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Heat Capacity and Other Properties of Hexagonal Close-Packed Helium-4 *

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The heat capacity of hcp helium has been measured for six molar volumes from 20.9 to 16.9 cm^3 between about 0.3°K and the melting point. The calorimeter, which uses magnetic cooling and thermometry, is described in some detail. The results, expressed as Debye thetas, level off at low temperatures to constant values, θ_0. The volume dependence of θ_0 gives a Grüneisen constant of 2.60 ± 0.05. The temperature dependence of θ, which is not qualitatively different from that found in other solidified inert gases, is such that θ/θ_0 is a single function of T/θ, irrespective of density. The results have been used with melting-curve data to give the internal energy, entropy, compressibility, and expansion coefficient. The values of the compressibility are in agreement with those obtained from the discontinuity in the heat capacity on melting. Comparison of θ_0 with the compressibility and velocity-of-sound data indicates that hcp helium is elastically anisotropic but approximately obeys the Cauchy relations.

I. INTRODUCTION

EXPERIMENTAL work on solid helium was begun more than 35 years ago, but was interrupted by the war and was not resumed again until about 1950. Since then both theoretical[1–5] and experimental interest have been persistent. Although solid helium is the simplest quantum mechanical solid, experiments on He^4 have revealed three allotropic crystalline forms[6]: the hexagonal close-packed structure[7] (hcp), the cubic close-packed[8] (ccp), and the body centered cubic[9] (bcc). The same three structures have been found in solid He^3. A great many experiments have been concerned with the volumes and pressures for these forms in equilibrium with the liquid and with each other. Other properties which have been investigated are the thermal conductivity, sound velocity, and specific heat. Since solid helium is so compressible, it has been possible to measure these properties over a very wide range of density.

The subject of the present paper is the heat capacity and other thermodynamic functions of hcp He^4 in the low-density range, that is, for molar volume V larger than 17 cm^3. Particular attention has been given to the temperature dependence of the Debye theta. The work was intended to complement the earlier, high pressure work of Dugdale and Simon[8] which was carried out in the range 15 to 10 cm^3 between 4 and 25°K. (Very recently the high-pressure region has been investigated again by Dugdale and Franck,[10] and Franck.[11]) It was also hoped to clarify the limiting form of the heat capacity at very low temperatures. Previous measurements of the heat capacity in the low-density region by Webb, Wilkinson, and Wilks[12] seem to show a maximum in the Debye theta at temperatures of the order of 1°K. A similar effect was observed by Heltemes and Swenson,[13] and Franck,[11] who analyzed their data in terms of an anomalous contribution to the specific heat, linearly proportional to T, as well as a Debye term which is approximately T^3. Franck has reported that in his experiments the linear term could be reduced by annealing.

In a second paper it is hoped to present measurements on the bcc phase of solid He^4 and on bcc and hcp He^3. The experimental technique used in all the measurements is described in the next section of the present paper. Section 3 describes and discusses the results on hcp He^4; a detailed intercomparison of bcc and hcp He^3 and He^4 is postponed to the second paper.

2. EXPERIMENTAL APPARATUS

The apparatus used in these measurements is the same as that in previous work[14–16] but with some modifications and improvements. As in previous work the samples of solid helium were contained in a copper calorimeter whose interior is partially filled with a porous sponge of sintered copper to promote thermal contact. The calorimeter was constructed[17] from a

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[17] Constructed by Micrometallic Division, Pall Corporation, Glen Cove, New York.

cylindrical copper cup which was filled with copper powder of uniform grain size, and then sintered just below the melting point to produce an average pore size in the sintered copper of about 10 μ and a surface area of about 0.2 m^2. This sort of construction was primarily intended to give extremely good thermal contact to solid He^3 at very low temperatures[15] and its use may possibly have contributed to the difficulty of annealing out pressure inhomogeneities in some of our samples. The volume of the calorimeter was found by filling it with liquid He^4 and then measuring the amount of gas evolved when it was warmed to room temperature, making a small correction for the filling tube. The volume was 0.2802±0.0006 cm^3. (This is different from the value in Refs. 14 and 15 because of some modifications in the construction of the calorimeter.) The filling tube is a 0.010-in. o.d., 0.005-in. i.d. stainless steel tube with a 0.003-in. niobium wire slipped inside it.

The calorimeter was cooled to 1.2°K using He^3 exchange gas in contact with a He^4 bath, and then to 0.1°K by magnetic cooling in which thermal contact between the calorimeter and the cooling salts was made by a superconducting thermal switch. The cooling salts remained below 0.2°K throughout the specific heat measurements and served to getter any residual exchange gas not pumped out after magnetization of the paramagnetic salts.

The disposition of some important parts of the apparatus is shown in Fig. 1. The cerium magnesium nitrate (CMN) thermometer is enclosed in a nylon case, screwed to the bottom of the calorimeter and contains about 60-#32 AWG enamelled wires which were soldered to the calorimeter. Thermal contact between the CMN crystals and the wires is made by silicone stopcock grease, which fills the nylon case. The two CMN single crystals together form a cylinder 2.7 cm long by 1.1 cm diam. and mass 5.8 g. The susceptibility of the crystals can be measured by mutual inductance coils wound on the vacuum jacket and connected to an electronic Hartshorn bridge.[18] The output of the bridge is relayed through a tuned amplifier and phase sensitive detector to a chart recorder which gives a continuous measurement of the calorimeter temperature during heat capacity determinations.

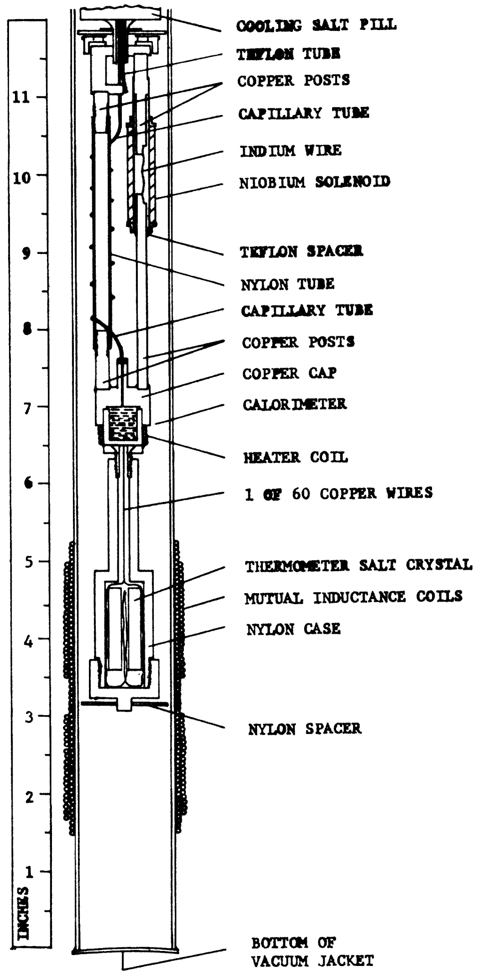

FIG. 1. Calorimeter.

During the measurements on the hcp solid, temperature rises of about one-twentieth of the temperature were measured within 1%. For the bcc solid between 1.4 and 1.8°K, which will be discussed in a second paper, temperature rises of about 0.006°K were measured with an accuracy of about 2%. The accuracy of the absolute temperature in the region 1 to 2°K (i.e., the region in which the thermometer was calibrated against the He^4 vapor pressure) was not worse than ±0.001°K and in the other temperature regions not worse than 0.2% of the temperature. The electrical measurements for the heater power were made to about 0.2% while the heating period was measured by an electronic counter to the nearest msec. The heater is varnished to the outside of the calorimeter, and connected by spot welding to niobium leads.

The calorimeter is mechanically supported by a thermally insulating nylon support tube from the cooling salt pill. This is a hermetically sealed metal case made after a design of Barnes, Heer, and Daunt[19] which contains 35 g of chromium potassium alum and used as a refrigerant and as an exchange-gas getter. The cooling salt pill, with the calorimeter rigidly attached to it, is suspended by the stainless steel filling tube from a guard or buffer salt pill case containing about 25 g of manganese ammonium sulphate. The guard salt acts as a thermal sink for the electrical leads and filling tube leading from the He^4 bath and also getters exchange gas. The guard salt in turn is suspended by the filling tube from the top of the vacuum jacket. The stainless steel

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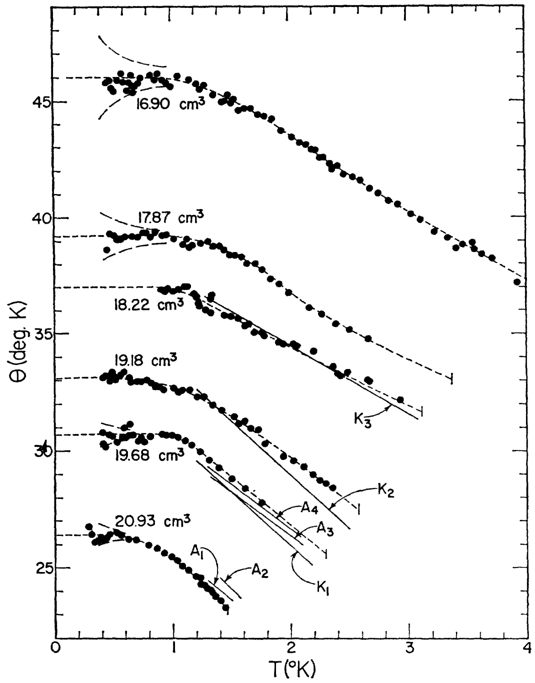

FIG. 2. The heat capacity of hcp He^4 given as the Debye θ, for six molar volumes. The short vertical lines give the melting temperature for each volume. The curved, dashed lines about the points at low temperature represent the effect of adding or subtracting 1% of the calorimeter heat capacity, and so give an idea of the approximate accuracy of the data. The solid lines give the results of previous workers: K_1, K_2, K_3, Keesom and Keesom (see Ref. 23) for $V=19.92, 19.34, 18.36$ cm³; A_1, A_2, A_3, A_4, Ahlers (see Ref. 24) for $V=20.921, 20.807, 19.884, 19.816$ cm³, respectively.

filling tube is brought into thermal contact with the He^4 bath at the top of the vacuum jacket and then continues to the top of the cryostat in a vacuum space. The electrical leads are brought out of the vacuum jacket via Kovar-glass seals into a small continuously pumped vacuum chamber (to guard against leaks) and then into the He^4 bath through another set of seals.

Thermal contact between the refrigerant salt and the calorimeter was obtained by a superconducting thermal switch of 99.999% pure indium. The indium ribbon of size 0.001 by 0.0005 by 0.75 in. was placed inside a small solenoid of about 2000 turns of 0.003 in. niobium wire along a length of 2.5 cm. A current of 0.3 A in the solenoid was sufficient to drive the indium switch normal and thus make thermal contact between the cooling salt pill and the calorimeter. The solenoid current was provided by a power transistor whose base current was controlled by a circuit resembling a Miller integrator.[20]

It may be useful to describe the method of making the thin indium ribbon used in the thermal switch. Stock indium wire about $\frac{1}{16}$ in. diam. was placed between two very smooth and clean blocks of tool steel and pressed in a large vise until it was squeezed down to a thickness of about 0.0005 in. The steel blocks were separated and displaced and then put back together with the indium sheet sticking out past the edge of one of the blocks. A feeler gauge, say 0.020 in., was set against the side of the displaced block with the 0.020 in. edge against the indium sheet. A good razor blade was set on the feeler gauge and pushed against the indium sheet to cut it. The feeler gauge was then changed from 0.020 to say 0.019 in. (depending on the size of switch desired) and a second cut with the razor blade was made. The second cut then formed a ribbon 0.001 in. wide and 0.0005 in. thick. The ribbon was much too small and fragile to solder; therefore it was installed on the terminals of the apparatus by pressing it on to larger indium tabs soldered onto the terminals of the calorimeter and cooling salt-pill case.

With the calorimeter in the temperature range above 1°K and the cooling salt pill below 0.1°K, there was a noticeable heat leak between the calorimeter and the cooling salt pill through the superconducting indium switch which cooled the calorimeter. This was cancelled when necessary by applying heat to the calorimeter through an auxiliary heating circuit which therefore controlled the temperature drift of the calorimeter.

Filling the Calorimeter

The very narrow filling tube to the calorimeter is connected outside the cryostat to a system with a relatively small dead volume, less than 1 cm³, consisting of a Consolidated Electrodynamics 5000-psi strain-gauge pressure transducer and a miniature needle valve connected to the gas handling system. The pressure transducer was chosen in preference to a Bourdon gauge because of its slightly higher accuracy and because it requires only a very small dead space. It was calibrated against a free piston gauge and was accurate to about ±0.2 atm. Since the equipment was designed for experiments on solid He^3 and solid He^3 and He^4 mixtures, the gas handling system included a small helium cryostat for condensing the specimen gas as liquid from low pressure storage bottles and vaporizing it at high pressure to fill the calorimeter. This technique had the secondary advantage of removing impurities which might otherwise have blocked the narrow calorimeter filling tube. As is usually done,[12] the calorimeter was filled with fluid or liquid helium at the desired density by maintaining it at a hundredth of a degree or so above the freezing temperature at the appropriate pressure as indicated by the data of Grilly and Mills[21,22]; then, by rapidly cooling the bath through the freezing point, the filling tube was blocked with solid helium. Afterwards it was usually observed that the sample remained at constant volume. This point could be checked by observing (a) the melting temperature, and (b) the freezing temperature by measuring the heat capacity while the

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filling tube was still blocked, and later by measuring directly the number of moles of helium in the calorimeter. This last could be done to within ±0.2% by expanding the contents of the calorimeter into a known volume connected to a mercury manometer and making the necessary corrections for the contents of the filling tube and dead volume. The density calculated from the filling pressure agreed with the three other measurements within the expected accuracy. Very little difficulty was experienced in maintaining the block in the capillary tube even when the average density of the helium in the calorimeter was less than the minimum melting density of the solid as in some of our experiments on bcc He^4. This agrees with previous experience with He^3 using the same apparatus[14,15]; however, as an additional precaution against the block's giving way, the liquid helium bath in the bcc He^4 measurements was held between the lower triple point and the melting temperature of the sample.

TABLE I. The Debye θ of hcp He^4.

	V_{meas} (cm^3/mole)					
T(°K)	16.90	17.87	18.22	19.18	19.68	20.93[a]
0.00	(46.0)[b]	(39.25)	(37)	(33.1)	(30.7)	(26.35)
0.50	...	39.25	...	33.1	30.7	26.3
0.75	46.0	39.25	...	33.0	30.7	26.1
1.00	46.0	39.2	36.9	32.8	30.6_5	25.4
1.25	45.7	38.9	36.4	32.3	29.7	24.3
1.50	45.0	38.5	35.8	31.5	28.8_5	(23.1)
1.75	44.4	37.7	35.0	30.6	27.8	
2.00	43.5	36.7	34.4	29.7		
2.25	42.7	35.9	33.8	28.8		
2.50	41.8	35.2	33.1	27.7_5		
2.75	41.1	34.5	32.5			
3.00	40.2	...	31.7			
3.25	39.4	...				
3.50	38.7					
3.75	38.1					
T_m(°K)	...	...	3.16	2.566	2.304	1.482[c]
T_F(°K)	...	4.388	4.019	3.329	2.993	...
P(atm)	...	160	129	99	78	49

[a] Determined from the pressure and the data of Grilly and Mills.
[b] Parentheses indicate extrapolated values of θ.
[c] Beginning of transition to bcc.

3. RESULTS AND DISCUSSION

The Heat Capacity

The heat capacity of the hexagonal phase of He^4 has been measured at six different molar volumes ranging from 20.93 to 16.90 cm^3. The results expressed as Debye thetas are given in Fig. 2 where we have also shown the data of Keesom and Keesom[23] (on the 1932 scale of temperature), and Ahlers[24] which are in good agreement with the present work. Smoothed values of θ at even temperature intervals are given in Table I. All of the measured samples were prepared in the way described in the previous section except for the highest density, molar volume 16.90 cm^3, which had a melting point and freezing point above 4.2°K. This sample was obtained by pressurizing the calorimeter to about 3500 psi when the cryostat was at liquid-nitrogen temperature; then liquid helium was slowly transferred into the cryostat in small quantities, taking about half an hour to reach 4.2°K. The molar volume of the sample was measured at the end of the experiment by expansion into the known volume in the same way as the less dense samples.

In some samples of hexagonal helium, interesting premelting effects were observed. In one sample, $V=19.68$ cm^3, these appeared when the temperature was still half a degree below the melting point, while in others they did not occur until very close to the melting temperature. The effects were observed as an "after heating," that is, in a specific heat measurement the temperature of the calorimeter continued to rise after the heating current was switched off, and would do so for several minutes until it levelled off in a quasi-exponential manner. However, the apparent heat capacity in such a case, when it was possible to measure it, was the same within the experimental error as that obtained in the absence of premelting effects. It was found that premelting could be avoided by annealing the sample for about half an hour or so just below the melting point before cooling it. The premelting was ascribed to parts of the sample having lower densities than the rest, which would melt on heating and then slowly refreeze again at a higher density as the sample became more homogeneous. The proportion of the sample involved was probably very small, less than a few percent, since the ratio of the heat involved in premelting to the total latent heat of melting was of that order or less.

An important feature of the results shown in Fig. 2 is that the Debye θ levels off at low temperatures and becomes independent of temperature, allowing one to determine θ_0, the value at 0°K, within 1 or 2%. We see no evidence in the present work for a contribution to the specific heat, AT, which is linear in the temperature (making the Debye θ decrease at low temperatures) comparable to that found by Heltemes and Swenson[13] in both solid He^4 and He^3. This confirms our earlier conclusions in work which included measurements of solid He^3.[15] The effect of adding or subtracting 1% of the calorimeter heat capacity to the present data is shown in Fig. 2 as the curved, dashed lines about the points at low temperatures. If a linear term in the specific heat exists in the present results, we estimate its order of magnitude to be less than 1% of our calorimeter (background) heat capacity which means that it is less than 5% of the linear term found by Heltemes and Swenson. J. P. Franck[11] has also reported a linear specific heat contribution in solid He^4 at high pressure. The largest molar volume investigated in his work was 16.30 cm^3, smaller than any in the present experiments. For all annealed samples, Franck found a coefficient A which was roughly one-third of that found by Heltemes and Swenson at the same density. On the other hand,

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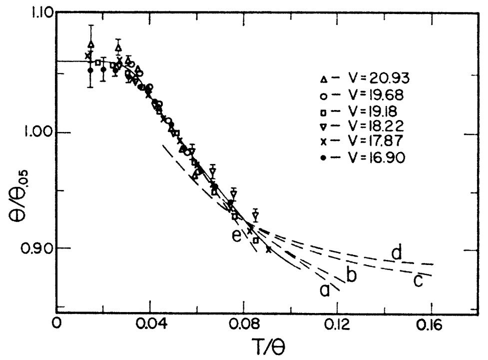

FIG. 3. The results of Fig. 2 plotted in a reduced form. $\theta_{0.05}$ is the value of θ when $T/\theta=0.05$. The dashed, lettered curves are the results of other workers: Dugdale and Franck (see Ref. 10); curve *a*, molar volume 16.25 cm^3; *b*, 14.55 cm^3; *c*, 12.22 cm^3; and *d*, 11.77 cm^3. Ahlers (see Ref. 24); *e*, 19.816, and 19.886 cm^3. The continuous line through the points is the curve used in calculating the thermodynamic functions.

for an unannealed sample the coefficient A was nearly as large as that found by Heltemes and Swenson, and so Franck has suggested that the linear term is associated with some form of lattice imperfection, which may be partly annealed out at higher temperatures. Again we have no affirmative evidence on this point, but this may be because our specimens were already sufficiently well annealed, or because our experiments do not extend to sufficiently high densities.

The curves of θ versus T in Fig. 2 are all similar in shape and can be represented in a reduced form, as shown in Fig. 3, in which we have plotted $\theta/\theta_{0.05}$ versus T/θ, where $\theta_{0.05}$ is the value of θ when $T/\theta=0.05$. All the experimental points lie close to the single, continuous curve in the diagram. The deviations from the curve do not depend systematically on molar volume and are probably within experimental error. This diagram allows us to compare our data with the recent measurements of the specific heat by Dugdale and Franck,[10] made at higher densities and temperatures. Since their data do not extend down to $T/\theta=0.05$, we have plotted their measurements as $\theta/\theta_{0.08}$ versus T/θ and then fitted the resulting curves to ours at $T/\theta=0.08$. Their lowest density curves, a and b in Fig. 3, join ours in a very satisfactory way, but at the higher densities the heat capacity can no longer be expressed in a reduced form, as shown by curves c and d. The measurements of Ahlers[24] at molar volumes between 19 and 20 cm^3 have also been plotted in Fig. 3, and can be seen to be in excellent agreement with the drawn curve.

In Fig. 4 we give the values of θ_0 (the extrapolated value of θ at 0°K) and of $\theta_{0.05}$ used in calculating the reduced plot, Fig. 3, as a function of molar volume. Both quantities have been estimated from the data of Fig. 2. The graph also shows the very good agreement with the measurements of other authors. (The linear terms found by Franck[11] and Heltemes and Swenson[13] have been subtracted out.) All the data can be represented by the empirical formulas

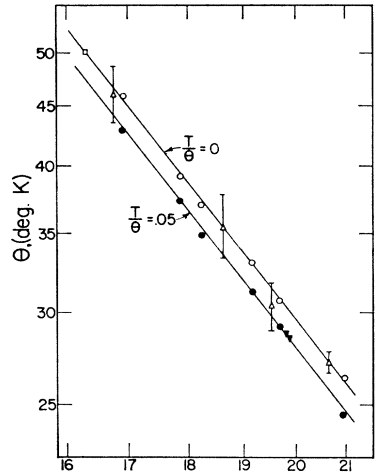

FIG. 4. The Debye θ at 0°K or $T/\theta=0$ (open symbols) and at $T/\theta=0.05$ (closed symbols) plotted as a function of molar volume. The circles are the results of the present work, the inverted triangles from Ahlers (see Ref. 24), the upright triangles from Heltemes and Swenson (see Ref. 13), and the square from Franck (see Ref. 11). The values from the last two references have been calculated after subtracting a linear contribution from the heat capacity. The two straight lines have slope −2.60 and represent Eqs. (1) in the text.

$$\theta_0=(7.12\times10^4)V^{-2.60},\quad \theta_{0.05}=(6.73\times10^4)V^{-2.60},$$
$$16.5(\text{cm}^3)\leq V\leq 21(\text{cm}^3),\quad (1)$$

shown as straight lines on the figure. The value of the Grüneisen constant $\gamma=2.60$ is estimated to be constant within ±0.05 in this range of molar volume. However, if the data of other workers,[8,10,11,13] measured at higher densities, are taken into account, it seems probable that γ is in fact a slowly varying function of V, varying from about 2.3 in the region of 12 cm^3 to 2.6 near 17 cm^3.

TABLE II. The thermal properties of hcp He^4 in reduced form.

$T/\theta_{0.05}$	$10^3C_v/R$	$10^3S/R$	$10^3(U-U_0)/RT$	$(K_0^{-1}-K^{-1})V/RT$
0.020	1.57	0.52	0.39	0.007
0.025	3.10	1.03	0.77	0.014
0.030	5.36	1.77	1.33	0.024
0.035	8.83	2.84	2.13	0.040
0.040	13.6	4.31	3.24	0.062
0.045	20.3	6.27	4.74	0.093
0.050	29.2	8.83	6.69	0.135
0.055	41.3	12.2	9.25	0.193
0.060	56.5	16.3	12.5	0.265
0.065	75.5	21.5	16.6	0.355
0.070	98.7	28.1	21.6	0.464
0.075	126	35.6	27.6	0.596
0.080	160	44.8	34.8	0.755
0.085	198	55.7	43.3	0.934
0.090	239	68.2	53.1	1.12
0.095	285	82.4	64.1	1.33
0.100	333	98.2	76.3	1.54

Table III. Thermodynamic properties of hcp He^4 at melting and at 0°K.

V cm^3/mole	T_m °K	P_0 atm	P_m-P_0 atm	U_0/R deg	$(U_m-U_0)/R$ deg	S_m/R	$K_0\times10^2$ atm^{-1}	$K_m\times10^2$ atm^{-1}	$\alpha_m\times10^2$ deg^{-1}
17.00	4.27	140.7	4.07	−2.56	0.324	0.0997	0.116	0.112	0.47
17.50	3.80	116.2	3.11	−3.32	0.255	0.0865	0.129	0.125	0.45
18.00	3.37	95.2	2.29	−3.98	0.193	0.0736	0.148	0.144	0.44
18.50	3.00	77.4	1.67	−4.50	0.145	0.0627	0.178	0.173	0.45
19.00	2.69	63.3	1.28	−4.93	0.114	0.0547	0.209	0.204	0.45
19.50	2.41	51.8	0.95	−5.28	0.0872	0.0468	0.246	0.241	0.43
20.00	2.13	41.1	0.67	−5.56	0.0627	0.0382	0.288	0.284	0.39
20.50	1.86	31.8	0.44	−5.78	0.0427	0.0298	0.334	0.330	0.35

Calculation of the Thermodynamic Functions and Equation of State

The specific heat at constant volume as a function of V and T, together with the melting curve measurements of Grilly and Mills[21,22] and one value of the internal energy, is sufficient to determine all the thermodynamic functions of hcp solid helium. Since the specific heat can be expressed in terms of a reduced temperature $\tau=T/\theta_{0.05}$, where $\theta_{0.05}$ is an analytic function of V [Eq. (1)], the calculations are like those first done by Dugdale and Simon.[8] From the solid curve in Fig. 3, which gives smooth values of $\theta/\theta_{0.05}$ as a function of T/θ, the specific heat has been expressed as a function of $\tau=T/\theta_{0.05}$, $C_v(\tau)$. The results have been integrated numerically to give the entropy, $S/R=\int_0^\tau(C_v/R\tau')d\tau'$, and the temperature-dependent part of the internal energy, $(U-U_0)/RT=(1/\tau)\int_0^\tau(C_v/R)d\tau'$, as functions of the reduced temperature τ. U_0 is the energy at 0°K and depends only on V. The results of these calculations are given in Table II. This table and Eq. (1), to give $\theta_{0.05}(V)$, can be used to determine S/R (shown in Fig. 5) or $(U-U_0)/RT$ for any values of V and T below the melting temperature and between $V=16.5$ cm^3 and $V=21$ cm^3. In addition, the change in pressure with temperature, $(p-p_0)$, can be determined from the equation

$$p-p_0=\gamma(U-U_0)/V, \tag{2}$$

with $\gamma=2.60\pm0.05$. This equation follows from the fact that C_v is only a function of τ. To complete the calculations the results of the melting curve measurements of Grilly and Mills[21,22] have been used. Grilly and Mills give P, V and T at melting from which, using Eq. (2) and Table II, we have obtained p_0, the pressure at 0°K as a function of V. Numerical integration of p_0 gives the variation of energy with volume at 0°K

$$U_0(V)-U_{0s}(V_s)=-\int_{V_s}^{V}p_0dV'. \tag{3}$$

The resulting values of U_0/R and p_0 are given in Table III; the energy diagram for solid helium is given in Fig. 6. For the reference value of the internal energy U_{0s} we have used a value for melting helium, $U_{0s}/R=-5.96$°K at $V_s=21.08$ cm^3, which is based on the

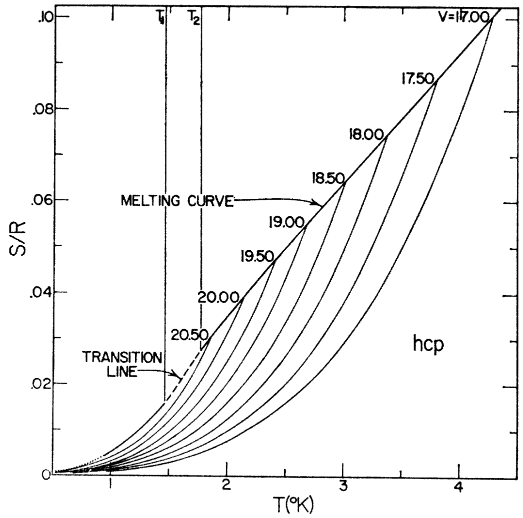

Fig. 5. The entropy diagram. The entropy of the hcp phase is given at melting, at the bcc-hcp transition line (dashed) and at constant molar volumes. The lower portion of the melting entropy curve is uncertain because of uncertainty in the molar volume at melting. T_1 and T_2 are the hcp-bcc-liquid triple point temperatures.

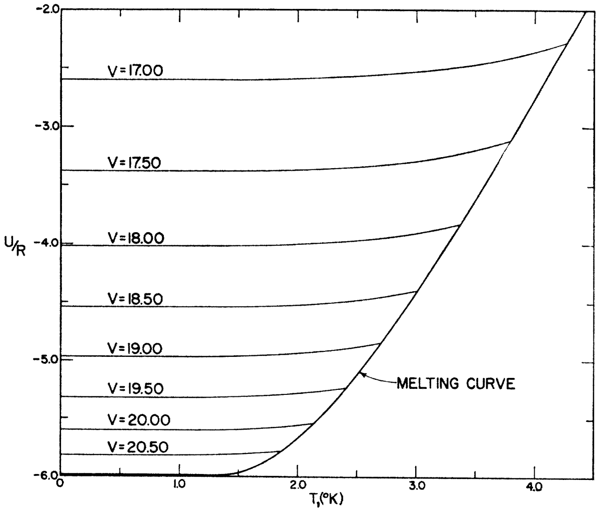

Fig. 6. The internal energy of hcp helium at constant molar volumes and at melting. The portion of the melting curve below 1.6°K is approximate.

earlier calculations of Swenson[25] who found the melting internal energy to be -5.99°K, believing that the melting point was at 25 atm and $V=21.18$ cm^3. The measurements of Grilly and Mills suggest that the melting and freezing volumes used by Swenson are too small by about 0.1 cm^3; therefore a small correction to his value of U_{0s}/R has been made. The correction is of the same order as the probable error in the data used by Swenson.

In addition to the properties of the solid at 0°K, Table III gives values of the entropy of the solid at melting S_m, the expansion coefficient of the solid at melting α_m, and the isothermal compressibility of the solid at melting κ_m. The expansion coefficient and compressibility can be obtained by applying Eqs. (4) and (5) to the melting curve data

$$\frac{dV}{dT}=\left(\frac{\partial V}{\partial P}\right)_T\frac{dp}{dT}+\left(\frac{\partial V}{\partial T}\right)_p=V\left(\alpha-\kappa\frac{dp}{dT}\right), \tag{4}$$

$$\alpha=\gamma\kappa C_v/V. \tag{5}$$

The Grüneisen Eq. (5) can be derived from Eq. (2) by differentiation. Values of dp/dT are tabulated by Grilly and Mills and dV/dT at melting was obtained by numerical and graphical differentiation of their data. Knowing the value of $\kappa_m(V)$ is possible to find the value of $\kappa(V)$ at any other temperature by applying the small correction given by the expression $(\kappa_0^{-1}-\kappa^{-1})V/RT$ in Table II. This quantity has been obtained by integrating the relation

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T\right]_V=\left[\frac{\partial}{\partial V}\left(\frac{\gamma C_v}{V}\right)\right]_T, \tag{6}$$

which yields

$$[\kappa^{-1}(V,T)-\kappa_0^{-1}(V)] \\ =(\gamma/V)[(\gamma+1)(U-U_0)-\gamma TC_v], \tag{7}$$

so that $(\kappa_0^{-1}-\kappa^{-1})V/RT$ is a function of τ only. In this way the values of the compressibility at 0°K, $\kappa_0(V)$, were obtained from the $\kappa_m(V)$ computed from Eqs. (4) and (5) and both are tabulated in Table III. It can be seen that the temperature dependence of κ is so small as to be negligible for most practical purposes, such as in the calculation of α from Eq. (5).

Tables II and III combined with Eq. (1) give sufficient information to calculate any thermodynamic property, including the Gibbs and Helmholtz free energies, for molar volumes $V\geqq 17$ cm^3. Dugdale and Franck[10] have given similar data for four volumes in the range $V\leqq 16.25$ cm^3. Although the two regions of measurement do not overlap, our values of $\theta_{0.05}$ and θ_0 can be extrapolated by means of Eq. (1) into the range covered by Dugdale and Franck, and the thermodynamic functions calculated by means of Table II. When this is done for $V=16.25$ cm^3, one of the molar volumes measured by Dugdale and Franck, it is found that at 3°K their specific heat is about 2% lower than the projection of the present data, their entropy is about 2.5% higher than ours, while their internal energy at 0°K and 17 cm^3 agrees within $\frac{1}{2}$% with ours. The difference becomes greater at higher temperatures, for at 5°K their specific heat is about 6% lower than the projection of our data. Dugdale and Franck estimate their error in C_v above 5°K to be about 1.5%, and greater at lower temperatures. Considering the error in the present results to be of the same order of magnitude, the difference between the two results does not appear to be too significant in view of the fact that the present results were projected outside the experimental range.

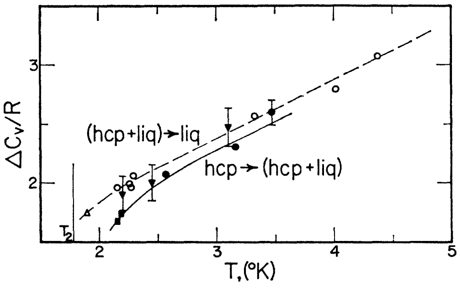

FIG. 7. The discontinuity in the heat capacity at constant volume on melting (full curve, closed symbols) and on freezing (dashed curve, open symbols). Present work, ○, ●; Keesom and Keesom (see Ref. 23), ▼; Ahlers (see Ref. 24), ■; Lounasmaa (see Ref. 27), △. T_2 is the upper hcp-bcc-liquid triple-point temperature.

The Melting Properties of hcp Helium

Whenever possible, the present heat-capacity measurements, which, it must be remembered, are at constant volume, were made through the melting point (at which melting begins), then the freezing point (at which melting is completed as the temperature is raised), and in the liquid phase. The melting and freezing temperatures can be calculated from the data using a lever rule and they are shown in Table I which gives T_m, T_F, and the initial or approximate freezing pressure for various molar volumes. These data are in good agreement with those of Grilly and Mills.[21] The molar volumes calculated from the melting and freezing temperatures agree with the measured molar volumes to within a root-mean-square deviation of 0.03 cm^3 which is within the experimental accuracy. The volumes which one would expect from the initial pressure do not agree quite so well, but are within an rms deviation of 0.09 cm^3. The measurements of C_v in the liquid agree with those of Lounasmaa[26] within 2–3%.

We have also obtained the discontinuities in the specific heat ΔC_v on melting and freezing. These are given in Fig. 7 with previous values taken from Keesom

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

[26] O. V. Lounasmaa, Cryogenics 1, 212 (1961).

and Keesom[23] and Lounasmaa.[27] It has been shown by Lounasmaa[27] and Goldstein[28] that, on passing from a single phase to a mixture of two phases at constant volume, the discontinuity in the heat capacity is given by

$$\Delta C_v = T(dV/dT)^2/V\kappa, \qquad (8)$$

where V and κ are the volume and isothermal compressibility of the single phase.

The Compressibility and Expansion Coefficient

Equation (8) with the smoothed values of ΔC_v at melting and the values of dV/dT derived from Grilly and Mills' data gives a set of values for the compressibility of melting hcp helium in addition to those obtained from Eq. (4) and tabulated in Table III. Furthermore, a third set can be derived from the equation

$$\kappa = V\Delta C_v / [\gamma C_v - V(dp/dT)]^2 T, \qquad (9)$$

which is obtained by eliminating (dV/dT) from Eqs. (4) and (8). All three sets of compressibilities, which depend on Grilly and Mills' and the present data in different ways, are in agreement within about ±7%, as is shown in Fig. 8. No values of κ are shown for $V > 20.5$ cm^3 since the value of (dV/dT) is very small and unreliable in this region and there are no values of ΔC_v available either. Figure 8 also shows the melting compressibility obtained by Stewart[29] at 4°K (triangle). Some preliminary, unpublished data of E. R. Grilly in the region of $V = 20$ to 21 cm^3 are in good agreement with the present data, although the value $(3.9 \pm 0.2) \times 10^{-3}$ atm^{-1} obtained by J. N. Kidder at $V = 20.5$ cm^3 is about 15% higher.[30] The compressibility of the freezing liquid was calculated with Eq. (8). The liquid has a compressibility which is considerably less than that of the solid at the same density but slightly larger than the solid which is in equilibrium with it, as shown in Fig. 8.

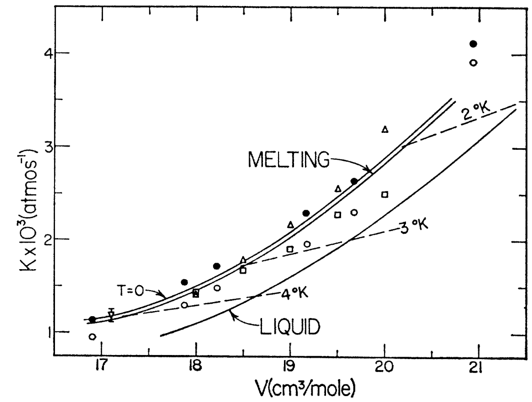

FIG. 8. The compressibility κ of hcp He^4 at melting and at 0°K, and of liquid He^4 at freezing. The full lines for the solid have been calculated from the melting curve data of Grilly and Mills and the specific heat using Eqs. (4), (5), and (7). The line for the liquid at freezing was calculated from ΔC_v and the melting curve data with Eq. (8). The dashed lines link the compressibilities for the liquid and solid in equilibrium at 2, 3, and 4°K. Other values for the compressibility of the melting solid are from ΔC_v and Eq. (8) (△), and from Eq. (9) (□). The circles represent values of the compressibility of the solid at 0°K calculated from the velocity of sound. The full circles ● are from the velocity of sound with Eq. (12) and the open circles ○ from the velocity of sound and the Debye theta at 0°K, θ_0, with the help of Eq. (11). The inverted triangle ▽ represents a direct measurement of the compressibility of the solid at 4°K by Stewart (see Ref. 29).

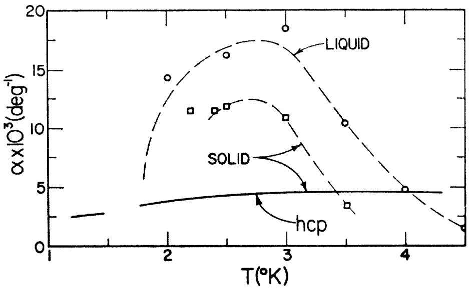

FIG. 9. The expansion coefficient α of solid He^4 at melting and of liquid He^4 at freezing. The full line was obtained from the Gruneisen Eq. (5) and the compressibility at melting as given by the full line of Fig. 8. The squares and the circles represent values for the hcp phase and the liquid calculated with Eq. (10); as explained in the text, these values are not very reliable.

The thermal expansion coefficient of the melting solid can be derived from the available experimental data in four different ways depending on which of the quantities, dp/dT, dV/dT, ΔC_v, C_v are dropped from the equations. Three of these simply use the Grüneisen Eq. (5) together with the three values of the compressibility discussed above. Since the three different ways of obtaining the compressibility are in substantial agreement with each other, they lead to substantially the same values of the expansion coefficient as those given in Table III which are shown as the full line in Fig. 9.

A fourth equation for α is obtained by substituting κ from Eq. (8) into Eq. (4), $dV/dT = V(\alpha - \kappa\, dp/dT)$, giving

$$\alpha = \frac{1}{V}\frac{dV}{dT} + \frac{T}{V\Delta C_v}\left(\frac{dV}{dT}\right)^2 \frac{dp}{dT}. \qquad (10)$$

The results from this equation, shown as open squares in Fig. 9, are not reliable because they are given by the sum of two large terms of opposite sign. The expansion coefficient of the freezing liquid has also been calculated with Eq. (10) (open circles); however, the same difficulty applies and the results should only be regarded as semiquantitative.

The Elastic Properties of hcp Helium

A hexagonal crystal has five elastic constants. At present, at any given density, we know only three

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

[28] L. Goldstein, J. Wash. Acad. Sci. 40, 97 (1950).

[29] J. W. Stewart, J. Phys. Chem. Solids 1, 146 (1956).

[30] J. N. Kidder, in *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 419; E. R. Grilly (unpublished). The authors are grateful to Dr. Grilly for his data in advance of publication.

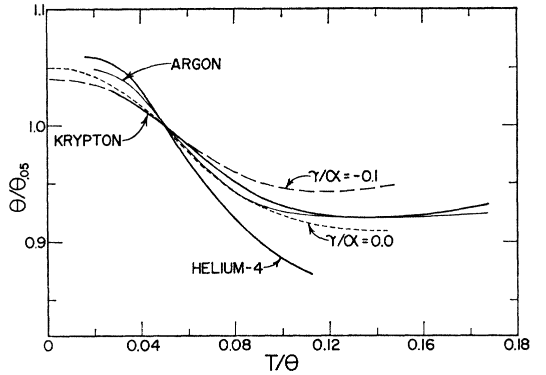

FIG. 10. The temperature dependence of the reduced Debye θ of hcp He^4 compared with that of solid argon, solid krypton, and the classical lattice model of Leighton for $\gamma/\alpha=0.0$ and -0.1. $\theta_{0.05}$ is the value of the θ at $T/\theta=0.05$.

quantities relating to the low-temperature elastic properties of hcp helium. They are the isothermal compressibility, the velocity of sound, measured by Vignos and Fairbank,[31] and the Debye θ at 0°K. To proceed further additional assumptions must be made: one that has been made frequently is that the crystal is, at least approximately, isotropic. The number of independent elastic coefficients is then reduced to two, for instance, the bulk modulus, κ^{-1}, and the rigidity modulus. The validity of this assumption is easily tested by calculating one of the three known quantities mentioned above from the other two. For an isotropic solid

$$\theta_0=\frac{h}{k}\left(\frac{6\pi^2N_0}{V}\right)^{1/3}\left(\frac{2}{3v_t^3}+\frac{1}{3v_l^3}\right)^{-1/3}, \qquad (11)$$

where v_t and v_l are the velocities of transverse and longitudinal sound at 0°K. Vignos and Fairbank found that the velocity of sound in their experiments did not depend on temperature, so we have assumed that their data apply at 0°K, and have used their measurements for v_l and the present measurements of θ_0 to calculate v_t from Eq. (11). It is found that the transverse velocity is approximately one-half of v_l at the same density, and that the low temperature heat capacity is dominated by the transverse modes. From v_l and v_t the compressibility κ of the supposedly isotropic solid can be found. The values of κ calculated in this way are shown as the open circles in Fig. 8. They should be compared to the other experimental values, bearing in mind the difference between the melting and 0°K compressibilities shown in the figure. On the average the points calculated from the velocity of sound and the Debye θ are 10% lower than the values from the specific heats and PVT data. This discrepancy, which is just outside the experimental uncertainty, indicates that the assumption of elastic isotropy is unjustified and shows that hcp helium is somewhat anisotropic. This conclusion is supported by the observations of Vignos and Fairbank who found that the variation in the measured velocity of sound from run to run was much greater than one would expect from the experimental uncertainty, and concluded that in each run they were obtaining a different configuration of elastically anisotropic crystals. On the other hand, Vignos and Fairbank[31] pointed out that if the average velocity of sound in their experiments was used in the equation

$$\rho v_l^2=5/(9\kappa) \qquad (12)$$

to calculate the compressibility κ, the results were in fair agreement with the values available from other methods. A comparison with the present values of κ is made in Fig. 8, where compressibilities from Eq. (12) are shown as closed circles; as can be seen the agreement is for the most part within experimental error. Equation (12) is appropriate for the velocity of longitudinal waves in an isotropic crystal whose elastic constants satisfy the Cauchy relations; however, agreement with Eq. (12) does not demonstrate the approximate isotropy of a single crystal, but only that the samples used in the velocity of sound experiments were probably polycrystalline. The elastic moduli of a polycrystalline sample can be calculated from those of the single crystal by means of the Voigt averages.[32] If the single-crystal elastic coefficients obey Cauchy's relations, then Eq. (12) can be derived from these averages. The agreement between the value of κ derived from Eq. (12) and the other values in Fig. 8 should therefore be interpreted as indicating that the velocity of sound samples were polycrystalline and that the single-crystal moduli satisfy the Cauchy relations, that is, $c_{13}=c_{44}$ and $c_{11}=3c_{12}$, for a hexagonal crystal. The number of independent elastic coefficients is thus reduced to three, but the experimental data available at the present time are insufficient to determine them separately.

Discussion of the Temperature Dependence of θ

Since the quantum dynamical-lattice problem for helium has not yet been solved, the best one can do in discussing the temperature dependence of θ is to compare it with the other solidified inert gases, and in a semiqualitative manner with classical lattice dynamical theory. Figure 10 presents in reduced form the temperature dependence of the Debye θ for krypton,[33] argon,[34] the present results for hcp He^4, and Leighton's[35] classical lattice model. Leighton's model is for a face-centered cubic crystal, like solid argon and krypton, and includes

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[31] J. H. Vignos and H. A. Fairbank, in *Proceedngs of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworth & Co. Ltd., London, 1963), p. 31.

[32] See H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 316.

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

[34] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1449 (1961).

[35] R. B. Leighton, Rev. Mod. Phys. **20**, 165 (1948).

next-nearest-neighbor as well as nearest-neighbor interactions. The ratio of the force constants for these interactions γ/α is related in the model to the compressibility and θ_0. If we ignore the fact that we are dealing with a hexagonal crystal and calculate this ratio from the present values of κ and θ_0, it varies between -0.10 to -0.15 depending on the density. It is obvious from the figure that the Debye θ varies much more strongly with temperature than either the other inert gases or the Leighton model with $\gamma/\alpha \sim -0.1$. A comparison with bcc He^4 and hcp and bcc He^3 will be made in another paper but we remark here that the relative temperature dependence of θ in these other forms of solid helium is only very slightly different from that in hcp He^4.

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Criteria for the Best Bogoliubov Quasiparticle*

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The principle of compensation of dangerous diagrams has previously been the only general criterion for determining the coefficients in the Bogoliubov canonical transformation to quasiparticles. In this paper it is shown that the criterion of maximum overlap of the true ground state with the BCS ground state gives the same condition for determining the coefficients. The criterion of diagonalizing the quadratic part of the reaction operator, which is a generalization of the Brillouin-Brueckner condition, is also equivalent to the above criteria. Finally these criteria are evaluated from the standpoint of "least labor for the most accuracy."

I. INTRODUCTION

THE problem of treating correlations in many-body systems is always difficult, but one of the most elegant methods is the canonical transformation to quasiparticles introduced by Bogoliubov eighteen years ago. The method was first used by Bogoliubov[1] in treating boson systems,[1] and it was successful in obtaining the phonon spectrum. Essentially the same idea was used over a decade later by Bogoliubov[2] and independently by Valatin[3] for fermion systems with attractive interactions to explain superconductivity. In this case the canonical-transformation method gave the energy gap[4] which was required.

In order to specify the quasiparticles completely, Bogoliubov[2,5] postulated the principle of compensation of dangerous diagrams (PCDD) which determined the coefficients in the canonical transformation. A quasiparticle (QP) annihilation operator for fermion systems is defined as[2]

$$\alpha_1 = u_1 a_1 + v_{-1} a_{-1}^\dagger, \qquad (1.1)$$

where a_1 and $a_1^\dagger$ are the annihilation and creation operators respectively for a fermion with momentum $\mathbf{k}_1$ and spin σ_1 and $(1) = (\mathbf{k}_1, \sigma_1)$. They satisfy the usual fermion anticommutation relations. In order for the QP to be fermions also, the coefficients must satisfy the relations

$$\begin{gathered} u_1^2 + v_1^2 = 1, \\ u_1 = u_{-1}, \\ v_1 = -v_{-1}. \end{gathered} \qquad (1.2)$$

The *principle of compensation of dangerous diagrams* states that the sum of all diagrams leading from the vacuum to the two QP state is zero. This condition gives an equation from which u_1 and v_1 can be obtained. The justification for postulating the PCDD is that divergences can be removed from the perturbation expansion of the ground-state energy.[5]

In his 1947 paper, Bogoliubov[1] used only the condition of diagonalizing the quadratic part of the Hamil-

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[1] N. N. Bogoliubov, J. Phys. (U.S.S.R.) **11**, 23 (1947).

[2] N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. **34**, 58 (1958) [English transl.: Soviet Phys.—JETP **7**, 41 (1958)]; Nuovo Cimento **7**, 843 (1958); Usp. Fiz. Nauk **67**, 549 (1959) [English transl.: Soviet Phys.—Usp. **2**, 236 (1959)].

[3] J. G. Valatin, Nuovo Cimento **7**, 843 (1958).

[4] See, e.g., D. H. Douglass, Jr., and L. M. Falicov, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. 4, Chap. III.

[5] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Academy of Sciences Press, Moscow, 1958) [English transl.: (Consultants Bureau, New York, 1959)]; Fortschr. Physik **6**, 605 (1958).