difficulties that arise when the slow-motion approximation is applied to other physical problems.

The ideas presented here arose during a study[8] of gravitational radiation damping, where the problem of runaway solutions had to be solved before work could safely proceed. I would like to thank Professor P. A. Lagerstrom for help with this problem.

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[†] Also member of the Board of Studies in Physics, U. of Calif. Santa Cruz, Calif.

[1] P. A. M. Dirac, Proc. Roy. Soc. (London) A167, 148 (1938).

[2] F. Rohrlich, *Classical Charged Particles* (Addison-Wesley, Reading, Mass., 1965).

[3] This is a routine problem in matching. See, for example, J. Cole, *Perturbation Methods in Applied Mathematics* (Blaisdell, Waltham, Mass., 1968).

[4] For a discussion of delay equations, see T. L. Saaty, *Modern Nonlinear Equations* (McGraw-Hill, New York, 1967), Chap. 5.

[5] D. J. Kaup, Phys. Rev. 152, 1130 (1966) has also discussed the role of higher terms in removing runaway solutions for the case of the classical electron. Here we are interested in addition with reconciling the approximate results with the correct results to improve the approximation scheme.

[6] See J. Cole, Ref. 3.

[7] G. N. Plass, Rev. Mod. Phys. 33, 37 (1961).

[8] W. L. Burke (unpublished).

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Thermodynamic Properties of hcp He^4

Guenter Ahlers
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Precision heat-capacity measurements at constant volumes for hcp He^4 are presented for molar volumes between 13.7 and 20.8 cm^3 and for temperatures between 1.3 °K and the melting temperature. These data are used to calculate the deviations of the equation of state for hcp He^4 from the Grüneisen equation of state. It is found that the reduced Debye temperature Θ/Θ_0 is *not* a volume-independent function of the reduced temperature T/Θ_0 and that the Grüneisen parameter γ is both volume and temperature dependent. It is observed that γ and Θ/Θ_0 at a given volume and T/Θ_0 are the same for hcp He^4 and hcp He^3, and it is suggested that the observed volume and temperature dependence of γ and Θ/Θ_0 are typical for close-packed van der Waals solids in general. The temperature-dependent contributions to other thermodynamic functions are given as well.

I. INTRODUCTION

In this paper detailed and precise constant-volume heat-capacity (C_v) measurements for hcp He^4 are reported. These data are sufficiently extensive to yield complete information about the temperature-dependent contributions to the equation of state for molar volumes greater than about 13 cm^3. The work was undertaken because a careful comparison of the thermal properties of hcp He^4 with available results[1] for hcp He^3 is expected to reveal any nonclassical isotope effect on the thermodynamic properties of the solids. If such nonclassical effects exist, they would be more noticeable in helium than in other simple solids, because the relative contribution of the zero-point energy to the total internal energy is larger here. If no such effects are observable, or if their nature is simple, it is not unreasonable to use solid helium as a model substance for the prediction of the properties of other close-packed solids whose binding is by van der Waals forces. There has been great temptation in the past[2] to look upon solid helium as such a model substance because its thermal properties can be studied readily over a large volume range. For most other solids, such an investigation would be very difficult because very large pressures would be required.

If solid helium is to be looked upon as a model solid, then it is of interest to examine the thermal properties of He^4 in detail and to compare them to simple equations of state such as the one proposed by Grüneisen.[3] If the isotope effect in helium is found to be essentially classical, it might be hoped that any observed deviations from the

Grüneisen model for the equation of state are not quantum effects peculiar to solid helium, but rather deviations to be expected in other close-packed van der Waals solids as well.

There have been several previous measurements of C_v for hcp He^4 over various volume and temperature ranges. All except the recent work by Edwards and Pandorf[4] and by Gardner, Hoffer, and Phillips[5-7] were reviewed recently, together with related work, by Dugdale.[2] However, all these results either were limited to a small volume range or are believed to be subject to probable errors of 1% or more. In principle it is possible to obtain data which are one order of magnitude more precise,[8] covering molar volumes which vary by a factor of 1.5 or 2. The measurements presented here generally have a precision of the order of 0.1%. They cover the volume range of the solid from 13.7 to about 21 cm^3/mole and extended from 1.37 °K to the melting line. As a result of the high precision of the data it was possible to determine both the volume and the temperature dependence of deviations from the Grüneisen equation of state, as reflected in the volume and temperature dependence of the Grüneisen parameter γ. Within the precision of previous C_v measurements on hcp He^4, γ was independent of volume and temperature.[4] It also was possible to make a meaningful comparison with the measurements on hcp He^3.[1] The isotope effect is essentially classical, except possibly for a small departure from the classical ratio between the Debye temperatures at 0 °K.

Some of the results of this work have been reported briefly elsewhere.[9-11]

II. APPARATUS

A. Thermometers

The thermometer and the temperature scale are the same as those used in previous measurements.[8,12,13] The thermometer calibration was checked before and after this work below 4.2 °K and at the n-H_2 triple point. It agreed with previous calibrations within experimental error [0.5×10^{-3} °K below 4.2 °K and 1×10^{-3} °K at the n-H_2 triple point].

B. Calorimeter

The calorimetric apparatus was a modification of that used previously[8,12,13] and is very similar to the one described by Senozan.[14] It is shown schematically in Fig. 1. A heavy-walled beryllium-copper cell with a volume of about 12 cm^3 was installed in the sample space. It was connected by a stainless-steel capillary of 0.08-cm o.d. and 0.028-cm i.d. to the external sample handling system. The capillary had its own vacuum jacket except for the lowest 15 cm, which passed through the main calorimeter vacuum. The special vacuum jacket could be filled with exchange gas. The capillary was attached thermally to the liquid-helium bath at the point where it left its vacuum jacket (A in Fig. 1) by means of a thin copper wire. At point A there was also a heater, which permitted raising the capillary temperature above the bath temperature by several degrees, and a thermometer. The lowest 18 cm of the capillary contained a stainless-steel wire of 0.025-cm diam. The primary purpose of this wire was to reduce the thermal conductance of the helium core in the capillary. The cell was cooled from the bottom by means of a mechanical heat switch. This arrangement permitted adequate control over the thermal gradient in the sample cell and the capillary, and made it possible to fill the cell with solid at nearly constant pressure, since freezing could be started at the bottom.

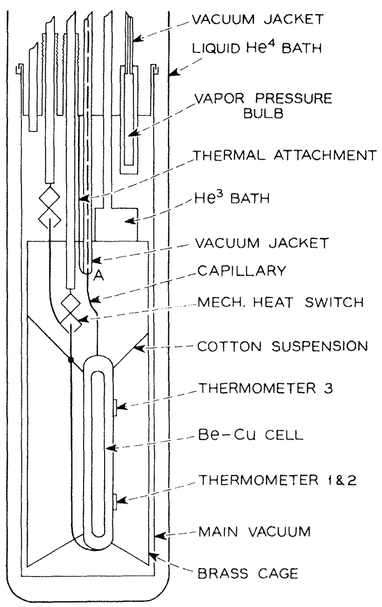

FIG. 1. Schematic diagram of the calorimeter.

C. Sample Cell

In precision calorimetry, it is desirable to make the sample as large as possible. In the present case, the cell volume was limited essentially by the necessary external gas-handling and compression system. This external system would become excessively large if the sample were larger than about 1 mole. It was therefore decided to make the cell volume about 12 cm^3.

The sample shape was dictated by several qualitative considerations. Although solid helium is very soft, it does have some shear strength, and any sample which is not solidified at absolutely constant pressure will have a density gradient. There is no information which would permit an estimate of the magnitude of this gradient. However, Edwards and Pandorf[4] used a copper "sponge" sample cell with an average pore diameter of 10^{-3} cm, and they observed considerable annealing effects, even at temperatures well below the melting temperature. Their experience shows that this type of cell is unsuitable for the precision measurements desired here. On the other hand, it is likely that samples for which the diameter is about equal to the length could have thermal relaxation times near the melting temperature which are excessively long. Previous experience[15,16] had indicated that a sample diameter of 0.95 cm resulted in thermal relaxation times of at most a few minutes. It was decided to make the sample diameter 1.27 cm, since thermal relaxation times of 5–10 min can be tolerated with the degree of thermal isolation attainable in the present calorimeter. The length of the samples, therefore, was about 10 cm. The heater (about 7000 Ω of 2.5×10^{-3}-cm-diam manganin wire) was wound over the whole length of the sample cell to minimize the necessary axial heat flow.

Obviously it is desirable to keep the cell walls as thin as possible to avoid an excessively large heat capacity of the empty cell. Since the minimum molar volume at which measurements can be made is dictated by the thickness of the cell walls and the strength of the material, a compromise between accuracy and volume range was necessary. A minimum volume of 13–14 cm^3/mole was considered small enough to yield adequate information and yet did not require excessively heavy cell walls. Beryllium-copper was used to construct the cell. Pressures up to 600 bar were required. The outside-to-inside-diameter ratio for the cell was made equal to 1.31, and the calculated burst pressure is about a factor of 3 larger than the maximum pressure to be used. This safety margin is desirable because of the serious consequences of a catastrophic failure. The cell was closed by a cap which was attached to the cell body by class-3 threads covered with soft solder. The capillary had been silver soldered into a hole in the cap prior to heat treating the beryllium-copper.

D. Pressure System

A schematic diagram of the pressure and sample-handling system is given in Fig. 2. The helium gas to be used originated in a commercial cylinder A. A sample could be condensed into the auxiliary cell B and reevaporated either into large evacuated containers C or through the manifold D into one arm of the stainless-steel U tube E. The U tube was half-filled with mercury, and the mercury could be pushed up or let down in the sample arm by means of oil in the other arm and the pumping system F. The sample could be compressed with the U tube into the cell in the calorimeter G. Pressure gauges H were available to monitor the process. The maximum attainable pressure is limited by the design pressure of the U tube, which is 700 bar. In principle this system is similar, but simpler, than one previously described,[17] and design details need not be repeated here.

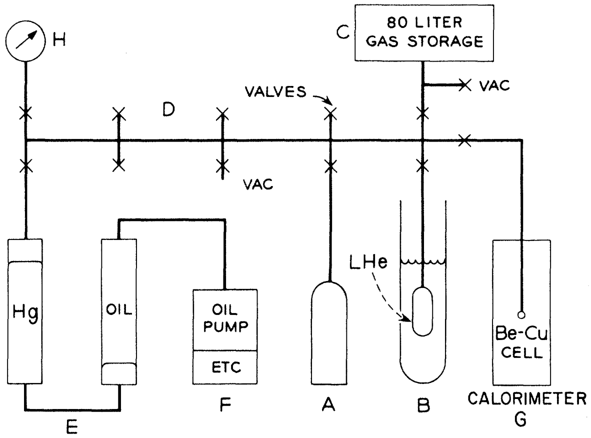

FIG. 2. Schematic diagram of the pressure system.

E. Gas Storage System

The gas storage system (C, Fig. 2) consisted of eight containers, two each of 2-, 5-, 10-, and 20-liter capacity, and a glass bulb of 2-liter volume, all connected through individual valves to a common manifold. The entire system was contained in an insulated box. Thermal gradients in the box never exceeded 0.1 °C. The manifold was connected to a mercury manometer, to the high-pressure manifold (D in Fig. 2), and to another external manifold useful for introduction of various gas samples. The volume of the 2-liter bulb was determined by weighing it empty and when filled with distilled water with an error of less than 0.01%. All other volumes in the system were calibrated against the glass bulb by expansion of helium gas and by measuring the pressure change on the mercury manometer. The volumes were calibrated several times, and the scatter in the data did not exceed ±0.1%.

F. Sample Preparation

During the course of this work, two gas samples were prepared. For the first one, an attempt at purification was made by condensing the helium in the auxiliary cell B and reevaporating it into the storage containers C. It was believed that any remaining impurities would condense in the capillary leading to the cell in the calorimeter when the solid sample was being prepared. Initial compression into the U tube E was achieved by a second condensation in B and reevaporation. Most of the measurements (solid samples 1–14) were carried out on this gas sample. However, careful analysis of the heat-capacity measurements suggested slightly anomalous behavior at the lowest temperatures and smallest volumes. A second gas sample therefore was prepared by replacing cell B by an adsorption cell with separate inlet and outlet. Helium from the cylinder A was passed through this cell at 15 °K at pressures from 0 to 100 bar directly into the U tube E. Solid samples 15–17 were prepared from this gas sample.

G. Cell Volume

The volume of the sample cell was determined by filling it with liquid hydrogen at several bar pressure and a temperature less than the normal boiling point. When the cell was full, the pressure was reduced to about 1 bar and the capillary temperature at point A (Fig. 1) was raised above the normal boiling point. This resulted in a cell filled with liquid and an essentially empty capillary. After pressure and temperature equilibrium was attained, the liquid sample was expanded into calibrated volumes in the gas storage system and the cell temperature was raised to 78 °K. The number of moles of gas was determined from the final gas pressure with an accuracy of 0.1%. Appropriate corrections for nonideal gas behavior at room temperature[18] were made. Both normal hydrogen and parahydrogen were used. From published values for the molar volumes,[18,19] the cell volume was calculated. For normal hydrogen, corrections for the ortho-para conversion[20] were made, and the compression from vapor pressure to the sample pressure was taken into account. The results are given in Table I.

TABLE I. Determination of cell volume.

Substance	T (°K)	P (bar)	Molar vol. (cm^3/mole)	Cell vol. (cm^3)
71.8% o-H_2	19.01	1.00	27.810	11.821
p-H_2	18.597	0.64	27.752	11.789
p-H_2	18.451	0.64	27.693	11.806
Average	...	...	...	11.806 ±0.016

Because it was considered desirable to confirm the above measurements with a different fluid, several molar volume determinations were made for liquid He^4 assuming a cell volume of 11.806 cm^3. The results are given in Table II. In this case, corrections for the difference between saturated vapor pressure and the sample pressure were made assuming a compressibility of 10^{-2} bar^{-1}. At the lower temperatures, the uncertainty in this correction is appreciable, and therefore the volume change due to the compression is given also in Table II in the column labeled ΔV. The results differ systematically by about 0.7% from the equation for the molar volume proposed by Kerr and Taylor.[21] This is well outside of the experimental error of this work. It implies that there exists a systematic error either in the molar volume determinations for hydrogen,[18,19] in the Kerr-Taylor equation for the molar volume of helium,[21] or in both. *Arbitrarily* the cell volume 11.806 cm^3 was retained for this work. A very small correction for the effect of pressure in the form $V = 11.806 \times (1 + 0.56 \times 10^{-5} P_M)$, where P_M is the melting pressure in bar, was applied.

TABLE II. Molar volume of liquid He^4 at saturated vapor pressure, based on a cell volume of 11.806 cm^3.

T (°K)	V (cm^3/mole)	ΔV (cm^3/mole)	V_{calc} (Ref. 21) (cm^3/mole)	Diff (%)
4.093	31.348	0.028	31.516	0.53
4.045	31.072	0.043	31.321	0.80
4.002	30.896	0.050	31.153	0.83
3.277	28.724	0.184	28.910	0.64
2.771	27.796	0.231	27.956	0.57

H. Procedure

While the apparatus was cooled, a sample pressure of 30–40 bar was maintained. During cooling exchange gas was used in the vacuum surrounding the capillary. It was hoped that this would serve to condense remaining impurities in the capillary rather than in the cell. The system was precooled with liquid nitrogen and liquid hydrogen. Depending on the desired density and corresponding temperature at which freezing would start, the sample pressure was raised either before or after liquid helium was transferred. For all except two samples, the sample pressure was adjusted to give the desired density in the fluid. The cell was then thermally isolated, and the bath was cooled well below the freezing temperature in order to block the capillary at point A (Fig. 1) with solid helium. The sample was then frozen at constant volume. This usually required several hours, and during freezing severe thermal gradients existed in the sample. After all the fluid had solidified, the

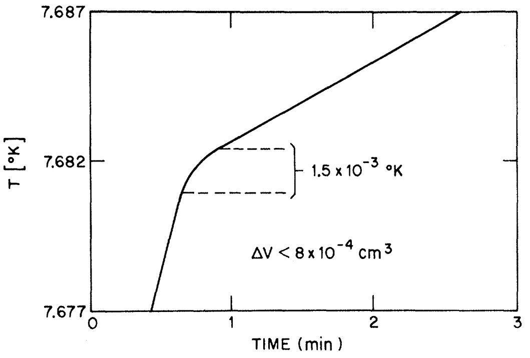

FIG. 3. Typical heating curve near the melting temperature. The temperature range over which the slope decreases from that characteristic of the solid to that characteristic of the two-phase region indicates that the molar volume of the solid is uniform within 8×10^{-4} cm^3.

sample was thermally isolated and heated slowly to determine the temperature at which melting started (T_M). The beginning of melting always was remarkably sharp, indicating that in spite of the thermal gradients and pressure changes during freezing the solid was of very uniform density. A typical heating curve is shown in Fig. 3. The temperature range over which the slope changes from that characteristic of the single-phase solid to that characteristic of the two-phase system is only 1.5×10^{-3} °K. Even this range may in part be due to changes in the small thermal gradients which are likely to exist during heating. If all of the temperature range is due to a density gradient in the solid, then the difference between the maximum and minimum molar volume is 8×10^{-4} cm^3.[22] Two samples (13.727 and 13.718 cm^3/mole) were frozen at almost constant pressure. The details have been given elsewhere.[9]

In spite of the extreme homogeneity of the samples, erratic heating was observed at the smaller volumes during preliminary measurements at the lowest temperatures when the sample had been cooled rapidly. This made accurate measurements very difficult; but indications were that the heat capacity was independent of the thermal history of the sample. It was decided to anneal each sample at a temperature about 10^{-2} °K less than the melting temperature for 12–18 h. After annealing, the samples were cooled as slowly as possible.[9]

The procedure used for the heat-capacity measurements was conventional[8] and need not be described. Most measurements were extended sufficiently far into the solid-liquid two-phase region to give the discontinuity in C_v at the melting temperature T_M. T_M was determined from the heat-capacity point which spans T_M and the heat capacities in the one- and two-phase regions with an error of less than 10^{-3} °K with respect to the working temperature scale. Sometimes it was larger by a few millidegrees than the value obtained from the heating curve prior to annealing. It is not clear whether this change is due to annealing of the sample or due to flow in the capillary. However, the change in molar volume calculated from the change in T_M[22–24] always was negligible (less than 0.002 cm^3).

It may be worth noting that afterheating similar to that reported by Edwards and Pandorf[4] also was observed in this work during the preliminary measurements on some unannealed samples, but never to the extent that accurate measurements could not be made. One particular sample which melted at 2.79 °K began to show the afterheating at 1.72 °K. When the sample was cooled a second time, no afterheating was observed. The heat-capacity results from the two sets of measurements agreed with each other within 0.1%. Local melting and subsequent relaxation of density gradients accompanied by refreezing, as suggested by Edwards and Pandorf,[4] cannot be the correct explanation of the relaxation effect observed in the present work because the sample is known to be very homogeneous. The melting volumes at 1.72 and 2.79 °K differ by almost 2 cm^3/mole.[23,24] No satisfactory explanation of this nonequilibrium effect can be offered at this time.

The molar volumes of the samples were determined from the melting temperatures T_M and the combined data for the molar volume at T_M of Grilly and Mills,[23,24] Dugdale and Simon,[22] and Gardner, Hoffer, and Phillips.[5–7] The data of Dugdale and Simon[22] differ by less than 0.04 cm^3/mole from those of Grilly and Mills[24] at 4 °K and above 14.7 °K, and the two sets of data, therefore, can be combined readily, and jointly span the desired temperature range. At large volumes ($V \gtrsim 20$ cm^3/mole) the recent measurements by Gardner, Hoffer, and Phillips[5–7] differ by at most 0.06 cm^3/mole from those by Grilly and Mills,[23] and probably are more accurate. Since Gardner *et al.* reported extensive heat-capacity results[5–7] in this range with which comparison of the present results will be made, their melting volumes[7] were used and joined smoothly onto those by Grilly and Mills.[23,24] The absolute errors of volumes are probably not larger than 0.04 cm^3/mole. However, volume differences between successive volumes are likely to be more accurate than this because the volumes were obtained from a large-scale smooth graph through the quoted data. The melting temperatures of all samples will be given so that any later improvements in the volume mea-

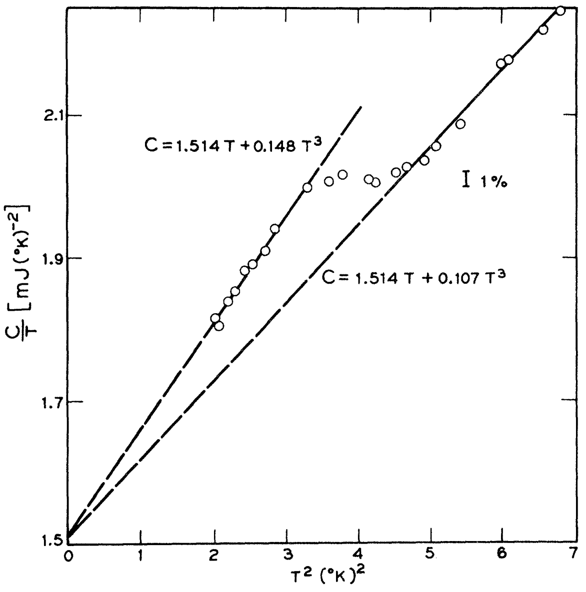

FIG. 4. Heat capacity of the empty calorimeter in the vicinity of the anomalous contribution from a germanium thermometer.

surements at the melting line can be used to adjust the results of this work. The number of moles of sample was calculated from the cell volume and the molar volume of the sample.

III. HEAT CAPACITY OF EMPTY CELL

The heat capacity of the empty cell was measured separately with random errors of less than 0.2%. Some necessary precautions during these measurements have been discussed elsewhere.[9] The low-temperature results are shown in Fig. 4. An anomaly is observed, which is believed to be due to the He^4 exchange gas in a germanium thermometer. There are actually three thermometers mounted on the cell. One of them, however, has been used in previous measurements[8,12,13] and is known to have no anomalous contribution to its heat capacity. Presumably it lost its exchange gas. The anomaly, therefore, is caused by at most two thermometers. Its magnitude is consistent with the measurements by Cochran *et al.*,[25] who observed a discontinuity of 8×10^{-4} J/°K in the heat capacity of an encapsulated Honeywell thermometer similar to those used here. The total enthalpy of the anomaly observed in the present work is estimated to be about 1.6×10^{-4} J. This corresponds to the heat of vaporization of 1.8×10^{-6} moles of helium gas, or 0.045 cm³ at 300 °K and 1 atm. This is about equal to the free volume in one thermometer.

The heat capacity of the empty cell never exceeded 20% of the total heat capacity and was less than 1% of the total heat capacity at large volumes near the melting line.

IV. RESULTS

A. Heat Capacities

Thirteen annealed samples (1–12 and 19, Table III) and four rapidly cooled samples (13–15 and 2′, Table III) were prepared from the first gas sample. The heat capacities of samples 1–15 were measured up to the melting temperature. The heat capacities of samples 2′ and 19 were measured below 3 °K only. Three further samples (16–18, Table III) were prepared from the second-more-pure gas sample, and their heat capacities were measured below 3 °K.

The molar volumes cover the range from 13.7 to 20.8 cm³, with a slightly closer spacing at the larger volumes. The observed melting temperatures T_M and the molar volumes deduced from these temperatures are given in Table III. Also given are the

TABLE III. Measured melting temperature T_M, heat-capacity discontinuities ΔC_{vM} at T_M, and molar volumes V derived from T_M.

Sample	T_M (°K)	ΔC_{vM} (J mole⁻¹ °K⁻¹)	V (cm³ mole⁻¹)
	Gas sample I, annealed		
1	9.331	31.80	13.727
2	7.690	29.24	14.513
3	6.675	28.13	15.097
4	5.490	25.61	15.913
5	4.492	23.54	16.770
6	3.746	21.63	17.550
7	3.162	19.50	18.270
8	2.601	17.06	19.135
9	2.412	16.18	19.455
10	2.251	15.17	19.735
11	2.080	13.85	20.036
12	1.852	11.40	20.472
	Gas sample I, rapidly cooled		
13	1.677[a]	...	20.725
14	2.726	17.72	18.926
15	3.102	19.48	18.350
2′	...	...	14.513
	Gas sample II, annealed		
16	...	...	13.718
17	...	...	14.208
18	...	...	14.815
	Gas sample I, annealed		
19	...	...	≈14.15

[a] Transition to bcc phase.

measured discontinuities ΔC_{vM} in the heat capacities at T_M.

The results for each volume were fitted with the equation

$$C_v = \sum_{i=1}^{N} a_i(V) T^{2i+1} , \tag{1}$$

and graphs of $\Delta C_v / C_v$, where ΔC_v is the difference between the value obtained from the equation and the observed value, were constructed. This procedure was followed primarily to facilitate data processing. Two typical difference graphs are shown in Fig. 5 and give an indication of the precision of the data. The diameters of the points are approximately equal to 0.1% It can be seen that individual points rarely differ by more than 0.1% from a smooth line through all the data except perhaps at the very lowest temperatures. Smoothed values of $\Delta C_v / C_v$ were obtained from the difference graphs. The coefficients of Eq. (1) and a table of $\Delta C_v / C_v$ were used for further data processing.

It does not appear useful to present in numerical form the results of individual heat-capacity measurements (over 1000 measurements were made), particularly since the heat capacity is not a very suitable function for interpolation because of its strong temperature and volume dependence. Instead we present in Table IV smoothed values of the Debye temperature as a function of T/Θ_0, where Θ_0 is Θ at 0 °K. The determination of Θ_0 will be discussed in Sec. IV D, and Θ was obtained from the smoothed C_v [Eq. (1) and smoothed values of $\Delta C_v / C_v$] with the aid of the relation[26]

$$C_v / 3R = 77.927 (T/\Theta)^3, \quad R = 8.314 \text{ J mole}^{-1} (^\circ\text{K})^{-1} \tag{2}$$

for $\Theta/T \geq 16$, and from numerical tables[26,27] for the appropriate Debye integral for $\Theta/T < 16$. Results of individual measurements are shown in Fig. 6 in the form of Θ as a function of T. Figure 6 gives an over-all view of the data, and indicates the extent of the measurements. For comparison, some smoothed results by others[4,16] are indicated by dashed lines.

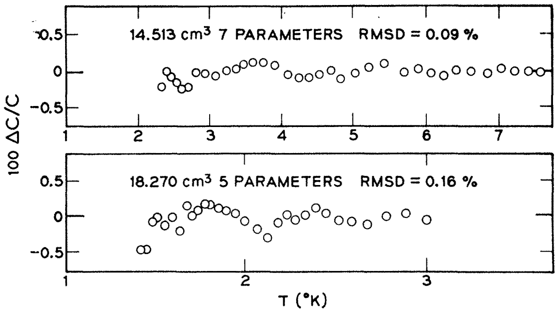

FIG. 5. Deviations in percent of individual heat-capacity measurements from a least-squares fit to Eq. (1). The diameters of the points correspond to about 0.1% of C_v.

Although the scatter in C_v when inspected as a function of T rarely exceeds ± 0.1%, small errors in V correspond to relatively large systematic errors in C_v; for at constant T we obtain

$$\delta C_v / C_v \cong 3\gamma (\delta V / V) , \tag{3}$$

where γ is the Grüneisen parameter and 3γ is approximately equal to 7. Since the volumes are known only to ± 0.2%, it follows that systematic errors in V could correspond to systematic errors in C_v of 1.4%. When additional possible systematic errors due to the cell volume and due to deviations of the working temperature scale from the thermodynamic temperature scale[13] are considered, it follows that on an absolute basis the heat capacity of hcp He^4 as measured here may be in error by about 2%. This error is propagated to all derived thermodynamic functions. Systematic errors of at least this magnitude are applicable to all previous measurements by other authors. However, the quantities of greatest interest are not always the absolute values of the major thermodynamic variables themselves, but rather their various derivatives with respect to volume and temperature. These often are not very sensitive to errors proportional to C_v or V. For these derived quantities, it is more important that C_v be a smooth function of V, and that *random* errors in V be small. In order to estimate the scatter in C_v as a function of V, an expression of the form $a + bV$ was subtracted from $\ln(C_v)$ at several values of T. This difference times 100 is shown in Fig. 7. Deviations from a smooth line through the data correspond to the scatter of C_v in percent. No physical significance is meant to be implied by this procedure, and it was used only to obtain sufficient resolution in the figure to display the scatter. It can be seen that C_v as a function of V is smooth within 0.5% of C_v. It follows that the values of V used here are smooth within 0.07% or about 0.01 cm^3/mole. Similarly it was found that values of $(\Delta \ln C_v / \Delta \ln V)_T$ computed from finite differences between succesive volumes when plotted against the average volume generally did not deviate from a smooth curve by more than 1%, except very near the melting line.

The results for the four samples which were not annealed are shown also in Fig. 7 and yielded heat capacities which agree with the annealed samples to ± 0.5%. Therefore, it can be concluded that rapid cooling of macroscopic samples has no appreciable effect on the heat capacity. The effect which ap-

TABLE IV. Debye temperatures for hcp He^4.

	V(cm^3/mole)						
T/Θ_0	13.727	14.513	15.097	15.913	16.770	17.550	18.270
0.000	73.90	65.41	59.86	53.02	46.80	41.88	37.87
0.010	73.89	65.39	59.86	53.01	46.79	41.84	37.83
0.015	73.84	65.35	59.84	52.98	46.78	41.80	37.77
0.020	73.70	65.23	59.77	52.89	46.69	41.72	37.67
0.025	73.44	65.00	59.60	52.71	46.52	41.57	37.51
0.030	73.02	64.63	59.25	52.40	46.24	41.33	37.29
0.035	72.42	64.09	58.72	51.96	45.82	40.98	36.98
0.040	71.65	63.39	58.02	51.35	45.27	40.48	36.52
0.045	70.72	62.54	57.19	50.62	44.63	39.88	35.93
0.050	69.68	61.61	56.32	49.76	43.90	39.21	35.30
0.055	68.65	60.67	55.43	48.96	43.14	38.51	34.70
0.060	67.68	59.80	54.62	48.20	42.44	37.85	34.06
0.065	66.81	59.01	53.89	47.53	41.82	37.24	33.47
0.070	66.05	58.33	53.26	46.94	41.28	36.70	32.94
0.075	65.43	57.73	52.68	46.41	40.77	36.21	32.44
0.080	64.92	57.22	52.19	45.95	40.31	35.76	31.96
0.085	64.48	56.80	51.76	45.52	39.88	35.30	...
0.090	64.05	56.43	51.38	45.11	39.43	...	...
0.095	63.69	56.06	51.01	44.69	38.92	...	...
0.100	63.39	55.68	50.62	44.18	...	...	...
0.105	63.08	55.29	50.18	...	...	...	...
0.110	62.72	54.85	49.71	...	...	...	...
0.115	62.33	54.42	...	...	...	...	...
0.120	61.92	...	...	...	...	...	...

	V(cm^3/mole)					
T/Θ_0	19.135	19.455	19.735	20.036	20.472	20.725
0.000	33.6	32.2	31.0	29.8	28.1	27.1
0.010	33.6	32.2	30.9	29.7	28.0	27.1
0.015	33.54	32.1	30.9	29.6	27.9	27.0
0.020	33.45	31.99	30.75	29.45	27.70	26.79
0.025	33.30	31.86	30.61	29.31	27.57	26.65
0.030	33.10	31.65	30.41	29.10	27.35	26.44
0.035	32.81	31.36	30.12	28.81	27.06	26.15
0.040	32.43	30.98	29.74	28.45	26.68	25.77
0.045	31.95	30.53	29.28	27.99	26.22	25.29
0.050	31.33	29.97	28.74	27.45	25.71	24.76
0.055	30.75	29.38	28.16	26.87	25.13	24.19
0.060	30.20	28.81	27.61	26.32	24.58	23.61
0.065	29.64	28.29	27.07	25.79	24.02	...
0.070	29.09	27.73	26.51	25.28	...	...
0.075	28.59	27.14	...	...	...	...

parently had been observed previously[9] was traced to a computational error for the quickly cooled sample. This error does not affect any other conclusions drawn in Ref. 9.

The results of this work are compared also with those of other authors in Fig. 7. Whenever the melting temperature for the work of others was quoted, the molar volumes were reevaluated from the melting temperature to assure consistency with the present work before the deviations were calculated. The heat capacities measured by Edwards and Pandorf[4] are from 1 to 6% higher than the present results, with an average difference of about 4%. This difference seems somewhat large since Edwards and Pandorf believed their precision to be ± 1% and since volume errors should not contribute more than about 0.5% to the heat-capacity error [see Eq. (3)]. It appears that the deviations from

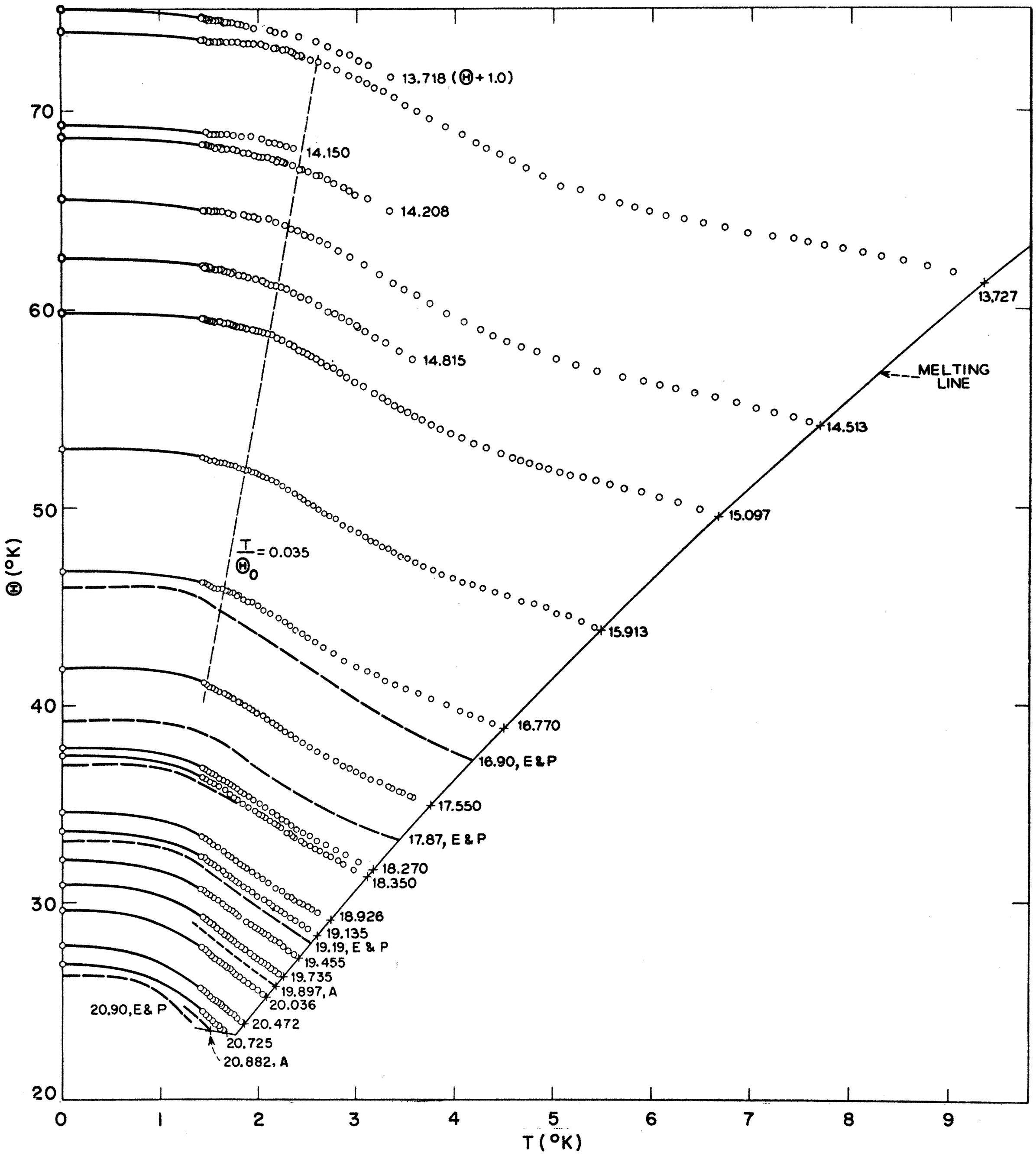

FIG. 6. The Debye temperature obtained from individual heat-capacity measurements as a function of the temperature. The numbers indicate the molar volumes. Note that the results at 13.718 cm^3/mole are displaced vertically by 1 °K. The dashed lines are smoothed results from Refs. 4 and 16.

the present data are systematic. The source of the systematic differences cannot be established with certainty; but it may be due to the nature of the sample container used by Edwards and Pandorf. At large volumes the results can be compared with the work by Gardner, Hoffer, and Phillips[5-7] and with previous measurements by this author.[15,16] All these data are in good agreement with each other, differing by less than 1%. At small volumes but fairly high-temperatures comparison can be made with the work of Dugdale and Franck.[28] The present results are about 10% higher than those of

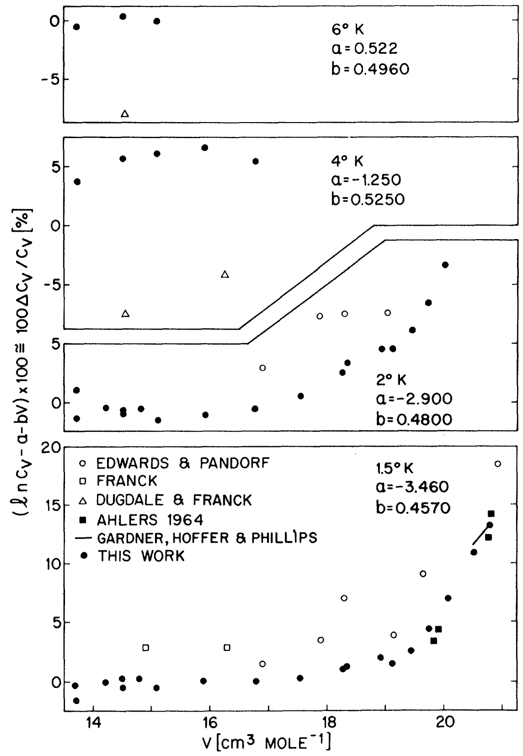

FIG. 7. Deviations of $\ln(C_v)$ from a linear function $a + bV$. This figure illustrates the scatter in C_v as a function of V. The present results are compared with those from Refs. 4, 5–7, 16, 28, and 29.

these authors. This is well outside of the quoted probable errors, particularly at 6 °K. At lower temperatures and small volumes the measurements by Franck[29] are about 3% higher than the present work.

B. Grüneisen Parameter at 0°K

On the basis of heat-capacity measurements, it is possible only to determine the temperature-dependent contribution to the equation of state. These contributions can be written conveniently in terms of the Grüneisen relation[3]

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\gamma C_v}{V} \quad . \tag{4}$$

It can be shown that at 0 °K γ assumes the value

$$\gamma_0 = -\frac{V}{\Theta_0}\frac{d\Theta_0}{dV} \quad . \tag{5}$$

In general, one would expect for real solids that γ is mildly temperature dependent; and although there is little experimental information for any solids, there is no reason why γ cannot also be mildly volume dependent. In previous heat-capacity measurements on hcp He^4, it was found that, within experimental error, the reduced Debye temperature Θ/Θ_0 is a universal function applicable at all volumes of the reduced temperature T/Θ_0.[4] If this is the case, it can be shown that γ is independent of T and equal to γ_0. This greatly simplifies the calculation of other thermodynamic properties, since γ_0 is not involved in integrations and differentiations of Eq. (4) with respect to T.

It is difficult to establish accurately the validity of Eq. (4) with γ independent of T on the basis of experimental data for Θ/Θ_0 because Θ_0 must be obtained from some extrapolation to 0 °K. This extrapolation will result in errors for Θ_0 greater than those for the measured Θ. For this reason, Edwards and Pandorf estimated that their error in Θ_0 may be as large as 2%.[4] Therefore, the universal dependence of Θ/Θ_0 on T/Θ_0 is at best established to ± 2% over the volume range covered by those authors. Alternately, one might attempt to compare Eq. (4) directly with experimental measurements in order to establish the temperature dependence of γ. One can obtain $(\partial P/\partial T)_v$ from

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\int_0^T \frac{C_v}{T}\,dT\right)_T \quad . \tag{6}$$

However, this requires extrapolation of C_v to 0 °K and is subject to errors similar to those encountered in determining Θ_0. For these reasons, it was decided to define a new Grüneisen-type parameter γ' which can be derived directly from the heat-capacity measurements without any need for extrapolation by the relation

$$\gamma' = \frac{V}{T}\left(\frac{\partial C_v}{\partial V}\right)_T \bigg/ \left(\frac{\partial C_v}{\partial T}\right)_v \quad . \tag{7}$$

γ' is a well-defined average over the frequency spectrum $g(\nu_i)$ of γ_i for the ith mode, and is given by

$$\gamma' = \sum_i \gamma_i \left(\frac{\partial C_i}{\partial T}\right)_v \bigg/ \sum_i \left(\frac{\partial C_i}{\partial T}\right)_v \quad ,$$

where

$$\gamma_i = \frac{V}{\nu_i}\frac{d\nu_i}{dV} \tag{8}$$

and where C_i is the heat capacity of the ith mode. At 0 °K, γ' is identical to γ_0. If γ' is independent of T, then Eq. (4) with γ independent of T is obeyed, and the universal function Θ/Θ_0 of T/Θ_0 exists. On the other hand, if γ' is dependent on T, the usual Grüneisen parameter γ will also be temperature dependent and in terms of γ' is given by

$$\gamma = C_v^{-1}\int_0^T \gamma' \left(\frac{\partial C_v}{\partial T}\right)_v dT \quad . \tag{9}$$

Values of γ' were calculated from the present heat-capacity data, using Eq. (7). Dimensionless logarithmic derivatives were used in the numerical work since these vary slowly with V and T and therefore facilitate data processing. The results already have been presented elsewhere.[10] It was found that γ' is temperature dependent, and therefore it can be concluded that γ in Eq. (4) is also temperature dependent. However, at sufficiently small volumes, γ' is almost independent of T except at high relative temperatures. It was possible to extrapolate γ' to 0 °K to obtain γ_0 over a sufficient volume range to establish the volume dependence of γ_0. This procedure was more reliable than the extrapolation of Θ to 0 °K, and the derivation of γ_0 from Θ_0. Within experimental error, γ_0 varies linearly with volume, and can be expressed by

$$\gamma_0 = 1.02 + 0.083V \quad . \tag{10}$$

Equation (10) for γ_0 can be compared with several measurements for He^4 by others. Edwards and Pandorf[4] obtained the value $\gamma_0 = 2.60 \pm 0.05$ from their estimates of Θ_0 for molar volumes between 16.9 and 20.9 cm^3. It appears the the probable error for γ_0 was underestimated by these authors. They believe that their values of Θ_0 are known to $\pm 2\%$. Such an error in Θ_0 corresponds to a 7% error in the total change of Θ_0 over the experimental volume range. Therefore an error of about ± 0.2 would seem more appropriate for Edwards and Pandorf's value of γ_0. Equation (10) predicts that γ_0 changes from 2.42 to 2.75, in very good agreement with Edwards and Pandorf if the larger error is accepted for their measurements.

At molar volumes between 20.5 and 20.9 cm^3, Gardner, Hoffer, and Phillips[5-7] obtained $\gamma_0 = 2.80 \pm 0.05$. Equation (10) yields values between 2.72 and 2.76 for this volume range, again in good agreement with the independent work. For molar volumes between 17.7 and 20.7 cm^3, Jarvis, Ramm and Meyer[30] measured $(\partial P/\partial T)_v$ for hcp He^4 and used these results together with either the specific-heat data reported here or those by Edwards and Pandorf[4] to obtain γ from Eq. (4). It is difficult to make a comparison of γ_0 as obtained from their work with the present results because γ as determined by them is not a monotonically increasing function of T, but has a minimum at $T/\Theta_0 \cong 0.05$. The magnitude of the initial decrease of γ with increasing temperature seems to be sensitive to the C_v data which are used to derive γ. However, when the present C_v results are used, Jarvis *et al.* obtain values of γ at 1.5 °K which differ from the present results by at most 2%.[30] These differences appear to be within the combined probable errors.

The volume dependence of γ_0 given by Eq. (10) is in accord with what is expected on the basis of rather limited theoretical information[31-33] for the volume dependence of γ for simple solids, in general. There seem to be no reliable measurements for classical solids with which comparison can be made. The recent measurements by Sample and Swenson[1] for hcp He^3 yield values of γ_0 which are only 2.4% higher and have the same volume dependence as those reported here for He^4. These results will be discussed in more detail in Sec. IV G. Further, it is interesting to note that for solid parahydrogen $d\gamma_0/dV$ was found to be 0.08,[34] in agreement with the present work for He^4. However, for the hydrogen measurements the possible volume errors were such that the volume dependence of γ_0 was not considered significant by itself. Nonetheless, on the basis of the limited available information it appears that Eq. (10) for γ_0 may predict at least qualitatively the volume dependence of γ_0 for other simple solids besides He^3 and He^4.

C. Temperature Dependence of C_v at Low Relative Temperatures

The general problem of the low-temperature behavior of the lattice heat capacity of solids has been discussed extensively by Barron and Morrison.[35] Their analysis of theoretical models and experimental data reveals that below $T/\Theta_0 = 0.02$ lattice heat capacities usually can be represented by Eq. (1) with two parameters, and three parameters are generally sufficient up to $T/\Theta_0 = 0.04$. Whether these conclusions are applicable to quantum solids needs to be determined experimentally. Barron and Morrison write the low-temperature heat capacity in the form

$$C_v = a_1 T^3 [1 + \alpha(T/\Theta_0)^2 + \beta(T/\Theta_0)^4] \quad . \tag{11}$$

In terms of a_1, Θ_0 is given by

$$\Theta_0^3 = 12\pi^4 R/5a_1 = (1.9437 \times 10^6) a_1 \quad , \tag{12}$$

where the units of a_1 are $mJ\ mole^{-1} (°K)^{-4}$ and R is the gas constant. Within the framework of certain models it is possible to calculate α and β.[35,36] Such calculations do not seem to have been carried out for the hcp structure; however, for isotropic cubic close-packed (fcc) crystals it appears that α is close to 50, and $\beta \approx 10^4$. It does not seem unreasonable to expect similar values for the hcp structure, provided the extreme anharmonicity of solid helium has no effect upon α and β.

At the smallest volumes the lowest relative temperature T/Θ_0 at which measurements were made is about 0.018. This is sufficiently low so that it should be possible to obtain meaningful estimates of the first three coefficients of Eq. (1). Since these coefficients are directly relatable to the frequency spectrum of the solid, it would be of interest to know whether quantum effects in hcp He^4 result in unusual values. The data for $T/\Theta_0 \leq 0.035$ for

TABLE V. Parameters for Eqs. (1) and (11) with three terms.

Sample	$a_1{}^{a}$	$a_2{}^{a}$	$a_3{}^{a}$	Θ_0	α	$10^{-4}\beta$
1	4.930	−0.0332	0.0093	73.32	−36	5.4
2	7.106	−0.0355	0.0166	64.91	−21	4.1
2′	7.055	−0.0192	0.0153	65.07	−11	3.9
19	6.041	−0.0611	0.0161	68.52	−48	5.9
16	4.771	0.0494	0.0041	74.13	57	2.6
17	6.041	0.0337	0.0061	68.52	26	2.2
18	7.970	0.0422	0.0151	62.47	21	2.9
ccp	...	...	...	...	≈ 50	≈ 1

[a] Units such that C_v is in mJ mole^{-1} °K^{-1} if T is in °K.

seven samples, therefore, were fitted to Eq. (1) with three parameters. The resulting coefficients a_1, a_2, a_3, α, β, and Θ_0 are given in Table V. The most striking feature of the results of this analysis is that a_2 and α for all four samples prepared from the first gas sample (1, 2, 2′, and 19) are negative. However, the values of a_2 and α for all three samples prepared from the second-more-pure gas sample are positive and of the magnitude expected for classical solids. The value of β also is reasonable.

It is clear that the samples prepared from the first gas sample exhibit an impurity effect in the low-temperature heat capacity. This effect is demonstrated further in Figs. 8 and 9. In Fig. 8, C_v/T^3 is shown as a function of T^2 for samples 1 and 17. The solid lines represent the equations obtained from the least-squares fit. For the "impure" sample 1 there is a strong deviation of the data from the equation immediately above the least-squares-fit temperature range. On the other hand, for the "pure" sample 17 the equation obtained at $T/\Theta_0 \leq 0.035$ fits the data up to $T/\Theta_0 = 0.045$, as expected from the behavior of other solids.[35] In Fig. 9, reduced Debye temperatures Θ/Θ_0 are shown as a function of T/Θ_0 for samples 1, 17, and 19. The values of Θ_0 used here are discussed in Sec. IV D. It is evident that samples 1 and 19, both prepared from the first gas sample, agree with each other, and in the vicinity of $T/\Theta_0 = 0.03$ show values of Θ/Θ_0 larger than those for the pure sample 17. Thus, it is seen that the impurity effect is a deficiency in C_v at $T/\Theta_0 \cong 0.03$. However, it should be emphasized that the difference in C_v between the pure and impure samples as indicated by Fig. 9 is quite small and never exceeds 1% of C_v for $T/\Theta_0 \geq 0.02$. Above $T/\Theta_0 = 0.04$ there is no noticeable impurity effect. It is possible that the effect observed here is related to the anomalous heat capacity observed at $T/\Theta_0 < 0.02$ by various other workers.[1,29,37] However, the effect is much too weak at relative temperatures greater than 0.02 to correspond to the "linear term" suspected by Heltemes and Swenson[37] and apparently observed by Franck.[29] This has been discussed elsewhere.[9] Franck's data would yield a clear maximum in Θ/Θ_0 in the vicinity of $T/\Theta_0 = 0.03$. Such a maximum is not present, as can be seen in Fig. 9. Furthermore, annealing has no appreciable effect on the impurity contribution, as can be seen by comparing the heat capacities of samples 2 and 2′. Franck's linear term could be affected by annealing.

The values found for α from the pure samples are very reasonable in view of what is known about other solids. It is possible that the spread in the values of α is within experimental error. Even for primary data of high precision, the errors in all coefficients for Eq. (1) except the first are fairly large because of the high parameter correlation over the narrow temperature range. However, values of α between 20 and 60 are quite acceptable and in models for an fcc lattice would correspond to a reasonable range for the anisotropy of the crystal.[36] It is interesting to note that the less accurate data available for solid parahydrogen[34] yield values of α between 50 and 100. In view of the fact that for these data the effects of the T^5 and T^7 terms are not clearly separable because of the lesser precision, this range for α is entirely in line with the values found here for hcp He^4. Recent precise heat-capacity measurements for argon and krypton by Finegold and Phillips[38] yield values for α of about 45 for both solids, again consistent with the present observations for hcp He^4. Unfortunately the results of Sample and Swenson for He^3 do not appear to be sufficiently precise at small relative temperatures to warrant a similar analysis.

The values of α found here for pure He^4 at small volumes are rather different from those deduced by Hoffer[7] from his C_v measurements for He^4 at much larger volumes. Hoffer finds $a_2 \cong 0$, and thus $\alpha \cong 0$. His values of a_3 correspond to $\beta \cong 4.6 \times 10^4$, which is larger than the values in Table V for the pure samples, but comparable to those for the impure samples. It is difficult to determine with certainty from the comparison whether α and β are really volume dependent, particularly since α and β are sensitive to impurities.

D. Debye Temperature at 0 °K

The results of Sec. IV C indicate that the first coefficient (a_1) of Eq. (1) can be determined accurately from the present data on the high-purity samples at small volumes. Knowledge of a_1 (or Θ_0) at one volume in conjunction with Eq. (10) is sufficient to calculate Θ_0 at all volumes. The value $\Theta_0 = (68.56 \pm 0.10)$ °K at $V = 14.208$ cm^3/mole, based primarily upon an analysis of the results for sam-

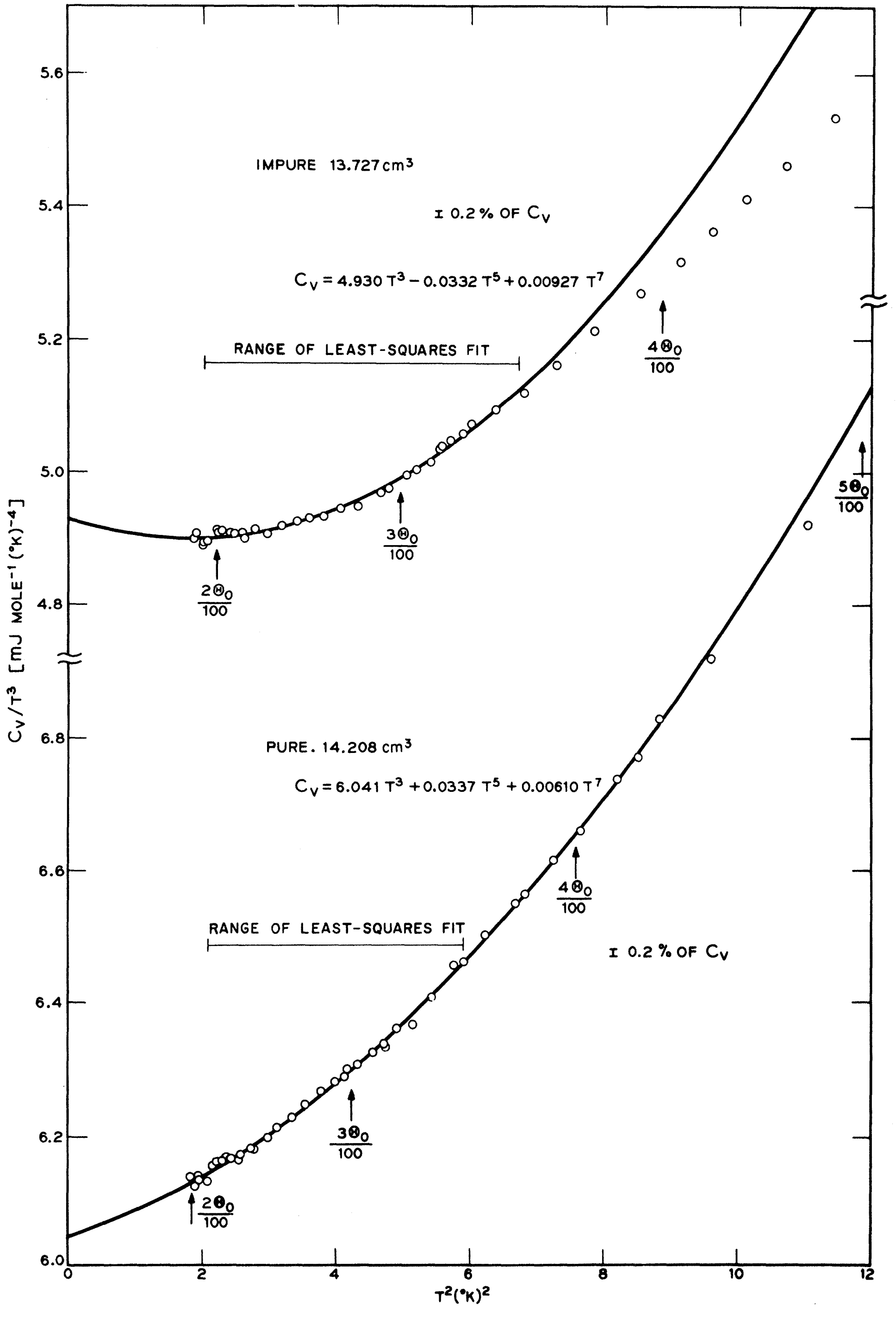

FIG. 8. C_v/T^3 as a function of T^2 for two samples of hcp He^4. The measurements at 13.727 cm^3/mole exhibit an impurity effect, as discussed in the text.

ple 17, has been adopted for this work. Then, by integration of Eq. (10), one has

$$\Theta_0(V)=68.56(V/14.208)^{-1.02} \times \exp[-0.083(V-14.208)] . \qquad (13)$$

Equation (13) is compared with estimates for Θ_0 by others[1,4,5,28,29] in Fig. 10. In general, there is reasonable agreement within the various experimental errors between the data and Eq. (13), except perhaps for the results of Sample and Swenson[1] and Dugdale and Franck.[28] It is particularly gratifying that the results near 21 cm^3/mole of Edwards and Pandorf[4] and of Gardner, Hoffer, and Phillips[5-7]

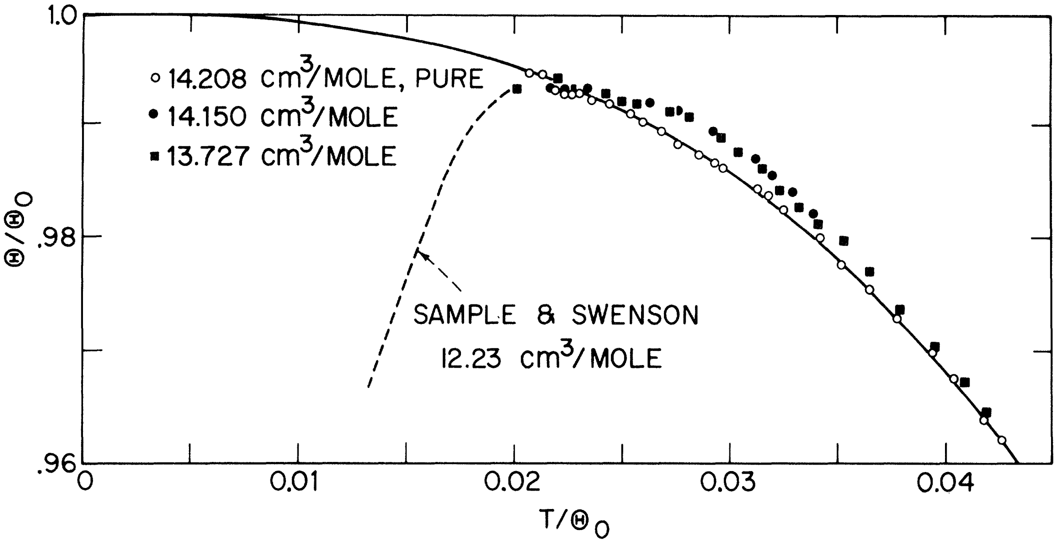

FIG. 9. Reduced Debye temperature Θ/Θ_0 as a function of the reduced temperature T/Θ_0 for three samples of hcp He^4. The solid symbols reflect an impurity effect as discussed in the text. The dashed curve is obtained from Ref. 1, and contains an "apparatus effect" for $T/\Theta_0 < 0.02$.

differ from Eq. (13) by less than 1% in Θ_0. In this volume range, Eq. (13) is based on an extrapolation of Eq. (10), and Eq. (10) is not directly supported by the present work for $V > 19$ cm^3/mole. We estimate that Eq. (13) is correct within about 0.5% for molar volumes between 13 and 19 cm^3 and within about 1% at 11 and 21 cm^3/mole.

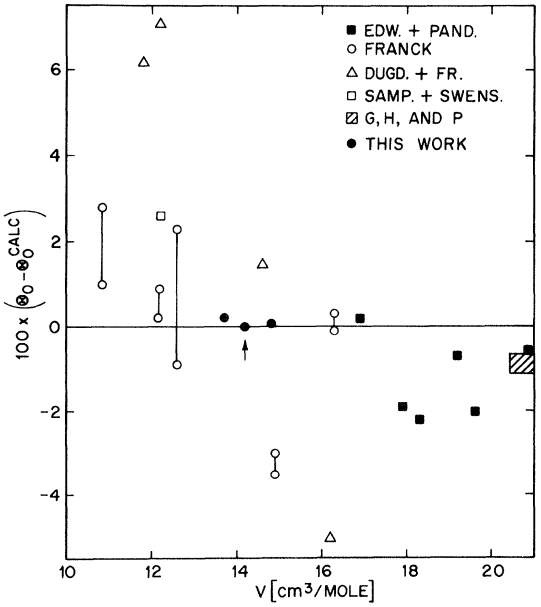

FIG. 10. Deviations in percent of Θ_0 reported in Refs. 1, 4, 5–7, 28, and 29 from Eq. (13). The solid circles are this work on samples 16–18. The parameters in Eq. (13) are based on the result indicated by the arrow. In Ref. 29, two independent estimates of Θ_0 are reported, and these are connected by a vertical line in this figure.

E. Reduced Debye Temperature

It was observed in Sec. IV B that the Grüneisen parameter γ at sufficiently high temperature is dependent upon the temperature. Therefore, we expect that Θ/Θ_0 at constant T/Θ_0 is dependent upon the molar volume. In Fig. 11, Θ/Θ_0 is shown as a function of T/Θ_0 at a few of the present experimental volumes as solid lines. Also shown as dashed lines are the curves corresponding to the measurement of Sample and Swenson[1] and of Gardner, Hoffer, and Phillips.[5-7] For this purpose, the value of Θ_0 corresponding to the Sample and Swenson results[1] was adjusted from their quoted value of 95.5 to 96.6 °K. This will be discussed in detail in Sec. IV G. For the Gardner-Hoffer-Phillips results, the value of Θ_0 quoted by the authors was used. If Eq. (13) were employed to obtain Θ_0 at 20.8 cm^3/mole, then values of Θ/Θ_0 for $T/\Theta_0 > 0$ would be slightly lower than shown in Fig. 11 for Gardner *et al.* Also shown in Fig. 11 are the curves for argon and krypton based upon the recent work by Finegold and Phillips.[38] The difference between the argon and krypton curves is within possible experimental errors. It is evident that Θ/Θ_0 at constant T/Θ_0 is a monotonically decreasing function of the molar volume. At sufficiently small volumes, Θ/Θ_0 for hcp He^4 approaches the experimental values for the classical solids.

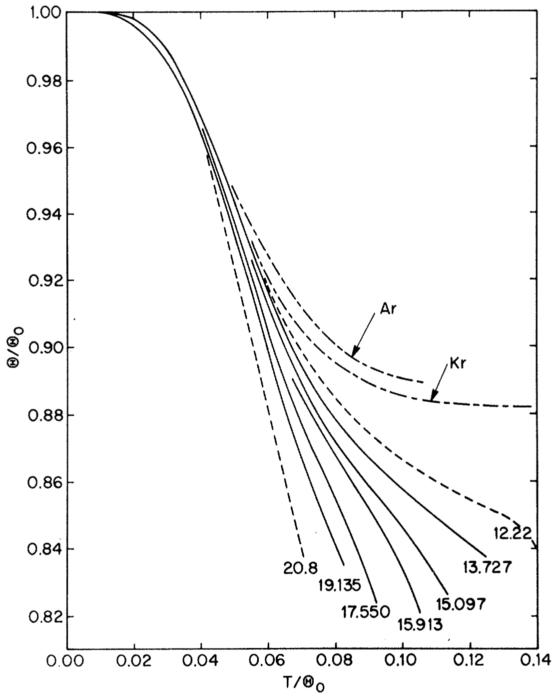

FIG. 11. Reduced Debye temperature as a function of the reduced temperature. The numbers in the figure indicate the molar volume. Solid lines: this work. Lower dashed line: Refs. 5–7. Dashed line at 12.22 cm^3/mole: Ref. 1. The argon and krypton results are from Ref. 38.

It will be noticed that at most volumes Θ/Θ_0 for hcp He^4 has two points of inflection. This is not a feature expected for the lattice heat capacity and is most likely caused by an excess heat capacity at large T/Θ_0 attributable to a premelting phenomenon.

F. Grüneisen Parameter γ

The determination of γ from Eq. (4) requires the integration from 0 °K of C_v/T. The values of Θ_0 and the temperature dependence of C_v at low relative temperatures discussed in Secs. IV C and D provide a reasonable guide for the required extrapolation of C_v for volumes less than about 19 cm^3/mole. The C_v measurements, therefore, were reanalyzed by a least-squares fit in which the first coefficient in Eq. (1) was held constant and set equal to the value predicted on the basis of Eq. (13). In order to exclude the data which might be affected by the low-temperature impurity effect discussed in Sec. IV C, only measurements for which $T/\Theta_0 \geq 0.03$ were used in this second least-squares analysis. New difference graphs of $\Delta C_v/C_v$ were constructed. The function $(T/C_v)(\partial C_v/\partial T)_v$, which varies by at most 23% over the entire temperature range over which the solid exists, was monotonically increasing with T below 1.4 °K and with decreasing T smoothly approached its 0 °K value of 3 with a vanishing temperature derivative for all volumes. It appears likely that this extrapolation of C_v is sufficiently accurate to introduce negligible errors into the required integral above 1.4 °K. Values of γ were then calculated from the relation

$$\gamma = \left[\frac{\partial}{\partial V}\int_0^T \left(\frac{C_v}{T}\right) dT\right]_T \frac{V}{C_v} . \tag{14}$$

We estimate that errors in γ are no larger than 1 or 2%. The smoothed results are shown as solid lines in the bottom half of Fig. 12. As was expected from the volume dependence of Θ/Θ_0 at constant T/Θ_0, and from the temperature dependence of γ', γ is dependent upon T as well as upon V. However, the temperature dependence of γ is not as strong as

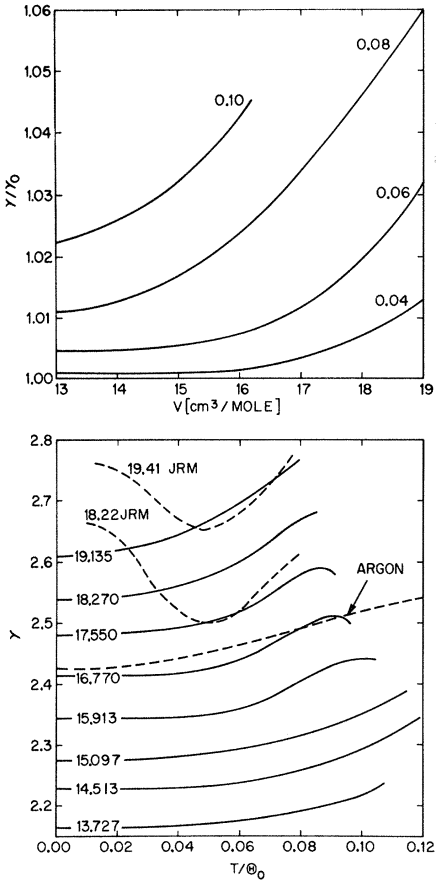

FIG. 12. Grüneisen parameter γ as a function of the reduced temperature T/Θ_0 at several molar volumes and the ratio γ/γ_0 as a function of volume at several T/Θ_0. The numbers in the upper figure are T/Θ_0, and those in the lower figure are the molar volume. The results for argon are from Ref. 39, and those labeled JRM are from Ref. 30.

that of γ'. It is questionable whether the maximum in γ at intermediate volumes and large relative temperatures is real. The existence of such a maximum is, however, not unreasonable since it occurs near the melting temperature and therefore may be attributable to excitations other than lattice vibrations. For comparison, the values of γ for argon which were derived recently by Tilford and Swenson[39] are also indicated in Fig. 12. It is evident that the temperature dependence of γ for He^4 at the smaller volumes is very similar to that for argon.

In Fig. 12, we also compare the present results for γ with some of those obtained by Jarvis, Ramm, and Meyer[30] from their own measurements of $(\partial P/\partial T)_v$ and the C_v measurements by Edwards and Pandorf.[4] Jarvis *et al.* observed a minimum in γ at $T/\Theta_0 \cong 0.05$, but their probable errors and those in the C_v measurements used by them were sufficiently large at small T that the existence of the minimum could not be established with certainty. The present results do not indicate a minimum in γ. However, at large volumes a considerable extrapolation of C_v was required to deduce γ, and an anomalous behavior of C_v for $T < 1.4$ °K at about 19 cm^3/mole would not have been detected by the present work and could result in an initial decrease of γ with increasing T. Such an anomalous behavior of C_v appears unlikely in view of the fact that C_v is well-behaved for $T/\Theta_0 \geqslant 0.02$, both at very small volumes and at 20.5 cm^3/mole.[5-7] For $T/\Theta_0 \geqslant 0.05$, the results of Jarvis *et al.* are similar to the present results.

It was observed by Sample and Swenson[1] that, within the precision of their work, γ/γ_0 at constant T/Θ_0 for He^3 is independent of volume. This is not the case for He^4 within the precision of the present work. In order to demonstrate this, γ/γ_0 is shown as a function of the volume in the top half of Fig. 12 for several values of T/Θ_0. Sample and Swenson's results would appear as horizontal lines on this graph, and they agree with the present results for hcp He^4 at about 16 cm^3/mole.

G. Comparison with hcp He^3

The most accurate data available for hcp He^3 are those reported by Sample and Swenson.[1] These authors also measured C_v for hcp He^4 at a molar volume of 12.23 cm^3. It had been hoped that comparison of the present results with Sample and Swenson's He^4 results might indicate that systematic errors in either set of measurements were small. Unfortunately, this comparison revealed a fairly large discrepancy. For this reason, we shall first discuss the comparison of the He^4 measurements.

Although the present results are only for volumes larger than 13.7 cm^3/mole, the success of Eq. (13) for Θ_0 from 13.7 to 20.8 cm^3/mole indicates that an extrapolation of Eq. (10) to about 12 cm^3/mole should introduce negligible errors. On the basis of this extrapolation of the present work, we predict $\Theta_0 = 94.1$ °K at 12.23 cm^3/mole. This value of Θ_0 cannot be compared directly with that quoted by Sample and Swenson. These authors observed a low-temperature anomaly in their measurements which they believed to be an apparatus effect and which prevented them from measuring accurately the temperature dependence of Θ for $T/\Theta_0 \lesssim 0.02$. Therefore, they assumed that Θ is independent of T in this temperature range. It seems likely that their measurements at $T/\Theta_0 = 0.03$ are not seriously affected by the anomaly, and we have chosen this temperature for comparison. The data in Fig. 11 indicate that $\Theta/\Theta_0 = 0.987$ at $T/\Theta_0 = 0.03$ for the smaller volumes of the present measurements and are virtually independent of volume in the range of interest. We use this information, and the value for Θ of 95.35 °K deduced from Sample and Swenson's quoted heat capacity at $T/\Theta_0 = 0.03$, to obtain $\Theta_0 = 96.6$ for their work. This differs by 2.6% in Θ_0 or almost 8% in C_v from the present results, and this difference is difficult to explain. It might be caused by a 1.3% error in the molar volume; but there is no obvious reason why such a large error in the volume might exist. The measurements of Sample and Swenson would be in agreement with the present work if their molar volume had been 12.08 cm^3/mole. It was demonstrated in Sec. IV E that if $\Theta_0 = 96.6$ °K is adopted for the purpose of comparing the temperature dependence of Θ/Θ_0 with that determined in the present work, then consistency between the two sets of measurements is obtained for $T/\Theta_0 \geqslant 0.03$.

Although there is a fairly large disagreement between the measurements by Sample and Swenson and the present results for He^4, a comparison of this work for He^4 with the He^3 results by Sample and Swenson is still worthwhile. Although the deduced ratios of Θ_0 for the two isotopes may be in error by 2.6%, this possible error should have relatively little effect upon Θ/Θ_0 and upon γ_0. Therefore, we have recalculated Θ_0 for He^3 from Sample and Swenson's measurements at $T/\Theta_0 = 0.03$, assuming that $\Theta/\Theta_0 = 0.987$ at this relative temperature. These values are compared with Θ_0 for He^4 as obtained from Eq. (13) in Table VI. It can be seen that Θ_{03}/Θ_{04} varies from 1.17 to 1.20 over the volume range covered by the measurements. When it is remembered that the ratio of Θ_0 for He^4 as determined by Sample and Swenson to that determined here is 1.026, one must conclude that there is no definite evidence for deviations of Θ_{03}/Θ_{04} from the value 1.154 which is expected for an harmonic solid.

The values of Θ_{03} in Table VI can be used to calculate γ_0. For this purpose, γ_{03} was approximated

TABLE VI. Comparison of the Debye temperature at 0 °K for hcp He^3 and hcp He^4.

V	Θ_{03}	Θ_{04}	Θ_{03}/Θ_{04}
19.05	39.7	34.0	1.168
17.13	52.1	44.4	1.174
15.29	68.7	58.1	1.182
13.71	88.1	74.1	1.190
11.42	129.7	108.0	1.201

by $-\Delta\ln\Theta_{03}/\Delta\ln V$, and this value was assigned to the average volume $\overline{V}$. In Table VII, γ_{03} is compared with values of γ_{04} obtained from Eq. (10). It is apparent that γ_0 has the same volume dependence for the two isotopes. The data indicate that γ_{03} is about 2.4% larger than γ_{04}; but this difference is probably no larger than possible systematic errors.

In order to compare the volume dependence of Θ/Θ_0, we show in Fig. 13 as solid lines Θ/Θ_0 for He^4 as a function of the volume at several values of T/Θ_0. Values of Θ/Θ_0 for He^3 were recalculated from C_v as quoted by Sample and Swenson, using Θ_0 in Table VI. These results are shown as circles in Fig. 13. It is evident that there is very good agreement for Θ/Θ_0 between the measurements for the two isotopes.

It was mentioned already that Sample and Swenson obtained values of γ/γ_0 which at constant T/Θ_0 are independent of the molar volume. It appears likely that Sample and Swenson did not observe the volume dependence of γ/γ_0 because of the lesser resolution of their work and that in fact γ/γ_0 at constant T/Θ_0 is about the same function of V for He^3 as it is for He^4. The values for γ/γ_0 reported by Sample and Swenson are approximately the same as those found here for He^4 at 16 cm^3/mole, and this volume is near the middle of the volume range covered by the He^3 measurements.

H. Other Themodynamic Functions

The entropy S, change in internal energy $U-U_0$, pressure coefficient $\beta_v=(\partial P/\partial T)_v$, change in pressure above 0 °K $P-P_0$, and the change in bulk modulus above 0 °K $B-B_0$ have been derived for each isochore for which the heat capacity had been measured, using the thermodynamic relations

$$S=\int_0^T T^{-1}C_v dT \quad , \tag{15}$$

$$U-U_0=\int_0^T C_v\, dT \quad , \tag{16}$$

$$\beta_v=V^{-1}\int_0^T C_v T^{-1} X dT \quad , \tag{17}$$

$$P-P_0=\int_0^T \beta_v\, dT \quad , \tag{18}$$

$$B-B_0=-\int_0^T\int_0^T C_v T^{-1}\left[V^{-1}X(X-1)+\left(\frac{\partial X}{\partial V}\right)_T\right] dT\, dT \quad , \tag{19}$$

where

$$X=\left(\frac{\partial \ln C_v}{\partial \ln V}\right)_T \quad . \tag{20}$$

Equations (17) and (19) were written deliberately in terms of the dimensionless logarithmic derivative X since this was used in the numerical work because of its small variation with V. It is estimated that no accuracy is lost in the integration and that each differentiation with respect to V increases the probable error due to random errors by one order of magnitude. Excluding the systematic errors discussed earlier, the errors in S and $U-U_0$ are, therefore, 0.1%, and those in β_v and $P-P_0$ are about 1%. Based on the relative contributions of $V^{-1}X(X-1)$ and $(\partial X/\partial V)_T$ to the term in the bracket of Eq. (19), it is believed that $B-B_0$ is subject to a possible error of about 5%. Numerical values of the thermodynamic functions are given in Table VIII at several values of T/Θ_0 for

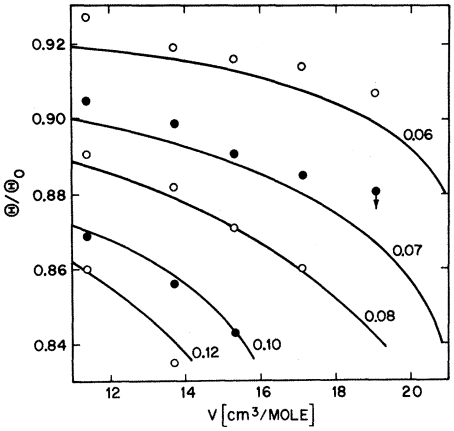

FIG. 13. Reduced Debye temperature as a function of molar volume at several values of the reduced temperature T/Θ_0. The numbers in the figure are the values of T/Θ_0. The solid lines are from this work and pertain to hcp He^4. Symbols are based on Ref. 1 and pertain to hcp He^3.

TABLE VII. Comparison of the Grüneisen parameter at 0 °K for hcp He^3 and hcp He^4.

$\overline{V}$	γ_{03}	γ_{04}	γ_{03}/γ_{04}
18.1	2.573	2.523	1.019
16.2	2.429	2.368	1.027
14.5	2.283	2.227	1.024
12.6	2.116	2.068	1.024

TABLE VIII. Thermodynamic functions for hcp He^4. The units are C_v – mJ $mole^{-1}\,°K^{-1}$; S – mJ $mole^{-1}\,°K^{-1}$; $(U-U_0)$ – mJ $mole^{-1}$; $(P-P_0)$ – bar; $(\partial P/\partial T)_v$ – bar $°K^{-1}$; (B_0-B) – bar.

T/Θ_0	C_v	S	$U-U_0$	$P-P_0$	$\left(\frac{\partial P}{\partial T}\right)_v$	B_0-B
Sample 1, $V=13.727$ cm^3/mole, $\Theta_0=73.870$ °K						
0.01[a]	1.94	0.65	0.36	0.0006	0.0031	0.0034
0.02	15.66	5.20	5.76	0.0090	0.0246	0.054
0.03	54.34	17.76	29.60	0.0463	0.0848	0.284
0.04	136.4	43.31	96.63	0.151	0.214	0.97
0.05	289.6	88.56	248.5	0.390	0.485	2.64
0.06	545.5	162.2	549.8	0.867	0.865	6.02
0.07	929.0	273.4	1086	1.72	1.48	12.0
0.08	1446	429.7	1955	3.10	2.31	21.7
0.09	2100	636.3	3256	5.18	3.36	35.7
0.10	2875	896.7	5086	8.12	4.64	55.3
0.11	3776	1212	7534	...	...	...
Sample 2, $V=14.513$ cm^3/mole, $\Theta_0=65.370$ °K						
0.01[a]	1.94	0.65	0.32	0.0005	0.0030	0.0030
0.02[a]	15.65	5.19	5.10	0.0078	0.0239	0.048
0.03	54.31	17.76	26.18	0.0399	0.0827	0.253
0.04	136.4	43.30	85.50	0.130	0.208	0.864
0.05	290.3	88.63	220.2	0.337	0.446	2.35
0.06	548.3	162.6	487.9	0.749	0.845	5.40
0.07	934.8	274.4	965.1	1.49	1.45	10.87
0.08	1462	432.0	1741	2.69	2.27	19.7
0.09	2126	641.3	2906	4.51	3.33	32.6
0.10	2932	905.7	4552	7.09	4.63	50.6
0.11	3881	1228	6770	10.62	6.19	74.8
Sample 3, $V=15.097$ cm^3/mole, $\Theta_0=59.813$ °K						
0.01[a]	1.94	0.65	0.29	0.0004	0.0029	0.0028
0.02[a]	15.58	5.18	4.65	0.0070	0.0234	0.045
0.03	54.0	17.67	23.83	0.0358	0.0810	0.233
0.04	136.3	43.12	77.92	0.117	0.204	0.793
0.05	291.2	88.52	201.3	0.302	0.439	2.16
0.06	551.3	162.8	447.3	0.674	0.834	5.01
0.07	940.5	275.2	886.6	1.34	1.43	10.2
0.08	1476	434.1	1602	2.44	2.26	18.5
0.09	2155	645.8	2681	4.10	3.33	30.9
0.10	2982	914.3	4209	6.47	4.64	48.2
0.11	3974	1244	6282	9.70	6.23	71.2
Sample 4, $V=15.913$ cm^3/mole, $\Theta_0=52.966$ °K						
0.01[a]	1.94	0.65	0.26	0.0004	0.0029	0.0025
0.02[a]	15.62	5.19	4.12	0.0061	0.0229	0.0403
0.03	54.18	17.71	21.16	0.0310	0.0794	0.210
0.04	136.4	43.23	69.17	0.101	0.201	0.716
0.05	293.0	88.75	178.8	0.263	0.431	1.95
0.06	556.6	163.6	398.4	0.586	0.823	4.54
0.07	954.0	277.4	792.1	1.17	1.42	9.29
0.08	1501	438.8	1435	2.14	2.26	17.1
0.09	2207	654.7	2410	3.62	3.37	28.9
0.10	3096	931.3	3804	5.75	4.75	45.6
Sample 5, $V=16.770$ cm^3/mole, $\Theta_0=46.752$ °K						
0.01[a]	1.94	0.65	0.23	0.0003	0.0028	0.0022
0.02[a]	15.61	5.18	3.64	0.0052	0.0225	0.0365
0.03	54.25	17.71	18.69	0.0270	0.0782	0.192
0.04	137.0	43.30	61.18	0.0881	0.197	0.650
0.05	293.5	88.96	158.2	0.228	0.425	1.77
0.06	561.2	164.2	353.0	0.511	0.816	4.14

TABLE VIII. *Continued.*

T/Θ_0	C_v	S	$U-U_0$	$P-P_0$	$\left(\frac{\partial P}{\partial T}\right)_v$	B_0-B
Sample 5, $V=16.770$ cm^3/mole, $\Theta_0=46.752$ °K (Continued)						
0.07	964.4	279.1	704.0	1.024	1.42	8.57
0.08	1528	442.8	1280	1.87	2.27	15.9
0.09	2266	663.5	2159	3.19	3.39	27.1
Sample 6, $V=17.550$ cm^3/mole, $\Theta_0=41.832$ °K						
0.01[a]	1.94	0.65	0.20	0.0003	0.0027	0.0020
0.02[a]	15.68	5.20	3.27	0.0046	0.0222	0.0331
0.03[a]	54.42	17.78	16.79	0.0238	0.0773	0.176
0.04	137.2	43.41	54.87	0.0780	0.196	0.602
0.05	295.0	89.24	142.0	0.202	0.421	1.64
0.06	566.7	165.1	317.7	0.453	0.813	3.85
0.07	982.3	281.6	636.2	0.913	1.42	8.03
0.08	1566	448.9	1163	1.68	2.30	15.1
0.09	2362	676.7	1975	2.88	3.47	26.1
Sample 7, $V=18.270$ cm^3/mole, $\Theta_0=37.819$ °K						
0.01[a]	1.94	0.65	0.18	0.0003	0.0027	0.0019
0.02[a]	15.74	5.21	2.96	0.0041	0.0220	0.0306
0.03[a]	54.74	17.86	15.25	0.0214	0.0773	0.164
0.04	138.2	43.64	49.89	0.0705	0.196	0.568
0.05	298.6	89.98	129.5	0.183	0.421	1.55
0.06	574.7	166.7	290.2	0.411	0.818	3.67
0.07	1003	285.3	583.4	0.831	1.45	7.71
0.08	1618	457.2	1073	1.542	2.36	14.70
Sample 8, $V=19.135$ cm^3/mole, $\Theta_0=33.574$ °K						
0.01[a]	1.94	0.65	0.16	0.0002	0.0027	0.0017
0.02[a]	15.72	5.21	2.63	0.0036	0.0217	0.0276
0.03[a]	54.79	17.86	13.54	0.0188	0.0764	0.150
0.04[a]	138.0	43.66	44.31	0.0619	0.194	0.522
0.05	299.0	89.84	114.8	0.161	0.418	1.44
0.06	576.7	166.8	258.0	0.362	0.814	3.45
0.07	1019	286.5	520.5	0.734	1.45	7.32
0.08	1643	461.8	963.6	1.37	2.40	14.12

[a] $T \leq 1.40$ °K, and data are based entirely upon the extrapolation described in the text.

the samples with volumes less than 19.2 cm^3/mole. For larger volumes, we do not regard the extrapolation to 0 °K of C_v to be sufficiently reliable to warrant a numerical presentation of the thermodynamic functions, and for $V \geq 20.5$ cm^3/mole accurate data are available from the work of Gardner *et al.*[5-7] It should be remembered that the results presented in Table VIII have not been smoothed with regard to the molar volume. Properties at the melting line are given for all volumes in Table IX.

It can be shown that $C_v, S, (U-U_0)/T, (P-P_0)/T, (\partial P/\partial T)_v$, and $(B-B_0)/T$ at constant T/Θ_0 are independent of V if the Grüneisen parameter γ is independent of T, and thus if the reduced Debye temperature Θ/Θ_0 at constant T/Θ_0 is independent of V. For hcp He^4, this is not the case; but it is expected that these thermodynamic variables are only mildly volume dependent at constant T/Θ_0. We have chosen the entropy to display this volume dependence in Fig. 14, and in this figure we also compare the present results with those of Gardner, Hoffer, and Phillips as quoted in Ref. 7. For this purpose, the entropy at the several molar volumes and at several values of T/Θ_0 was divided by the entropy at 13.727 cm^3/mole and at the same values of T/Θ_0, and this ratio is shown as a function of V. The numbers 0.03, . . . , 0.11 indicated in the figure are the values of T/Θ_0 which correspond to the ratios. The volume dependence of S at constant T/Θ_0 is apparent. If smooth lines are drawn through the data, then the scatter about these lines is less than 0.5% of S. This scatter reflects the random volume errors of 0.07% discussed earlier. The measurements by Hoffer *et al.* also agree with the present results within 0.5%.[40] This is very gratifying since it indicates that the present extrapolation procedure to

TABLE IX. Thermodynamic properties of hcp He^4 at the melting temperature T_M.

V (cm^3 mole^{-1})	T_M/Θ_0	S_M [J mole^{-1}(°K)$^{-1}$]	$U_M - U_0$ (J mole^{-1})	$P_M - P_0$ (bar)	$\frac{\partial P}{\partial T}_{V,M}$ [bar (°K^{-1})]	$B_0 - B_M$ (bar)
13.727	0.1263	...	...	...	...	...
14.513	0.1176	1.516	8.907	14.0	7.57	98.3
15.097	0.1115	1.302	6.668	10.3	6.51	75.4
15.913	0.1035	1.049	4.438	6.72	5.34	53.1
16.770	0.0960	0.8289	2.879	4.27	4.22	36.2
17.550	0.0894	0.6643	1.930	2.81	3.41	25.5
18.270	0.0835	0.5342	1.311	1.89	2.77	18.1
19.135	0.0775	0.4122	0.832	1.18	2.13	12.1
19.455	0.0749	0.3708	0.6940	1.02	1.98	11.0
19.735	0.0726	0.3363	0.5876	0.878	1.83	9.9
20.036	0.070	0.2988	0.4817	0.721	1.64	8.4
20.472	0.066	0.2494	0.3578	0.503	1.31	5.7
20.725[a]	0.062	0.1988	0.2577	0.346	0.98	3.8

[a] hcp → bcc transition.

0 °K yielded reliable results, even at the larger volumes and smaller values of T/Θ_0 where the present entropy is based entirely upon extrapolated values of C_v.

The present results are compared with the measurements of $(\partial P/\partial T)_v$ by Jarvis *et al.*[30] at two volumes in Fig. 15, where $(\partial P/\partial T)_v/T^3$ is shown as a function of T/Θ_0. The molar volumes are two of those used by Jarvis *et al.* and were reevaluated from the melting line used in this work and the reported[30] melting temperatures. The Debye temperatures at 0 °K are from Eq. (13). The smoothed data in Table I of Ref. 30 were used. For the present work, an interpolation in Table VIII of $(\partial P/\partial T)_v$ at constant T/Θ_0 was employed. It is evident that the general agreement is quite reasonable, and for $T/\Theta_0 \geq 0.035$ differences do not exceed 3% of $(\partial P/\partial T)_v$. This is within approximate estimates of the combined probable errors. For $T/\Theta_0 < 0.035$, the data by Jarvis *et al.* reveal a temperature region where $(\partial P/\partial T)_v \propto T^3$. The present work near these volumes is based upon an extrapolation of C_v in this

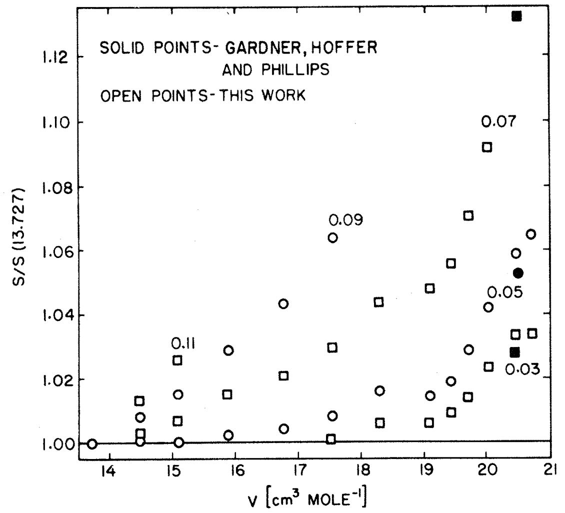

FIG. 14. Volume dependence of the entropy at several values of the reduced temperature T/Θ_0. The ratio shown here would be equal to unity if the Grüneisen parameter were temperature independent. The numbers are the value of T/Θ_0. The solid symbols are based on Refs. 5–7.

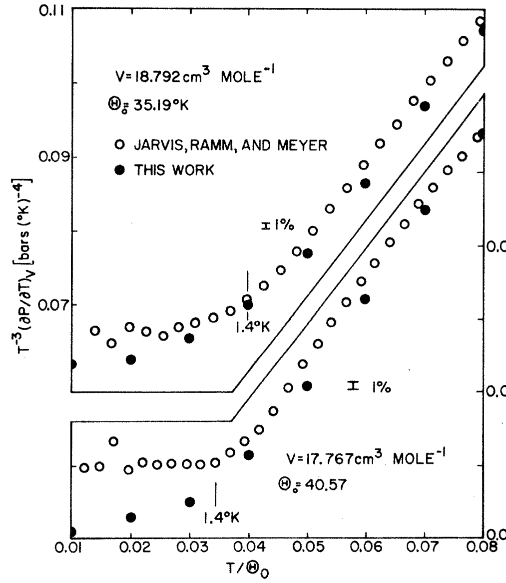

FIG. 15. Comparison of the present results for $(\partial P/\partial T)_v$ with the direct measurements reported in Ref. 30.

temperature range; however, the reasonable extrapolation of C_v employed here results in values of $T^{-3}(\partial P/\partial T)_v$ which are dependent upon T/Θ_0 even for $T/\Theta_0 \leq 0.035$.

In addition to the thermodynamic variables presented above, it is possible to derive some other variables at T_M[4,16,34,41] from the discontinuity ΔC_{vM} in C_v at T_M and from the P-V-T relations at melting.[5–7,22–24] Table I contains the required ΔC_{vM}. The calculations will not be carried out in detail here.

V. SUMMARY AND CONCLUSIONS

We have reported in this paper extensive high-precision measurements of the heat capacity at constant volume for hcp He^4. The results are for molar volumes between 13.7 and 20.7 cm^3. They were used to determine the deviations of the temperature-dependent contributions to the equation of state from the Grüneisen model and these deviations were expressed in terms of a temperature- and volume-dependent Grüneisen parameter γ. The temperature and volume dependences of γ were compared where possible with those for hcp He^3, parahydrogen, argon, and krypton. The following conclusions can be drawn.

(a) γ_0 (γ at 0 °K) for hcp He^4 increases about linearly with volume and is the same within about 2% for hcp He^3 and hcp He^4 at the same volume. The volume dependence of γ_0 is given by $d\gamma_0/dV = 0.08$ $(cm^3/mole)^{-1}$. This latter value is also consistent with what is known about solid parahydrogen. No information is avaliable for heavier hcp van der Waals solids; but the absence of an isotope effect in $d\gamma_0/dV$ for hcp helium makes it seem likely that γ_0 has a similar volume dependence for heavier inert-gas solids.

(b) At a fixed volume, γ for hcp He^4 is temperature dependent. The dependence of γ upon the reduced temperature T/Θ_0 is weaker at small volumes than it is at large volumes, and it is at least qualitatively the same as in hcp He^3. At the smaller volumes, the dependence of γ upon T/Θ_0 for hcp He^4 is very similar to that for solid argon.

(c) The reduced Debye temperature Θ/Θ_0 at constant T/Θ_0 is volume dependent, and this volume dependence is very similar in hcp He^3 and hcp He^4. As the molar volume decreases, Θ/Θ_0 at a fixed value of T/Θ_0 approaches the corresponding values for argon and krypton.

The above observations indicate that quantum and anharmonic effects are unimportant for the volume and temperature dependence of γ and Θ and indicate that hcp helium may reasonably be looked upon as a model for other close-packed van der Waals solids whose properties cannot be studied readily over a large volume range.

We have also presented in this paper values of thermodynamic functions S, $U - U_0$, $P - P_0$, $(\partial P/\partial T)_v$, and $B - B_0$ for hcp He^4 and for molar volumes between 13.7 and 19.2 cm^3.

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Connection between Elementary Collective Coordinates and the Vlasov Equation*

Jerome K. Percus

Courant Institute of Mathematical Sciences, New York University, New York 10012

and

George J. Yevick

Physics Department, Stevens Institute of Technology, Hoboken, New Jersey 07030

(Received 12 March 1970)

A naive collective coordinate analysis leads to no damping of the acoustic modes of a classical fluid. A similar analysis of the linearized Vlasov equation leads to the well-known phenomenon of Landau damping. The qualitative form of Landau damping is, however, inaccurate for nonsingular forces and probably for low-k propagation in plasmas. Comparison of the two approaches shows that retention of the velocity variable in the Vlasov equation allows for an accurate description of positional fluctuations due to velocity dispersion by itself, but a poor assessment of collective forces. If, instead, the phase mixing of collective modes due to velocity dispersion is taken into account, a damping mechanism is introduced with the anticipated hydrodynamic form in fluids at low k, and with a k^4 dependence for plasmas.

I. INTRODUCTION

It is well known that the elementary collective coordinate approach[1] to the theory of fluids in general and of plasmas in particular yields steadily oscillating normal modes. On the other hand, even the very crude linearized Vlasov equation[2] generates Landau damping. The reasons for this discrepancy are essential to an understanding of the time-dependent properties of fluids and plasmas. In this paper we propose to elucidate clearly why there is no damping in the elementary collective coordinate approach, to examine the primitive nature of the Landau damping mechanism, and to offer a heuristic modification of the collective coordinate analysis which leads to a very simple physically reasonable damping effect.

II. COLLECTIVE COORDINATE APPROACH

The longitudinal acoustic phonons of a solid or a continuum fluid suggest that the oscillatory normal modes of a real fluid or plasma be described by the set

$$q_{\vec{k}}(t) \equiv \textstyle\sum_i e^{i\vec{k}\cdot\vec{x}_i(t)} , \qquad (1)$$

where i runs over the N identical particles (the mobile electrons in a plasma) of the system. Differentiating twice with respect to time and making use of Newton's equations of motion, we have

$$\ddot{q}_{\vec{k}} + \sum_i (\vec{k}\cdot\dot{\vec{x}}_i)(\vec{k}\cdot x_i) e^{i\vec{k}\cdot\vec{x}_i} + (i\vec{k}/m) \sum_{i\neq j} \nabla\varphi(\vec{x}_i - \vec{x}_j)\, e^{i\vec{k}\cdot\vec{x}_i} = 0 , \qquad (2)$$

where $\varphi(\vec{x})$ is the interaction potential. Equation (2) is, of course, an exact representation of the many-body problem.

Suppose that the system is not far from equilibrium. Then the Bohm-Pines approximation[3] involves making an ensemble equilibrium average of suitable terms in order to extract a pure $q_{\vec{k}}$ dependence. Thus we have