results are presented in this manner, the Θ_0 being taken by interpolating the results of Ref. 3, Table I. As can be seen, there is a large discrepancy between our more direct data and those of Edwards and Pandorf.[3] It is also quite apparent that the reduced expression for the compressibility coefficient used above is not a function of T/Θ_0 independent of volume.

TABLE II. The coefficient of thermal expansion in $10^3(°\text{K})^{-1}$ in hcp He^4 at various molar volumes as a function of temperature.

$T \diagdown V$	17.77	18.22	18.80	19.41	19.93	19.97	20.40	20.72
0.50	0.007	0.010	0.015	0.024	0.034	0.035	0.048	0.060
0.60	0.013	0.018	0.026	0.041	0.058	0.060	0.082	0.103
0.70	0.020	0.029	0.042	0.065	0.092	0.045	0.131	0.165
0.80	0.030	0.043	0.063	0.097	0.139	0.143	0.197	0.249
0.90	0.043	0.061	0.090	0.137	0.200	0.206	0.285	0.360
1.00	0.059	0.083	0.123	0.190	0.279	0.287	0.400	0.509
1.10	0.079	0.111	0.166	0.255	0.379	0.391	0.550	0.705
1.20	0.102	0.145	0.218	0.337	0.506	0.523	0.740	0.962
1.30	0.130	0.185	0.282	0.441	0.667	0.691	0.984	1.30
1.40	0.163	0.233	0.360	0.570	0.870	0.901	1.30	1.73
1.50	0.203	0.292	0.454	0.730	1.12	1.16	1.70	2.28
1.60	0.250	0.362	0.576	0.925	1.43	1.49	2.19	2.97
1.70	0.306	0.446	0.705	1.16	1.81	1.88	2.77	3.83
1.80	0.374	0.544	0.869	1.44	2.27	2.36	3.49	
1.90	0.453	0.660	1.06	1.77	2.76	2.92	4.34	
2.00	0.546	0.792	1.28	2.14	3.40	3.60		
2.10	0.650	0.948	1.54	2.58	4.22	4.38		
2.20	0.769	1.12	1.84	3.12				
2.30	0.902	1.32	2.17	3.70				
2.40	1.05	1.55	2.55	4.38				
2.50	1.22	1.80	2.98					
2.60	1.41	2.09	3.45					
2.70	1.61	2.40	4.00					
2.80	1.83	2.76	4.60					
2.90	2.09	3.15						
3.00	2.36	3.57						
3.10	2.66	4.04						
3.20	2.99							
3.30	3.35							
3.40	3.76							
3.50	4.21							

From the calculated $P(V)$ curve at $T=0$, the internal energy $U_0(V)/R$ was calculated for the various molar volumes using

$$U_0(V)-U_{0s}(V_s)=-\int_{V_s}^{V} PdV. \tag{6}$$

The standard internal energy U_s of the solid at the melting curve was taken to be $U_s=-5.96$°K as calculated by Edwards and Pandorf[3] based on the results of Swenson.[19] The consistency of U_0 with the tabulation of Edwards and Pandorf is then excellent. Several relevant thermodynamic quantities at the melting point and at the absolute zero are presented in Table III for the various molar volumes. First it should be noted that the melting-curve data (P_m versus T_m) are in excellent agreement within experimental error, with those of Grilly and Mills.[16] The thermal expansion at the melting curve is systematically higher than that found by Grilly[20] by up to 50%. The thermal expansion at T_m agrees well with the data of Edwards and Pandorf[3] except above 19 cm³/mole, where the present data are systematically higher.

We further define the Grüneisen coefficient γ from the relation

$$(\partial P/\partial T)_V=\gamma C_v/V. \tag{7}$$

It is well known that if the specific heat C_v can be represented by $C_v(T,V)=f(T/\Theta_0)$, where Θ_0, the Debye temperature at 0°K, is a function of V only,

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[19] C. A. Swenson, Phys. Rev. **79**, 626 (1950).

[20] E. R. Grilly, in *Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, 1966* (Viniti, Moscow, 1967).

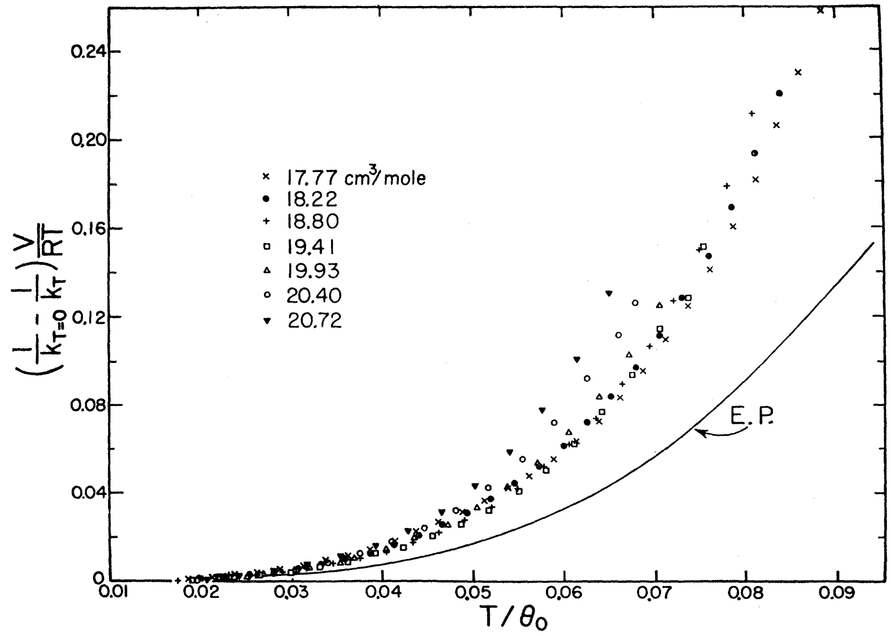

FIG. 3. Plot of the reduced compressibility change versus T/Θ_0. Solid line: Edwards and Pandorf (Ref. 3).

TABLE III. Thermodynamic properties of hcp He^4 at the melting curve and at 0°K.

T_m (°K)	P_m (bar)	V [a] cm^3/mole	$(\partial P/\partial T)_{V_m}$ (bar/°K)	α_{pm} (10^3 °K^{-1})	k_m (10^3 bar^{-1})	$k_T(T=0)$ (10^3 bar^{-1})	$P_m - P_0$ (bar)	Θ_0 [b] (°K)	γ [c]	$U_0(V)/R$ (°K)
3.560	109.2	17.77	3.26	4.54	1.39	1.31	2.53	39.8	2.60	−3.69
3.200	91.1	18.22	2.87	4.56	1.59	1.51	2.00	37.0	2.62	−4.22
2.808	70.5	18.80	2.38	4.62	1.94	1.85	1.47	34.7	2.67	−4.76
2.450	54.5	19.41	2.00	4.76	2.38	2.29	1.05	32.2	2.75	−5.22
2.146	42.7	19.93	1.63	4.61	2.82	2.73	0.73	30.1	2.80	−5.52
2.124	43.1	19.97	1.61	4.60	2.86	2.77	0.71	29.9	2.80	−5.54
1.912	34.3	20.40	1.36	4.45	3.27	3.17	0.54	28.2	2.87	−5.74
1.753 [d]	29.7	20.72	1.22	4.36	3.58	3.47	0.44	26.9	2.92	−5.85

[a] Determined from the V-T_m data of Grilly and Mills (Ref. 16).
[b] Obtained by interpolation of the data of Edwards and Pandorf (Ref. 3) in Table I of their paper.
[c] Value at $T=0$°K, obtained using Eq. (7) and the specific-heat data of Edwards and Pandorf (Ref. 3).
[d] hcp-bcc phase boundary.

then the coefficient γ is constant with temperature and is given by $\gamma = d\ln\Theta_0/d\ln V$. In Fig. 4 we have plotted the γ obtained from Eq. (7) by combining our data of $(\partial P/\partial T)_V$ with the specific-heat results of Edwards and Pandorf,[3] taken from their Table I. These authors, on the basis of specific-heat data alone, found the Grüneisen constant to be $\gamma = 2.60$ and independent of molar volume. Combination of thermal and pressure data is a more direct way of obtaining γ and indicates both a volume and temperature dependence. Figure 4, combined with the appropriate values of Θ_0, shows that the minimum of γ is situated near $T/\Theta_0 \approx 0.05$. The existence of this minimum is somewhat outside the experimental error claimed in both experiments. Ahlers[6] has recently made precise measurements of C_v at several molar volumes down to 1.35°K, and from his data he obtained γ as a function of T and V. His extrapolated C_v data at 1.0°K and below agree well with those of Edwards and Pandorf. However, there is a systematic discrepancy which increases with temperature, the specific-heat data of Ahlers being smaller by about 3–5% at 1.50°K.

Use of the data of Ahlers in Eq. (7) in combination

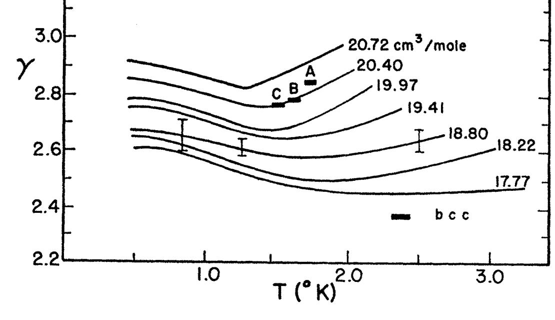

FIG. 4. Plot of the Grüneisen factor γ versus T for various molar volumes in the hcp and bcc phases, as obtained from $(\partial P/\partial T)_V$ data and interpolated C_V of Edwards and Pandorf (Ref. 3). Rectangles mark molar volumes in the bcc phase: (C) 20.96 cm^3/mole; (B) 20.92 cm^3/mole; (A) 20.91 cm^3/mole.

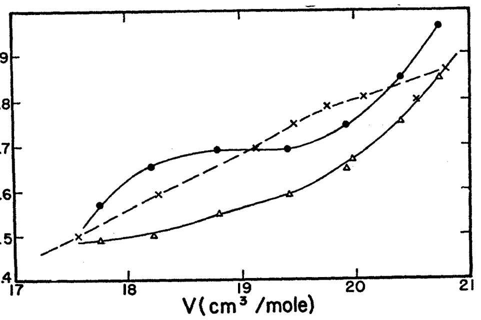

FIG. 5. The Grüneisen factor γ versus molar volume in the hcp phase at 1.50°K. Solid circles: from $(\partial P/\partial T)_V$ data and C_v data of Ahlers (Ref. 6). Triangles: from $(\partial P/\partial T)_V$ data and C_v data of Edwards and Pandorf (Ref. 3). Crosses: from C_v data alone of Ahlers (Ref. 6).

with the present $(\partial P/\partial T)_V$ results gives a less pronounced minimum for γ and a larger temperature increase above this minimum. At 1.5°K, γ so obtained is then consistent to within 2% with the γ obtained from specific-heat data alone. This is shown in Fig. 5.

Another useful thermodynamic result can be obtained from the relation

$$C_P/C_V-1=(\partial P/\partial T)^2{}_V V k_T T/C_V. \qquad (8)$$

The quantity $(C_P/C_V)-1$ was obtained by again making use of the present strain-gauge data together with the C_V results of Edwards and Pandorf.[3] The ratio is plotted against T/Θ_0 in Fig. 6 and, like other quantities derived, it cannot be expressed as a reduced curve.

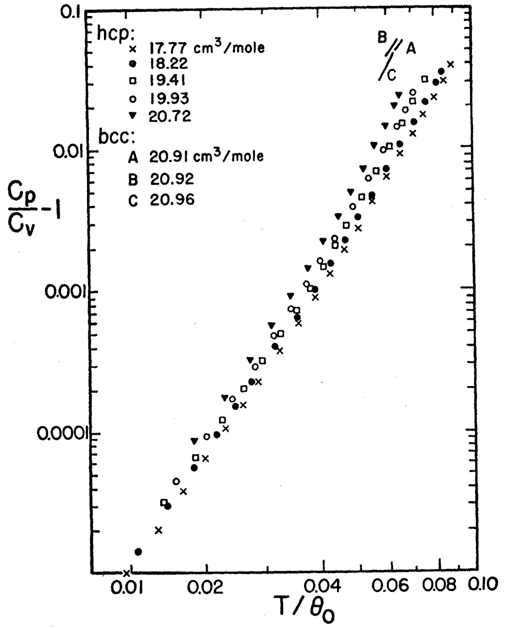

FIG. 6. Plot of the ratio $(C_p/C_v)-1$ calculated from Eq. (5) for hcp and bcc He^3. The lettering for the bcc phase is the same as for Fig. 4.

Sample and Swenson[7] have been able to express their specific-heat data in bcc He^3 as the sum of a lattice T^3 term and the low-temperature approximation of an Einstein function $E(\Phi/T)$. The excitation energy Φ was found to be 13.2°K for $V=20.2$ cm^3/mole and decreasing to 7°K at 23.80 cm^3/mole. We have also attempted such an empirical fit using this simple model together with Eq. (7) and assuming a temperature-independent $\gamma=\gamma_0$. An excellent fit was obtained for all densities, the excitation energy being about 0.49 Θ_0, which is $\Phi=12.7$°K for a crystal under $P=27.4$ bar. It is somewhat tempting to relate this energy to the average energy of the low-lying optical mode found from neutron scattering in hcp He^4.[2] However, the fit of the simple model outlined above to the data must be considered fortuitous, because no account is taken of the dispersion in the acoustical modes which gives a temperature variation of Θ_D. Also, pending more extensive neutron-scattering data along different crystallographic directions, it is hardly possible to estimate the effect of the optical modes on thermal properties.

Solid bcc He^4

Once the molar volume was determined from the melting temperature T_m, the $P(T)$ data in this phase were taken in the same manner as the hcp phase. The cooling rates were made slower, ranging from 0.5 to 2 m°K per min. The temperature resolution was 10^{-5}°K, and data points were recorded every 0.2 m°K, in order to produce sufficient data for the numerical-differentiation procedure. The most striking part of the measurements in this phase was the strong tendency of the phase to supercool. The slopes measured in the supercooled region were very reproducible and have accounted for a large amount of data taken in this phase. The maximum width of the bcc phase at constant volume is about 0.035°K. The supercooled region could often be made to extend more than 0.05°K below

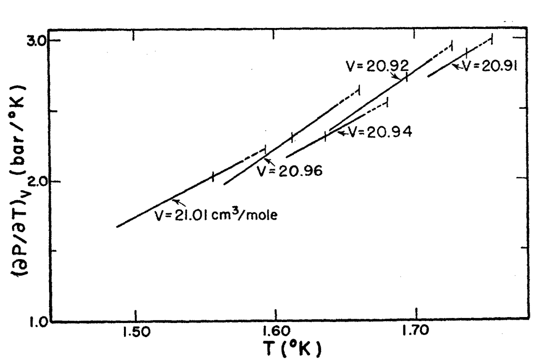

FIG. 7. Plot of $(\partial P/\partial T)_V$ in the bcc phase as a function of T. The vertical dashes represent the equilibrium bcc phase boundaries. The dashed portions of the $(\partial P/\partial T)_V$ lines represent extrapolations into regions where "rounding off" of the boundaries occurs. The scatter of the experimental points (not shown) about the lines is about ±2%.

TABLE IV. The thermal-expansion coefficient α_p (10^3 °K^{-1}) in the bcc phase of He^4 for several molar volumes, as a function of temperature. The highest temperature given for each molar volume is the melting temperature. V is in cm^3/mole.

$V=20.91$		$V=20.92$		$V=20.94$		$V=20.96$		$V=21.01$	
T	α_p	T	α_p	T	α_p	T	α_p	T	α_p
1.71	10.3	1.65	9.1	1.60	8.2	1.56	7.4	1.49	6.4
1.73	10.9	1.67	9.7	1.62	8.7	1.58	8.0	1.51	6.8
1.75	11.5	1.69	10.5	1.64	9.2	1.60	8.5	1.53	7.2
1.755	11.8	1.71	10.9	1.66	9.7	1.62	9.0	1.55	7.6
		1.726	11.3	1.68	10.3	1.64	9.6	1.57	8.0
				1.686	10.4	1.662	10.1	1.593	8.4

the equilibrium phase boundary, more than doubling the equilibrium width of the phase.

When data were taken for warming from the hcp-bcc mixed-phase region, some rounding of the transition was noted, i.e., the slope dP/dT did not change suddenly, but only gradually over a temperature interval of about 5 m°K. The same phenomenon was also noticed when warming from the bcc solid to the melting curve. In this case, the temperature range of the "curving" was about 10 m°K. It was hence on cooling that the most extensive data could be obtained, owing to the supercooling phenomenon.

The values of $(\partial P/\partial T)_V$ for several molar volumes in the bcc phase are presented in Fig. 7. Taking the compressibility values given by Grilly and Mills,[16] the thermal expansion α_p was calculated and is presented in Table IV. There is agreement within experimental error with Grilly's data and also with those calculated by Edwards and Pandorf.[4] In Fig. 4, the Grüneisen γ for the bcc phase is plotted and is seen not to be greatly different from that obtained for a similar molar volume in the hcp phase.

V. CONCLUSION

Measurements of the change of pressure with temperature along different isochores in solid He^4 have complemented the specific-heat data. On the whole, there is good consistency with the results and conclusions of Edwards and Pandorf, namely, both α_p and k_T are "well behaved" in both solid phases. The inconsistency worth mentioning is that of the temperature variation of k_T, which in our work is approximately double that calculated in Ref. 3. The Grüneisen factor, determined by combination of our $(\partial P/\partial T)_v$ data with the C_v data of Edwards and Pandorf,[3,4] is found to be volume- and temperature-dependent with a shallow minimum near $T/\Theta_0 \sim 0.05$. Combination of our $(\partial P/\partial T)_v$ data of Ahlers gives a Grüneisen constant consistent with that derived by him[6] from his C_v data alone.

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