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Liquid and Solid He^3

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I. INTRODUCTION

HELIUM has two stable isotopes, He^3 and He^4. The macroscopic properties of He^4 are very interesting, and they have been the subject of many experimental and theoretical investigations over the last fifty years. On the other hand, research on the properties of He^3 has been handicapped by the fact that the concentration of He^3 in natural helium gas is at most of the order of one part per million.[1] Only in recent years has He^3 been produced artificially and become available in large amounts from the β decay of tritium H^3.

Sydoriak, Grilly, and Hammel[2] were the first to liquify (97% pure) He^3. Using 20 cm^3 (NTP) of artificially produced He^3 gas, they were able to determine the critical constants of He^3 vapor pressure and density of the liquid.

The attractive interactions between a pair of helium atoms are so weak (at most of the order of 10°K) that neither isotope forms diatomic molecules[3] or solidifies under its own vapor pressure. In fact, an appreciable external pressure (of the order of 25 atm for He^4 and 30 atm for He^3) is required in order to solidify the liquid at the lowest temperatures.

One point of interest in the bulk properties of He^3 is that, having a nuclear spin of $\frac{1}{2}$, it represents the simplest known system of interacting identical fermions, and hence it displays the influence of the interactions on properties such as specific heat and magnetic susceptibility. It is interesting also in He^3 to contrast its properties with those of He^4, which has zero nuclear spin. From the point of view of the many-body problem, the essential difference between the two isotopes is that He^4 is a boson, whereas He^3 is a fermion. Since the interactions between two He^3 atoms or two He^4 atoms are the same, these isotopes offer the possibility of studying the effects of statistics on the macroscopic properties of a system. The difference in atomic masses is not very important and can be regarded simply as a multiplicative factor in the strength of interaction [Eq. (4)].

Fortunately, the strength of the attractive interactions between helium atoms is not strong enough to bind either isotope to a lattice. Otherwise, helium would solidify under its own vapor pressure, and the difference in statistics would not lead to any strikingly different properties between the two isotopes. As a matter of

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[1] For a review of the early work on liquid He^3, see J. G. Daunt, Phil. Mag. Suppl. **1**, 209 (1952).

[2] S. G. Sydoriak, E. R. Grilly, and E. F. Hammel, Phys. Rev. **75**, 303 (1949); E. R. Grilly, E. F. Hammel, and S. G. Sydoriak, *ibid.* **75**, 1103 (1949).

[3] N. Bernardes and H. Primakoff, J. Chem. Phys. **30**, 691 (1959).

fact, the attractive interactions are so weak that in the early days some authors[4] conjectured that He^3 might not condense into a liquid. However, de Boer and Lunbeck,[5,6] by extrapolating the critical constants of the other inert gases, made theoretical predictions regarding the critical constants of He^3, and in a short time their predictions were fully verified by the experiments of Sydoriak, Grilly, and Hammel.[2]

In this review, we discuss the available experimental data as well as the current theoretical situation for both liquid and solid He^3. We place the emphasis on basic facts and ideas, rather than on an exhaustive presentation of the existing literature. Some aspects of the properties of He^3 are mentioned only briefly, and we refer the reader to the original papers. A list of books and review papers can be found at the end of this paper.

II. STATEMENT OF THE THEORETICAL PROBLEMS

1. Quantum-Mechanical Equations of Motion

According to the theorem of Born-Oppenheimer, an approximate quantum-mechanical description of a system of N helium atoms can be given in terms of a Schrödinger equation for the motion of N interacting nuclei,

$$\left\{\left(-\frac{\hbar^2}{2m}\right)\sum_{i=1}^{N}\Delta_i^2+\mathcal{E}(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_N;\boldsymbol{\sigma}_1,\boldsymbol{\sigma}_2,\cdots\boldsymbol{\sigma}_N)\right\}\times\psi(\mathbf{r},\boldsymbol{\sigma})=E\psi(\mathbf{r},\boldsymbol{\sigma}),\quad(1)$$

where m is the nuclear mass, the $\mathbf{r}$'s and $\boldsymbol{\sigma}$'s the position and spin coordinates of the N nuclei regarded as fixed, and $\mathcal{E}(\mathbf{r};\boldsymbol{\sigma})$ is the lowest electronic-energy eigenvalue which depends on the positions $\mathbf{r}$ and $\boldsymbol{\sigma}$ of the N nuclei. $\mathcal{E}$ also includes the Coulomb repulsions among all nuclei. Since the ionization potential of a helium atom is sufficiently large compared to the average Coulomb interaction between the constituents of neighboring helium atoms (except at extremely high pressures), the electronic-energy eigenvalue $\mathcal{E}(\mathbf{r};\boldsymbol{\sigma})$ can be written, to a good approximation, as a superposition of central and spin-independent "two-body potentials,"

$$\mathcal{E}(\mathbf{r}_1,\mathbf{r}_2\cdots;\boldsymbol{\sigma}_1,\boldsymbol{\sigma}_2\cdots)=\sum_{i<j}^{N}\sum^{N}V(r_{ij}).\quad(2)$$

Equation (2) corresponds to neglecting the so-called many-body forces.

According to this separation the two-body potential $V(r_{ij})$ should be obtained from the solution of a two-atom Schrödinger equation. To neglect the many-body forces is equivalent to neglecting the influence of the medium (i.e., of the remaining N-2 atoms) on the motion of the four electrons in question, which simplifies the problem considerably.

An analysis of the gas-phase experimental data of all the inert gases shows that the theoretical, two-body, interatomic potentials obtained in the way described in the foregoing give only a fair description of the electronic interations and, hence, of a macroscopic system of atoms. A better description of the gas-phase data can be obtained by introducting slight empirical modifications in the theoretical, two-body, interatomic potentials.[6] For the heavier inert gases, the same phenomenological interatomic potential is capable of describing the properties of both the gaseous and solid phases, and this may be taken as an indication of the unimportance of many-body (density-dependent) forces.

Among the variety of analytical forms proposed by different authors, the simplest satisfactory form of the empirical interatomic potential involves two phenomenological constants, which can be taken as: (1) the minimum value $-\epsilon$ of the interatomic potential, and (2) the interatomic distance r_0 at this minimum. Any of these two-body interatomic potentials can be written as

$$V(r_{ij})=\epsilon v(r_{ij}/r_0)\equiv\epsilon v(x_{ij}),\quad(3)$$

and hence, Eq. (1) can be written as

$$\{-\lambda^2\sum_{i}^{N}\Delta_i^2+\sum_{i<j}^{N}\sum^{N}V(x_{ij})\}\psi(\mathbf{x},\boldsymbol{\sigma})=E\psi(\mathbf{x},\boldsymbol{\sigma}),\quad(4)$$

where $\lambda^2\equiv\hbar^2/2m\epsilon r_0^2$, Δ_i^2 is now the Laplacian with respect to $\mathbf{x}_i$, and E is measured in units of ϵ. Despite the many different analytical forms used by different authors, the value of the constant λ is rather insensitive to the particular form of v_{ij}. A typical interatomic potential is the so-called 12-6 Mie-Lennard-Jones potential

$$v(x_{ij})=(x_{ij}^{-12}-2x_{ij}^{-6}),\quad(5)$$

with parameters ϵ and r_0 as adjusted for helium by de Boer,[6,7]

$$\epsilon=10.2°\text{K},\quad r_0=2.87\ \text{Å},\quad(6)$$

for which $\lambda=0.269$ for He^4 and $\lambda=0.310$ for He^3.

Even though the results of theoretical calculations which "start from the origin" are sensitive to the detailed behavior of the interatomic potential at short interatomic distances, we may expect a 12-6 potential to provide a fair description of the bulk properties of either helium isotope. For gross estimates of the effects of the interatomic forces, one may use nonsingular potentials which fit the 12-6 potential near r_0, for instance a Morse potential,

$$v(x)=e^{-12(x-1)}-2e^{-6(x-1)}.\quad(7)$$

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[4] F. London and O. K. Rice, Phys. Rev. **73**, 1188 (1948); L. Tisza, Phys. Today **1**, 26 (1948).

[5] J. de Boer and R. J. Lunbeck, Physica **14**, 318 (1948); **14**, 510 (1948); **14**, 520 (1948).

[6] J. de Boer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, Netherlands, 1957), Vol. II.

[7] In many instances, we use units such that Boltzmann's constant k is equal to unity. In this case, energies are measured in °K.

For a system of He^3 atoms, one is interested only in the antisymmetric solutions of Eq. (4), i.e., those that change their sign when the coordinates $\mathbf{r}$ and $\boldsymbol{\sigma}$ of any two atoms are interchanged.

There are two main difficulties in obtaining approximate solutions of Eq. (4) in the case of helium. First, the strong singularity of the interatomic potential at the origin rules out any approximation based on an independent-particle model with overlapping wave functions. Second, the relatively large value of λ for helium, which implies large zero-point motion, enhances the importance of correlations between neighboring atoms.

If one includes in Eq. (4) terms corresponding to external interactions (such as an external pressure exerted by the walls of a container or an external magnetic field), one should be able to answer questions such as: the nature (gas, liquid, or solid) of the system at $p=0$ and $T=0$, the volume, cohesive energy, compressibility, specific heat, and nuclear-magnetic susceptibility as functions of pressure, etc. Unfortunately, theorists have not had much success with this difficult task, and, for the liquid, we only know one serious attempt to numerically calculate these properties from first principles.[8]

The simplest theoretical approach consists of disregarding completely the interactions among helium atoms and treating the (liquid) system of N He^3 atoms as an ideal Fermi-Dirac gas. For purpose of reference, we summarize in the next section the properties resulting from such a simple model.

2. Ideal Fermi-Dirac Gas Model for the Liquid

According to this model, the energy, E is purely kinetic and, hence, positive, and at $T=0°K$ it can be written as

$$E=(3/5)NkT_F, \tag{8}$$

where the Fermi temperature T_F is given by

$$kT_F=(\hbar^2/2m)(3\pi^2N/V)^{\frac{2}{3}}. \tag{9}$$

Substituting the numerical values, we obtain

$$T_F \cong 5(V_0/V)^{\frac{2}{3}}{}^\circ\mathrm{K}, \tag{10}$$

where $V_0=V_{\mathrm{liq}}(p=0)=36.7\ \mathrm{cm}^3/\mathrm{mole}$.[9] Therefore, the energy, pressure, and compressibility at 0°K are given by

$$E=3(V_0/V)^{\frac{2}{3}}Nk, \tag{11}$$

$$p=2V_0^{-1}(V_0/V)^{5/3}Nk, \tag{12}$$

and

$$K=(3/10)V_0(V_0/V)^{-5/3}/Nk. \tag{13}$$

Equation (11) obviously cannot represent the latent heat of the liquid at 0°K. Adding a negative energy, corresponding to an average potential, to the right-hand side of Eq. (11) would not have much value since the ideal Fermi-Dirac (F-D) gas model does not provide a way of calculating this (negative) energy as a function of V and T. According to Eq. (11) the zero-point energy of the liquid at 0°K and $V=V_0$ is equal to 3°K/atom. Since the maximum interaction between two helium atoms at a distance $1.7r_0$ (corresponding to the average interatomic separation 5 Å in the liquid at $p=0$ and $T=0$) is of the order of $-0.8°K$, even a coordination number as large as 8 will make the liquid only barely bound ($3-3.2=-0.2°K$/atom). The experimental value for the latent heat at 0°K is, on the other hand, 2.5°K/atom.[9]

Again at 0°K and $V=V_0$, Eq. (13) gives a compressibility $K=13\%\ \mathrm{atm}^{-1}$, compared to measured values of about $3.7\%\ \mathrm{atm}^{-1}$. The velocity of sound is proportional to $K^{-\frac{1}{2}}$, and hence the theoretical velocity is smaller than the experimental value by a factor of about 2. At 0°K and $V=V_0$, the actual liquid has a zero pressure while Eq. (12) gives $p(V_0)\cong 5$ atm.

According to the ideal F-D gas model, the specific heat C_V at sufficiently low temperatures is linear in T, and is given by

$$C_V/R\cong 5(T/T_F), \tag{14}$$

which for $V=V_0$ gives

$$C_V\cong 2T\ \mathrm{cal/mole}^\circ\mathrm{K}, \tag{15}$$

contrasted to an experimental value, below 0.1°K, of about $5T$ cal/mole°K. The equations above also show that, at very low temperatures, $C_V^{-1}[\partial C_V/\partial p]_T=-8\%\ \mathrm{atm}^{-1}$ according to the ideal F-D gas model, while experimental values are about $+1\%\ \mathrm{atm}^{-1}$. At higher temperatures, the specific heat of an ideal F-D gas tends smoothly to $(3/2)R$, while the specific heat of liquid He^3 above 0.5°K is quite complex. [See Fig. 10.]

The ideal F-D gas model also predicts a positive thermal-expansion coefficient,

$$\alpha_p\equiv V^{-1}(\partial V/\partial T)_p,$$

given by

$$\alpha_p=\gamma KC_v/V, \tag{16}$$

where K is the compressibility and

$$\gamma=-d\ln T_F/d\ln V=\tfrac{2}{3}.$$

From Eqs. (10), (13), and (16), we may write

$$\alpha_p=(1/5)(V/V_0)^{4/3}T^\circ\mathrm{K}^{-1}, \tag{17}$$

which, for $V=V_0$, gives $\alpha_p=0.2T/°K$, compared to experimental values α_p of the order of $-0.1T/°K$.

According to the theory of the magnetic properties of an ideal F-D gas,[10] one expects the ground state to have a zero total spin; i.e., we expect the liquid not to show spontaneous nuclear magnetization. All the experimental data on the nuclear-magnetic susceptibility

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[8] K. A. Brueckner and J. L. Gammel, Phys. Rev. **109**, 1040 (1958).

[9] Some experimental values are quoted in this section without reference to the original papers which can be found in Chaps. III and IV.

[10] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1954).

down to 0.02°K confirm this prediction. The theory of the ideal F-D gas predicts, furthermore, a value for the small paramagnetic-spin susceptibility χ, which at constant volume is given by

$$\chi(T)=(N\mu^2/kT)F_{\frac{1}{2}}'(\xi)/F_{\frac{1}{2}}(\xi), \tag{18}$$

where μ is the nuclear-magnetic moment of a He^3 nucleus, $\xi=T_F/T$, a prime denotes differentiation, and

$$F_s(\xi)\equiv\int_0^\infty \frac{x^s dx}{e^{x-\xi}+1}. \tag{19}$$

According to Eqs. (18) and (19), the low- and high-temperature limits of the susceptibility are given, respectively, by

$$\chi(0)=(3N\mu^2/2kT_F), \tag{20}$$

and by

$$\chi(\infty)=N\mu^2/kT, \tag{21}$$

the latter coinciding with the classical value given by Curie's law. From Eqs. (20) and (21), we can see that $\chi(0)/\chi(\infty)$ assumes a value equal to $\frac{1}{2}$ at $T\cong T_F(0)/3$; i.e.,

$$[\chi(T)kT/N\mu^2]_{T=T_F(0)/3}\cong\tfrac{1}{2}, \tag{22}$$

where $T_F(0)=T_F(T=0)$.

Hence, according to the ideal F-D gas model, we may expect strong deviations (~50%) from Curie's law at temperatures as high as 2°K. Early experiments[11] showed that, within a few percent, $T\chi(T)$ is independent of T down to 1.2°K, and subsequent experiments[12] showed that the nuclear-magnetic susceptibility of liquid He^3 under its own saturated vapor pressure is such that Eq. (22) is satisfied for $T=0.2$°K, indicating a value of $T_F(0)\cong0.6$°K, or ten times smaller than the one given by the ideal F-D gas model [see Eq. (10)].

One might expect that the predictions from the ideal F-D gas model can be improved by introducing an effective mass m^*. It is very easy to see that such a concept does not improve the situation at all. In fact, the values of m^*/m necessary to make the predictions of the ideal F-D gas model fit the experimental data should be, approximately, 2.5 from C_V, 0.3 from K or v_{sound}, and 10 from χ. Furthermore, each of these effective masses should have quite different temperature and pressure dependence.

Another important feature of the experimental data is that the specific heat of liquid He^3 above 0.5°K (see Fig. 10) does not resemble, even qualitatively, the specific heat of an ideal F-D gas, whereas the magnetic susceptibility up to 2°K can be described[13] by Eq. (18) with an empirical, temperature-independent, effective mass of about 10. Hence, the specific-heat data show that the $\epsilon(k)$ spectrum is quite unusual and that the fit to the magnetic-susceptibility data is only fortuitous. Therefore, not much meaning should be attached to the magnetic value 10 for m^*/m. Thus, we may conclude that an effective mass is not a useful concept, except as a quick guide to certain experimental data.

Strictly speaking, one cannot make theoretical predictions about transport properties (such as thermal conductivity κ, viscosity η, and self-diffusion D) on the basis of the ideal F-D gas model, since interparticle scattering is an essential factor determining these properties. Nevertheless, this simple model is capable of giving the *temperature dependence* of these properties. Only a detailed knowledge of the scattering and interatomic forces would allow one to calculate the numerical constants involved.[13,14] The qualitative predictions of the ideal F-D gas model for very low temperatures are[13,14]

$$\kappa\sim T^{-1}, \tag{23}$$

$$\eta\sim T^{-2}, \tag{24}$$

and

$$D\sim T^{-2}. \tag{25}$$

To some extent, Eqs. (23)–(25) agree with experimental data, but we postpone a discussion for Secs. III.9, 10, and 14.

3. Influence of the Interactions on the Properties of the Liquid

The simplest way to include the effects of interactions is given by first-order perturbation theory. For a single Slater determinant of plane waves, the energy E in first order is given by

$$\begin{aligned}E=(\hbar^2/2m)\textstyle\sum_{\mathbf{k}}&[n_+(\mathbf{k})+n_-(\mathbf{k})]k^2+\tfrac{1}{2}N\gamma_0\\ &-(1/2N)\textstyle\sum_{\mathbf{k}}\sum_{\mathbf{k}'}n_+(\mathbf{k})n_+(\mathbf{k}')\gamma(\mathbf{k}-\mathbf{k}')\\ &-(1/2N)\textstyle\sum_{\mathbf{k}}\sum_{\mathbf{k}'}n_-(\mathbf{k})n_-(\mathbf{k}')\gamma(\mathbf{k}-\mathbf{k}'),\end{aligned} \tag{26}$$

where + refers to "spin-up," − to "spin-down," and $n_\pm(k)$ is equal to 1 or 0, depending on whether or not the state k is present in the determinant. $\gamma(\mathbf{k})$ is the Fourier transform of the interatomic potential,

$$\gamma(\mathbf{k})\equiv(N/V)\int e^{i\mathbf{k}\cdot\mathbf{r}}V(r)d\mathbf{r}. \tag{27}$$

If all states $\mathbf{k}_\pm$ up to a certain $\mathbf{k}_\pm{}^F$, and no other, are present in the determinant, the summations in Eq. (26) can be restricted to $k_\pm\leq k_\pm{}^F$, and the $n_\pm$ taken equal to 1, where

$$(4/3)\pi(k_\pm{}^F/2\pi)^3=N_\pm/V. \tag{28}$$

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[11] W. M. Fairbank, W. B. Ard, H. G. Dehmelt, W. Gordy, and S. R. Williams, Phys. Rev. **92**, 208 (1953).

[12] A. A. Abrikosov and I. M. Khalatnikov, J. Exptl. Theoret. Phys. (U. S. S. R.) **32**, 1084 (1957) [translation, Soviet Phys.—JETP **5**, 745 (1957)].

[13] W. M. Fairbank, W. B. Ard, and G. K. Walters, Phys. Rev. **95**, 566 (1954).

[14] A. A. Abrikosov and I. M. Khalatnikov, Repts. Prog. in Phys. **22**, 329 (1959).

[15] S. Tomonaga, Z. Physik **110**, 573 (1938); K. S. Singwi and L. S. Kothari, Phys. Rev. **76**, 305 (1949); R. A. Buckingham and H. N. V. Temperley, *ibid.* **78**, 482 (1950); I. I. Pomeranchuk, J. Exptl. Theoret. Phys. (U. S. S. R.) **20**, 919 (1950).

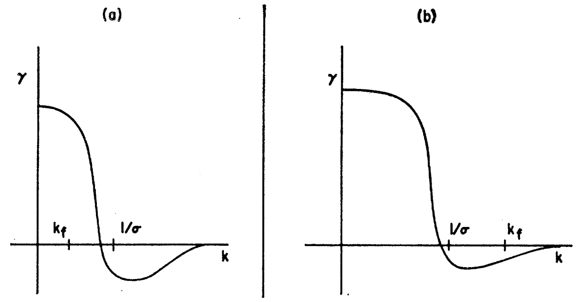

FIG. 1. Two possible relations between the Fourier transform γ of the interatomic potential and the Fermi momentum.

If $n(\mathbf{k})$ is replaced by a Fermi-Dirac distribution function, E represents the thermodynamic average energy, and we may write

$$E(V,T)=\tfrac{1}{2}N\gamma_0(V)+\sum_k n_+(\mathbf{k})[T_k-J_+(\mathbf{k})] \\ +\sum_k n_-(\mathbf{k})[T_k-J_-(\mathbf{k})], \quad (29)$$

where $T_k\equiv\hbar^2k^2/2m$ and

$$J_\pm(\mathbf{k})\equiv(1/2N)\sum_{k'} n_\pm(\mathbf{k}')\gamma(\mathbf{k}-\mathbf{k}'), \quad (30)$$

the so-called exchange energy, depends on volume, temperature, and total magnetization.

Equations (29) and (30) do not include any correlation between different particles, and the γ's are meaningless for a singular interatomic potential like the one in Eq. (5). In this case, one has either to include an arbitrary cutoff[16] in the interatomic potential or to replace it by a nonsingular potential like the one in Eq. (7). Cutoff factors have the disadvantage that they are useful only in *a posteriori* theories. On the other hand, replacing a singular interatomic potential by one in which the singularity has been removed does not introduce any extra parameter into the theory, and *a priori* calculations are still possible. Nevertheless, in the present case, even a soft potential like the Morse potential retains much interatomic repulsion, and the term $\tfrac{1}{2}N\gamma_0$ will dominate the right-hand side of Eq. (29), which will be positive. Hence, we may expect that the effects of correlation are important for a calculation of the cohesive energy.

A qualitative discussion of the effects of the exchange energy on the specific heat (effective mass or density of states) and magnetic susceptibility can be given as follows. If the ground state is ferromagnetic ($N_+=N$, and $N_-=0$), the Fermi momentum $k_F(\uparrow\uparrow)$ will be larger than $k_F(\uparrow\downarrow)$ for the antiferromagnetic state ($N_+=N_-=N/2$) by a factor of $2^{\frac{1}{3}}$; i.e.,

$$k_F(\uparrow\uparrow)=2^{\frac{1}{3}}k_F(\uparrow\downarrow), \quad \text{and} \quad E_F(\uparrow\uparrow)=2^{\frac{2}{3}}E_F(\uparrow\downarrow). \quad (31)$$

If the range of the repulsive forces σ is much smaller than $1/k_F$, as shown in Fig. 1(a), then the exchange energies E_x will be independent of k_F, and they will be roughly

$$E_x(\uparrow\uparrow)\approx(1/2N)N^2\gamma_0, \quad (32)$$

and

$$E_x(\uparrow\downarrow)\approx(1/2N)[(N^2/4)+(N^2/4)]\gamma_0, \quad (33)$$

and, hence

$$E_x(\uparrow\uparrow)\approx 2E_x(\uparrow\downarrow). \quad (34)$$

Thus, if γ_0 is sufficiently large and positive, we have $E(\uparrow\uparrow)=(3/5)E_F(\uparrow\uparrow)-E_x(\uparrow\uparrow)<E(\uparrow\downarrow)$, which means that the ground state will be ferromagnetic in spite of the increase in kinetic energy. If $\gamma_0<0$ the antiferromagnetic ground state is likely to be favored.

On the other hand, if $\sigma\gg k_F^{-1}$ [see Fig. 1(b)], we have $E_x(\uparrow\downarrow)\cong E_x(\uparrow\uparrow)\cong N\gamma_0/4(k_F\sigma)^3$, and the decrease in kinetic energy will favor an antiferromagnetic ground state, independently of the sign of γ_0.

In the case of liquid He^3, we have $k_F(\uparrow\downarrow)\cong 2/\sigma$, and hence we expect the ground state to be antiferromagnetic, as in fact it is.

From the experimental values for C_V, one can infer the behavior of $\epsilon(k)$ near k_F. In fact, since $m^*(C_V)\approx 2.5m$, we may conclude that

$$(dJ_\pm/dk)_{k=k_F}\cong\hbar^2k_F^2/4m\cong 4°\text{K Å}. \quad (35)$$

Equations (29) and (30) allow us to predict the behavior of the magnetic susceptibility and, hence, to understand the reasons for the large difference in effective masses [$m^*(C_V)\cong 2.5$, and $m^*(\chi)\cong 10$], as follows.

In order to calculate the magnetic susceptibility, one has to calculate $N_+-N_-\equiv 2\nu$ as a function of the external, applied magnetic field H, where

$$N_+=\sum_k n_+(\mathbf{k}), \quad N_-=\sum_k n_-(\mathbf{k}), \quad N_++N_-=N,$$

and for an antiferromagnetic ground state and weak magnetic fields $N_+\cong N_-\cong N/2$. Since $J_\pm(k)$ depend on $n_\pm(k)$, we see that $J_\pm(k)$ will depend on the external magnetic field or, more precisely, on the magnetization $M=\chi H$. If $N_\pm=\tfrac{1}{2}N_\pm\pm\nu$, we may write

$$J_\pm(\mathbf{k},\mathbf{k}_\pm{}^F)=J_\pm[\mathbf{k},\mathbf{k}_F(\tfrac{1}{2}N\pm\nu)] \\ \cong J_\pm[\mathbf{k},\mathbf{k}_F(N)]\pm(\partial J/\partial k_F)\Delta\mathbf{k}_F(\nu). \quad (36)$$

From Eq. (30), we have

$$\frac{\partial J}{\partial k_F}=(2\pi)^{-3}\left(\frac{V}{2N}\right)\left(\frac{\partial}{\partial k_F}\right)\int_{k_1<k_F}\gamma(\mathbf{k}-\mathbf{k}_1)d\mathbf{k}_1 \\ +O\left(\frac{T}{T_F{}^*}\right)\cong\frac{3\gamma(\mathbf{k}_0-\mathbf{k})}{4k_F}, \quad (37)$$

where $|k_0|<k_F$, and where the factor $\frac{3}{4}$ was introduced for convenience only. Above $T_F{}^*/10$, the terms $O(T/T_F{}^*)$ are not negligible and, hence, our final results, Eq. (45), are applicable only below 0.2°K. Since $\Delta k_F(\nu)/k_F=(\nu/3)/(N/2)$, we obtain from Eqs. (36) and (37),

$$J_\pm(\mathbf{k},\nu)=J_\pm(\mathbf{k},0)\pm(\nu/2N)\gamma(\mathbf{k}_0-\mathbf{k}). \quad (38)$$

Therefore, we may write, in the presence of a magnetic

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[16] L. Goldstein and M. Goldstein, J. Chem. Phys. 18, 538 (1950).

field H,

$$E(H)=\tfrac{1}{2}N\gamma_0+\textstyle\sum_{\mathbf{k}}\left[n_+(\mathbf{k})\epsilon_+(\mathbf{k},\nu)+n_-(\mathbf{k})\epsilon_-(\mathbf{k},\nu)\right], \quad (39)$$

where

$$\epsilon_\pm(\mathbf{k},\nu)=\epsilon^*(\mathbf{k})\mp\Delta_k=\hbar^2k^2/2m \\ -J_\pm(\mathbf{k})\mp(\nu/2N)\gamma(\mathbf{k}_0-\mathbf{k})\mp\mu H, \quad (40)$$

and

$$\Delta_k\equiv(\nu/2N)\gamma(\mathbf{k}_0-\mathbf{k})+\mu H. \quad (41)$$

The magnetization M is given by

$$M=(N_+-N_-)\mu=\mu\textstyle\sum_{\mathbf{k}}\left[n(\epsilon^*(\mathbf{k})-\Delta_k)-n(\epsilon^*(\mathbf{k})+\Delta_k)\right] \\ =2\mu\Delta(\bar{k})(\partial/\partial\epsilon_F^*)\textstyle\sum_{\mathbf{k}} n[\epsilon^*(\mathbf{k})]+O(\nu^2/N), \quad (42)$$

where the term $O(\nu^2/N)$ is completely negligible for usual magnetic fields. When the effects of exchange are partially neglected, we have $\Delta_k=\mu H$, and

$$M=2\mu^2H(\partial/\partial\epsilon_F^*)\textstyle\sum_k n[\epsilon^*(\mathbf{k})]\equiv\chi^*H, \quad (43)$$

where χ^* is the ideal F-D gas susceptibility, given by Eq. (18), except that [since $J(\mathbf{k})$ is included in $\epsilon^*(\mathbf{k})$ of Eq. (42)] the Fermi energy ϵ_F^* is the one given by the specific-heat data.

If the effects of exchange are taken into account, both in $\epsilon^*(k)$ as well as in Δ_k, then $\Delta(\bar{k})=(\nu/2N)\bar{\gamma}+\mu H$, and Eq. (42) become, in view of Eq. (43),

$$M=\chi^*(H+\nu\bar{\gamma}/2N\mu), \quad (44)$$

or, since $2\nu\mu=M$, and $M\equiv\chi^{**}H$,

$$\chi^{**}=\frac{\chi^*}{1-(\bar{\gamma}/4N\mu^2)\chi^*}. \quad (45)$$

At very low temperatures ($T\ll 0.2$°K) [see Eq. (20)], $\chi^*/2N\mu^2=\frac{3}{4}T_F^*$, and, hence, from Eq. (45)

$$\chi^{**}(T)=\frac{\chi^*(T)}{1-3\bar{\gamma}/8kT_F^*(0)} \quad (T\ll T_F^*). \quad (46)$$

Since C_V data indicate that T_F^* may be as small as 1.5°K, and since the susceptibility remains finite at all temperatures, we may conclude that

$$\bar{\gamma}<4°\text{K}. \quad (47)$$

An estimate of $\bar{\gamma}$ can be obtained from specific-heat and magnetic-susceptibility data. From susceptibility data, $\chi_0^{**}/\chi_0\approx 9$, from C_V data $\chi_0^*/\chi_0=T_F/T_F^*\cong 2.4\pm 0.4$; and hence from Eq. (46)

$$1-3\bar{\gamma}/8kT_F^*\cong 0.31, \text{ or since } T_F^*\cong 1.7°\text{K},$$

we may conclude that at zero pressure

$$\bar{\gamma}\cong 3.7°>0. \quad (48)$$

At temperatures above 0.2°K, Eq. (45) is not expected to apply to liquid He^3 because of the terms neglected in Eq. (28).

Since no interatomic potential appropriate to the gas phase would give such a small value for $\bar{\gamma}$, we may conclude that the effects of correlations are very important, and that $\gamma(k)$ should be regarded as the Fourier transform of some effective (softer) interatomic potential instead of the actual interatomic potential appropriate to the gaseous phase.

4. Theories of the Liquid Phase

Many authors have discussed the influence of particle interaction on the properties of liquid He^3.

Goldstein[17] assumed that these interactions do not destroy the relation

$$S=R\ln 2[\chi(T)/\chi_0(T)] \quad (49)$$

between the magnetic susceptibility and entropy of an ideal F-D gas,[18] where χ_0 is the ideal paramagnetic Langevin susceptibility. Goldstein assumes that Eq. (49) gives not the total entropy of the liquid but only the "partial spin-entropy," and that to obtain the total entropy one should add a "nonspin entropy," about which this theory does not make any assertion. Despite its interesting features and consequences, this theory rests on a basis of questionable assumptions, viz., (1) that the entropy of the liquid can be separated into spin and nonspin parts, and (2) that the spin entropy is related to the magnetic susceptibility by the ideal F-D gas relation of Eq. (49). Even though Eq. (49) may be quite general, the entropy-separation hypothesis is rather vague.

Landau[19–21] proposed a phenomenological theory of the properties of liquid He^3 that contains a phenomenological interaction function $f(\mathbf{k},\mathbf{k}',\boldsymbol{\sigma},\boldsymbol{\sigma}')$. If the energy of an excitation, when the system is characterized by a distribution function $n(k)$, is given by $\epsilon_0(k,\sigma)$, then Landau assumed that the energy of this excitation when the distribution is altered by an amount characterized by δn is given by

$$\epsilon(\mathbf{k},\boldsymbol{\sigma})=\epsilon_0(\mathbf{k},\boldsymbol{\sigma})+\int\delta n(\mathbf{k}',\boldsymbol{\sigma}')f(\mathbf{k},\mathbf{k}',\boldsymbol{\sigma},\boldsymbol{\sigma}')d(\mathbf{k}',\boldsymbol{\sigma}'), \quad (50)$$

which is a generalization of Eq. (29).

Equation (50) is quite general. The only restriction on its applicability to a real system is that the width Δ of the level $\epsilon(\mathbf{k},\boldsymbol{\sigma})$ has to be sufficiently small compared to the spread kT of the derivative of the Fermi distribution. If one assumes that the lifetime $\tau(\cong\hbar/\Delta)$ is of the order of the relaxation time for thermal conductivity or diffusion, one then expects Eq. (50) to be applicable at

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[17] L. Goldstein, Phys. Rev. **96**, 1455 (1954); **102**, 1205 (1956); **112**, 1465 (1958); **112**, 1483 (1958); **117**, 375 (1960); Ann. Phys. **8**, 390 (1959).

[18] F. Bloch, Z. Physik **53**, 216 (1929); L. Goldstein, Phys. Rev. **96**, 1455 (1954).

[19] L. D. Landau, J. Exptl. Theoret. Phys. (U. S. S. R.) **30**, 1058 (1956) [translation Soviet Phys.—JETP **3**, 920 (1957)].

[20] L. D. Landau, J. Exptl. Theoret. Phys. (U. S. S. R.) **32**, 59 (1957) [translation, Soviet Phys.—JETP **5**, 101 (1957)].

[21] L. D. Landau, J. Exptl. Theoret. Phys. (U. S. S. R.) **35**, (1958) [translation Soviet Phys.—JETP **35**, 70 (1959)].

temperatures such that $T \gg \hbar / k\tau(T)$. Thermal-conductivity data [see Eq. (64)] give $\tau(T) = 6\times 10^{-3} T^{-2}$ sec. Hence, we expect Landau's theory to be applicable only well below 0.1°K.

From C_V and χ data, Landau was able to infer some of the features of the interaction function f. The results of this theory are essentially the same as the ones given by the simple-exchange model discussed in the foregoing, if $f(\mathbf{k},\mathbf{k}',\boldsymbol{\sigma},\boldsymbol{\sigma}')$ is taken to be proportional to $-\gamma(\mathbf{k},\mathbf{k}')(1+\boldsymbol{\sigma}\cdot\boldsymbol{\sigma}')$. The generality of Landau's theory resides in the unspecified interaction function f. Despite its generality, this theory serves only as an *a posteriori* theory, since the function f cannot be simply calculated from first principles, and even its rough features can only be inferred from C_V and χ experimental data. The most interesting and the unique feature of Landau's work is in regard to the propagation of sound in liquid He^3. This is discussed at the end of this section.

The only serious attempt to numerically calculate the properties of liquid He^3 from first principles has been the work of Brueckner and Gammel.[8] Their results contain the same qualitative features as those of Landau's theory or of the simple-exchange model. However, no phenomenological parameters are introduced in their calculations which start from a Schrödinger equation with a given interatomic potential. Even though these interatomic potentials may be singular, Brueckner and Gammel's method of calculation removes the singularity by the use of a reaction matrix. Hence, these authors were able to calculate the ground-state energy as a function of volume and, thus, the density as a function of pressure, cohesive energy, and compressibility at 0°K. Two interatomic potentials,

$$V(r) = V_0[(R/r)^{12} - (R/r)^6], \qquad V_0 = 40.88\,^\circ\mathrm{K}, \quad R = 2.55\ \text{Å}, \tag{51a}$$

and

$$V(r) = V_0\left[1200e^{-4.82r} - \frac{1.24}{r^6} - \frac{1.89}{r^8}\right], \qquad V_0 = 7250\,^\circ\mathrm{K}, \quad r \text{ in Å}, \tag{51b}$$

were used in the calculations. Even though the potentials of Eqs. (51a, b) are almost identical, except near the origin, the results were found to be very sensitive to the behavior of $V(r)$ near the origin. Brueckner and Gammel also calculated C_V and χ for the potential of Eq. (51b), which gives a cohesive energy $\cong 1$°K, compressibility $\cong 5.3\%$ atm, $(m^*/m)_{C_V} \cong 1.84$ and $(m^*/m)_\chi \cong 12$. The reason for the large apparent m_χ^* is the same as explained by the simple-exchange model. Brueckner and Atkins[22] extended the calculations of Brueckner and Gammel, and calculated the thermal-expansion coefficient α_p of the liquid at low temperatures which depends on dm^*/dV. All the results on the basis of this theory are applicable only below 0.1°K, and the theory does not offer any explanation for the properties of the liquid above 0.1°K.

As mentioned in the foregoing, the most interesting result of Landau's theory concerns the propagation of sound in liquid He^3. At sufficiently low temperatures ($T < 0.05$°K, see Sec. III.9), both the relaxation time and the mean free path of excitations near the Fermi surface will increase as T^{-2}. Therefore, at sufficiently low temperatures, the relaxation time τ (or mean free path $l \cong v_F\tau$) is much larger than the period $T \cong \omega^{-1}$ (or wavelength $\lambda = v_s/\nu \cong v_F/\omega$), and a steady state cannot be reached within a period of oscillation (or within a wave's length). Consequently, an ordinary, compressional sound wave cannot propagate in liquid He^3 if $\omega\tau \gg 1$. In this case, a different kind of disturbance propagates through the liquid, as discussed in the following.

If we consider a small disturbance δn proportional to $\exp i(\mathbf{k}\cdot\mathbf{r} - \omega t)$ of the equilibrium distribution n_0, under conditions of long relaxation time τ and high frequency ω, $\omega\tau \gg 1$, we obtain from Boltzmann's transport equation an integral equation for δn,[14,20] viz.,

$$(\mathbf{k}\cdot\mathbf{v} - \omega)\delta n = \mathbf{k}\cdot\mathbf{v}\frac{\partial n_0}{\partial \epsilon}\int f\delta n' d(\mathbf{k}',\boldsymbol{\sigma}), \tag{52}$$

where $\hbar\mathbf{v} = \mathrm{grad}_{\mathbf{k}}\epsilon(\mathbf{k})$.

Taking the direction of propagation $\mathbf{k}$ for polar axis and defining $c = \omega/k$ (the velocity of sound) and $s = c/v$, we may write Eq. (52) as

$$(s - \cos\theta)\delta n = \cos\theta\frac{\partial n_0}{\partial \epsilon}\int f\delta n' d(\mathbf{k}',\boldsymbol{\sigma}'). \tag{53}$$

If Eqs. (52) or (53) have a solution, we see that the disturbance is confined to the Fermi surface [since from Eqs. (52) or (53) $\delta n \sim (\partial n_0/\partial\epsilon)$]. Landau has given the name zero sound to this peculiar disturbance.

In the simple case that f is independent of angles and spins, we have

$$\delta n \sim \frac{\cos\theta}{s - \cos\theta}\left(\frac{\partial n_0}{\partial \epsilon}\right). \tag{54}$$

Hence, the disturbance is confined to the Fermi surface and, if $f > 0$, mainly in the forward direction as contrasted to a compressional sound wave, in which case $\delta n \sim \cos\theta$, which means a rigid displacement of the Fermi surface. In order that Eq. (53) have a real solution, i.e., s real, $f(0)$ [which is similar to our $-\gamma_0$] must be positive, which seems to be the case for liquid He^3. Landau[20] has shown that, for a nearly ideal F-D gas, as $f(0) \to 0$, $s \to 1$, and hence, $c \to v_F \to 3^{\frac{1}{2}} v_s$. Since the condition $\omega\tau \gg 1$ is not easily met, there has been no experimental verification of these ideas. Since $\tau \cong 6\times 10^{-13} T^{-2}$ sec, we can expect that zero sound of 10 Mc/sec will be observed only below 0.002°K.

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[22] K. A. Brueckner and K. R. Atkins, Phys. Rev. Letters 1, 315 (1958).

5. Superfluid Phase Transition

Different authors[23] have expressed various opinions on the question of whether or not Bose-Einstein statistics are an essential factor for the superfluidity of liquid He^4. Therefore, the existence or nonexistence of superfluidity (as we know it for He^4) in liquid He^3 would clarify the role played by the statistics in this phenomenon. Early experiments[23a] did not reveal any sign of superfluidity in liquid He^3 down to 0.5°K, and the specific heat having become linear[24] in T below 0.1°K seemed to show that He^3 behaved qualitatively like a system of free fermions.

However, the phenomenon of superconductivity shows that a system of nearly free fermions may undergo a different kind of phase transition at sufficiently low temperatures.

Based on the ideas leading to the superconductivity theory by Bardeen, Cooper, and Schrieffer,[25] Cooper, Mills, and Sessler[26] were the first to suggest that below a certain critical temperature T_0 the properties of the liquid might be remarkably different from those above T_0. Lately, other authors[27,28] have discussed the possibility of such a phase transition in liquid He^3 at very low temperatures.

Since the viscosity of this low-temperature phase is expected to decrease with T (instead of increasing as T^{-2}, appropriate to a normal Fermi liquid), the word superfluid has been used in reference to this abnormal low-temperature phase. The existence of weak *attractive* interactions between He^3 atoms is a *sine qua non* ingredient for this transition. However, this superfluid phase transition of He^3 is expected to be quite different from the superfluid λ transition of He^4. According to the several authors,[28] the thermal properties of this transition of He^3 should be more similar to a superconducting phase transition, and, for instance, the specific heat should suffer only a finite jump across T_0.

Since, in the case of He^3, the s-wave phase shift is negative[29] and the d-wave phase shift is positive, one may expect the energy gap (for excitation of single particles near the Fermi surface) for He^3 to be strongly angle-dependent and to vanish for certain momentum directions.[28] This anisotropy is expected to give rise to an unusual structure for the liquid. For instance, the liquid is expected to break up in small domains having dimensions comparable to the (superfluid) correlation length which has been estimated to be 2×10^2 Å. Since the correlation function is anisotropic, the liquid may have a small, net angular momentum, which may be thought of as arising from a noncancellation, near the walls, of weak, circulating currents.[28]

The transition temperature T_0 is given by

$$T_0 \cong T_F^* \exp(T_F^*/V), \tag{55}$$

where V is an appropriate (negative) interaction matrix element at the Fermi surface. Estimates of V give $T_0 \cong 0.1$°K at zero pressure, and it should increase with pressure.[28] Nevertheless, small variations of T_F^* and V have a large effect on T_c, and a factor of n in the exponent of Eq. (55) will reduce T_0 by a factor of about $(20)^{n-1}$. Bardasis and Schrieffer[30] estimated that the finite lifetime of the Fermi excitations may reduce T_0 by a factor of 60. But, according to a recent[31] revision of their calculations, these authors believe that these effects should reduce T_0 by a factor of about 3 only.

Possibly either specific-heat, magnetic-susceptibility, or viscosity experiments should reveal this phase transition. Existing data for C_V and χ, for T as low as 0.005°K have not yet shown any sign of this phase transition. Recent measurements of the sound velocity[32] v_s, have shown a large discontinuity in v_s at high pressures, but it should not be related to the superfluid phase transition, since the ratio of the compressibilities at 0°K (and hence of v_s^2) of the two phases should be at most $(1-T_0/T_F)$ and hence very close to unity, unless T_0 is unexpectedly large. (However, see note added in proof.)

6. Solid Phase

The question of whether or not liquid He^3 will solidify under its own vapor pressure at very low temperatures ($V_{\text{liq}} \cong 36$ cm^3/mole) can be discussed as follows. Neglecting any volume change across the melting curve, the volume per atom V/N would be about 60 Å^3. Hence, each atom would occupy a sphere of radius $R_0 \cong 2.5$ Å, and the nearest-neighbor distance would be $2R_0 \cong 5$ Å. At this interatomic distance, the potential energy of interaction of two He atoms is about 0.4°K/atom, and, hence, even a close-packed lattice would have a (static) cohesive energy of about 5°K/atom. If the solid is to be stable with respect to the liquid at zero pressure, one

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[28] For a review, see A. M. Sessler, in *Helium Three*, edited by J. G. Daunt (The Ohio State University Press, Columbus, Ohio, 1960), p. 81.

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[30] A. Bardasis and J. R. Schrieffer, Phys. Rev. Letters **7**, 79 (1961).

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must have $E(\mathrm{sol}) = -5°\mathrm{K} + E_{\mathrm{zp}} < E(\mathrm{liq}) = -2.5°\mathrm{K}/$atom. Hence, the zero-point energy E_{zp} of the solid (or its Debye temperature) should be less than 2.5°K/atom. Neglecting anharmonic corrections, we may conclude that the average kinetic energy in the solid should be about $(\frac{1}{2}E_{\mathrm{zp}})$ 1.2°K/atom; hence, each atom should have an rms deviation δ from its lattice site of the order of 3 Å ($3\hbar^2/4m\delta^2 < 1.2°\mathrm{K}$), which is about 60% the average interparticle separation. Therefore, we may expect that such necessarily large δ will prevent the liquid from freezing at zero pressure.

Actually, the liquid at $T < 0.5°\mathrm{K}$ solidifies under an external pressure of the order of 30 atm. At this pressure, the volume of the liquid is 26 cm^3/mole, and that of the solid is 25 cm^3/mole. The cohesive energy of the solid can be estimated as follows. The work W to compress the liquid to the melting pressure can be taken as $W \cong (1/2) \times 30 \times (36\text{–}26)$ atm cm^3/mole$\cong$1.7°K/atom; hence, the cohesive energy of the liquid at $T = 0°\mathrm{K}$ and $p = 30$ atm, is about 0.8°K/atom. At $T = 0°\mathrm{K}$, the solid will have a cohesive energy of 0.8°K/atom$- 30 \times (26\text{–}25)$ atm cm^3/mole$=$0.5°K/atom. For this volume of 25 cm^3/mole, a solid He^3 lattice will have static potential energy of about -12°K/atom.

From the preceding argument, we may conclude that the zero-point energy in solid He^3 (or its Debye temperature), at 30 atm, will be about 11.5°K/atom, of which one-half (6°K) may be taken as kinetic energy. Hence, the rms displacement of an atom from its lattice site should be about 1.4 Å, which is about 30% of the average distance between particles.

If one neglects zero-point motion in a solid, one can assume the atoms to be more or less bound to lattice sites, and, hence, they are almost distinguishable. In other words, the proper symmetry of the nuclear wavefunction is not very important for a solid. An example of a solid in which the nuclear spins have, for instance, any effect on the lattice-vibration spectrum is not known. The phonon wavefunction (which is symmetric with respect to normal-mode coordinates) does not have any definite symmetry with respect to interchange of the coordinates of two atoms.

Pomeranchuck,[15] in his paper on liquid He^3, assumed that the He^3 atoms in the solid are rigidly bound to definite lattice sites, and, therefore, that the nuclear spin system will behave classically. Thus, the susceptibility of the solid should be given by Curie's law down to a temperature T_0 below which the nuclear magnetic dipole-dipole interaction ($kT_0 \approx \mu^2/R^3$) would tend to align the spins in some kind of antiparallel arrangement. For low pressures, one can estimate $T_0 \approx 10^{-7}$ °K for solid He^3. According to these ideas, the entropy of the nuclear-spin system, in the absence of an external magnetic field, should be $R \ln 2$ and independent of T down to $T_0 \approx 10^{-7}$, below which it would drop to zero in an unspecified manner. Except for a numerical factor of the order of unity, which accounts for effects such as m^*, $\partial S/\partial p$, and $\partial^2 S/\partial T^2$, the entropy of the liquid is roughly RT. Consequently, Pomeranchuk concluded that above $T \approx \ln 2 = 0.7°\mathrm{K}$, $S_{\mathrm{liq}} > S_{\mathrm{sol}}$, and that, below 0.7°K, $S_{\mathrm{liq}} < S_{\mathrm{sol}}$. Thus, Pomeranchuk concluded that (unless $V_{\mathrm{liq}} - V_{\mathrm{sol}}$ changes its sign at the same T) the melting curve ($dP_m/dT_m = \Delta S/\Delta V$) should have a minimum around 0.7°K. Taking $\Delta V = 1$ cm^3/mole and independent of T, one can estimate $d^2P/dT^2 = R/\Delta V \cong$ 80 atm °K^{-2}; hence, at very low T, P_m should rise about 20 atm below its minimum value at 0.7°K. Therefore, the effect is quite large, and it should be easily detected. Early melting-curve data[33] down to 0.16°K failed to show any rise in P_m, and the data indicated $dP_m/dT_m = 0$ for $0.16°\mathrm{K} < T < 0.4°\mathrm{K}$, which, if taken literally, would imply $S_{\mathrm{liq}} = S_{\mathrm{sol}}$ (and, hence, $S_{\mathrm{sol}} < R \ln 2$, or equivalent, large deviations from Curie's law) in this temperature range. However, Sydoriak pointed out that the traditional, blocked-capillary, experimental set-up used in the determination of the melting curve of helium would not reveal a minimum in P_m; the flat portion of the melting curve would be meaningless.

Primakoff[34] used a tight-binding approximation to estimate the exchange energy in the solid, and he concluded that it was of the order of 0.3°K/atom and thereby much larger than the magnetic dipole-dipole interaction energy. Bernardes and Primakoff[35] discussed the properties of the solid phase on basis of a Heitler-London localized, single-particle wavefunction. According to their results, the exchange energy $-T_C$ at 30 atm is about -0.1°K/atom and favors antiferromagnetic configurations. According to their calculations,[35] the solid should show anomalies in C_V, χ, and α_p near 0.1°K. None of these results have been confirmed by experiment, which seems to indicate that T_C is about ten times smaller than the theoretical estimate of 0.1°K/atom. In this case, the anomalies in C_V, χ, and α_p should occur at about 0.01°K instead of 0.1°K. According to their original calculations, the minimum in the melting curve should occur at 0.37°, as compared to an experimental value of 0.325 ± 0.05°K.

The disagreement in the value of T_C is not surprising due to the many approximations in the theory. However, the disagreement regarding the temperature of the minimum in the melting curve deserves some attention, and it seems to indicate that the experimental values for the entropy of the liquid under pressure are too small by about 10% (see Sec. III.8).

According to Bernardes and Primakoff, the entropy of the antiferromagnetic solid at very low temperatures is given by $A\,(T/T_C)^3$, whereas the entropy of the liquid (in the absence of a superfluid transition) is linear in T. Therefore, at sufficiently low temperatures, the entropy of the solid will again be less than that of the liquid, and a maximum is then to be expected in the melting pres-

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sure. According to their calculations,[35] this maximum should occur at 0.08°K. However, this maximum has not been found down to 0.06°K. If T_C is smaller than the theoretical value by a factor of ten, the temperature of the maximum should be smaller by a factor of $10^{\frac{2}{3}}=4.6$ and the maximum should occur near 0.01°K.

The large-mean-square deviation is the essential reason why the exchange energy ($\cong$0.01–0.1°K/atom) is much larger than the magnetic dipole-dipole interaction. A simple estimate of the relations between mean-square deviation and exchange energy has been given by Bernardes,[36] who concludes that, for all inert gases except for solid He^3, the dipole-dipole magnetic interaction is predominant. In solid hydrogen (HD), the exchange energy is slightly larger than the dipole-dipole energy, but is still too small (or the order of 10^{-5} °K/atom) to affect the classical Curie susceptibility.[36,37]

Saunders[38] estimated the exchange integral J for a pair of He^3 atoms in an anisotropic harmonic potential and found a tendency for parallel spin alignment. However, he also found that the effect of nearest neighbors is such as to make the antiparallel spin state have the lower energy.

Goldstein[17] also discussed the properties of solid He^3 (along the melting curve). His results are presented in conjunction with the experimental data in Sec. IV.

One of the unusual features of solid He^3 is its crystallographic structure. The heavy inert gases, Ne, A, Kr, and Xe, solidify at low pressures in a face-centered cubic lattice. Solid He^4 shows at least one phase transition,[39] but for pressures less than 1500 atm it has a hexagonal close-packed lattice,[40] except possibly for a small region near the melting curve[41] where it may be body-centered cubic. On the other hand, He^3 for pressures between 30 and 100–150 atm solidifies in a bcc lattice, and for pressures between 150–1800 atm it solidifies in a hcp lattice.[42,43] For pressures larger than 1800, a transition to an fcc lattice occurs[43,44,45] similar to solid He^4.

The reasons why He^3 at low pressures solidifies in a bcc lattice rather than in a close-packed lattice are not understood.[46] In order to appreciate the delicate energy balance, we observe that the difference in free energy at 0°K, $\Delta F_0=p\Delta V$, is about 100 atm×0.1 cm^3/mole[46a] $\cong$0.1°K/atom and, hence, is much less than the zero-point energy (30°K/atom) of either phase.[44] Therefore, the zero-point energies will have to be calculated with an accuracy better than 0.3% in order to provide a meaningful answer to the question of the relative stability of the two phases.

Bernardes and Primakoff[35] suggested that this crystallographic phase transition may be accompanied by a magnetic transition related to a change in sign of the exchange integral. There is no experimental evidence for this magnetic transition; if it occurs, it does not seem to contribute to the latent heat (see Sec. IV.5).

One interesting feature of these phase transitions is that they occur at molar volumes which are about the same for both He^3 and He^4; hence, they seem to be due mainly to a volume effect.[45]

Unfortunately, only a small amount of experimental data is available for the solid phase. A more detailed presentation and discussion of these data is given in Sec. IV.

7. He^3-He^4 Mixtures

Prior to the time that He^3 was artificially produced from the β decay of tritium, all the experiments were done with very dilute (less than 1%) solutions of He^3 in He^4 obtained from successive enrichments of natural-helium gas.[1] Daunt and collaborators[47] in 1947 observed that the small amount of He^3 contained in natural helium did not partake of the superfluid motion of the liquid through a porous plug. They were able to filter the He^4 from the solution and obtain solutions enriched with He^3. Many authors[1,48] have investigated this phenomenon as a possible means of He^3 enrichment. Nevertheless, isotope separation by this method is possible only below the λ point of the solution; this is the main limitation of the method. Many authors have investigated the temperature of the λ point as a function of He^3 concentration[49] as well as the phase separation of mixtures.[49] The results, shown schematically in Fig. 2, are very complex. They can be roughly described by the equations

$$T_\lambda(c)=T_\lambda(0)(1-c) \tag{56}$$

for the λ point T_λ of the solution, and

$$T_s(c)=[0.8-4(c-0.5)^2]°\mathrm{K} \tag{57}$$

for the temperature T_s below which phase separation occurs for a solution of mole fraction

$$c=N(He^3)/[N(He^4)+N(He^3)].$$

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[46a] E. R. Grilly and R. L. Mills, Ann. Phys. **8**, 1 (1959).

[47] J. G. Daunt, R. E. Probst, and H. L. Johnston, J. Chem. Phys. **15**, 759 (1947); J. G. Daunt, R. E. Probst, H. L. Johnston, L. T. Aldrich, and Alfred O. Nier, Phys. Rev. **72**, 502 (1947).

[48] For a discussion of the problem of enrichment, see the review by V. P. Peshkov and K. N. Zinov'eva, Repts. Prog. Phys. **22**, 504 (1959).

[49] *Helium Three*, edited by J. G. Daunt (The Ohio State University Press, Columbus, Ohio, 1960).

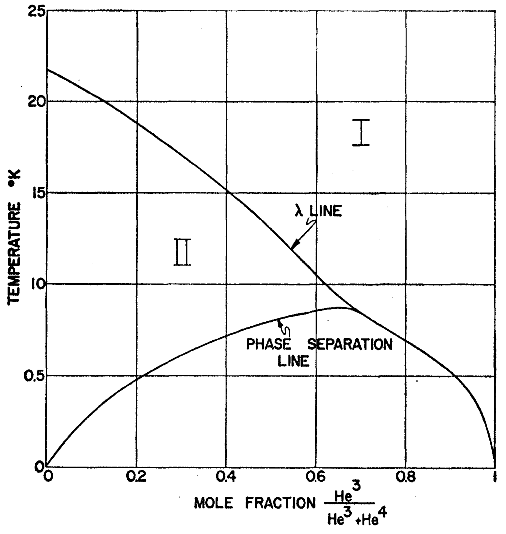

FIG. 2. Phase-separation line and λ line for He^3—He^4 mixtures.[49,50]

Other properties of He^3—He^4 solutions, such as specific heat, zero-sound velocity, vapor pressure, etc., have been measured. We refer the reader to other reviews.[1,48–50]

III. LIQUID PHASE: EXPERIMENTAL DATA

1. Vapor Pressure and Critical Constants

The first liquefaction of He^3 was carried out in 1948 by Sydoriak, Grilly, and Hammel.[2] Their measurements of vapor pressure and critical constants confirmed the prediction of de Boer and Lunbeck[5] that He^3 would liquefy under its own vapor pressure in spite of its large zero-point energy. More precise measurements were made soon afterwards by Abraham, Osborne, and Weinstock[51] in the temperature range 1.0° to about 3.35°K, and were extended down to 0.45°K by Sydoriak and Roberts.[52] In Fig. 3, the vapor pressure of liquid He^3 is compared with that of He^4 as a function of temperature. From a practical point of view, a useful feature of liquid He^3 is its relatively much higher vapor pressure which enables constant temperature baths using liquid He^3 to reach about 0.3°K without difficulty, particularly since a superfluid film is absent. For comparison, liquid He^4 baths cannot be used much below 1°K. Several references to He^3-cryostat design have been given recently by Peshkov and Zinov'eva.[48]

The normal boiling point as recalculated by Sydoriak and Roberts[52] from the data of Abraham *et al.*[51] is $T=3.19$°K. Critical pressures determined by Sydoriak *et al.*[2] and by Abraham *et al.* give an average of 875 mm Hg. The critical temperature and density are $T_c=3.33$°K and $\rho_c=0.0413$ g/cm^3. Using an optical method, Peshkov[53] obtained $T_c=3.38\pm0.03$°K, $p_c=930\pm20$ mm Hg, and $\rho_c=0.041\pm0.001$ g/cm^3.

2. Latent Heat of Evaporation

The latent heat of evaporation L has been determined both by direct measurement and from the Clausius-Clapeyron equation

$$L=T(V_v-V_l)(dp/dT), \tag{58}$$

where dp/dT is the slope of the vapor-pressure curve. The latter calculations are likely to give less accurate results than direct measurements, because of the uncertainties in the temperature scale and in the second virial coefficient.

The only direct measurements of latent heat are due to Weinstock, Abraham, and Osborne.[54] In Fig. 4, a comparison is made between the direct measurements (considered to be accurate to 0.2%) and the calculations from the vapor pressure.[2,51,55,56] The latter are about 1% higher at 1.2°K and 0.5% lower at 2.1°K. Precise measurements of the latent heat are important inasmuch

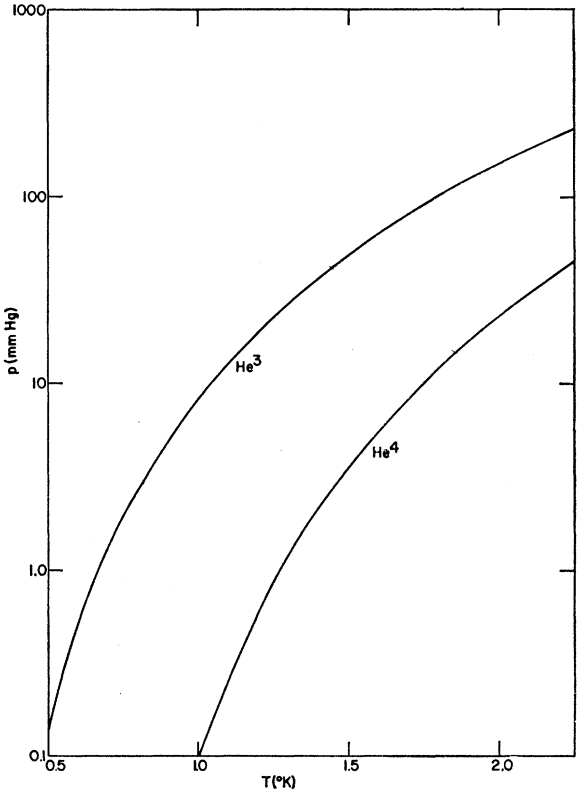

FIG. 3. Vapor pressures of He^3 and He^4.

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[50] *Proceedings of the VIIth. International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallet (The University of Toronto Press, Toronto, Ontario, Canada, 1961).

[51] B. M. Abraham, D. W. Osborne, and B. Weinstock, Phys. Rev. **80**, 366 (1950).

[52] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

[53] V. P. Peshkov, J. Exptl. Theoret. Phys. (U. S. S. R.) **33**, 833 (1947); Soviet Phys.—JETP **6**, 645 (1947).

[54] B. M. Abraham, D. W. Osborne, and B. Weinstock, Physica **24**, S-132 (1958).

[55] E. C. Kerr, Phys. Rev. **96**, 551 (1954).

[56] T. R. Roberts and G. S. Sydoriak, Phys. Rev. **98**, 1672 (1955).

as they can be used to calculate the entropy of the liquid, as was done by Weinstock, Abraham, and Osborne.[54] The extrapolated latent heat of vaporization at 0°K is $L_0 \cong 5$ cal/mol.

3. Density

Soon after their first liquefaction of He^3, Grilly, Hammel, and Sydoriak[2] measured the saturated liquid and vapor densities by an indirect method. Since then, several authors have measured the normal liquid density using a variety of methods. Kerr[55] and Ptukha[57] (who also determined densities of He^3—He^4 solutions) used a pyknometer in the temperature range of about 1.3° to 3.2°K, measuring the amount of gas needed to fill the pyknometer with liquid up to a known volume. The early results of Grilly, Hammel, and Sydoriak[2] and those of Kerr are shown in Fig. 5. By using a liquid He^3 bath, Taylor and Kerr[58] were able to extend the temperature range down to 0.29°K, and, with a small adaptation for adiabatic demagnetization, to about 0.21°K. The variation of density with temperature was determined optically by Peshkov,[53] who counted the passage of fringes of equal optical thickness between a glass wedge during a series of operations to fill the wedge with liquid at 2.00°K. Hence, the change in refractive index was found, and, using Kerr's value of the density at this temperature, the molar polarization A was calculated, gave $A = 0.123$ cm^3/mole. Using this value and by counting the passage of fringes as the temperature changed, Peshkov determined the change in density with temperature between 1.4 and 3.2°K.

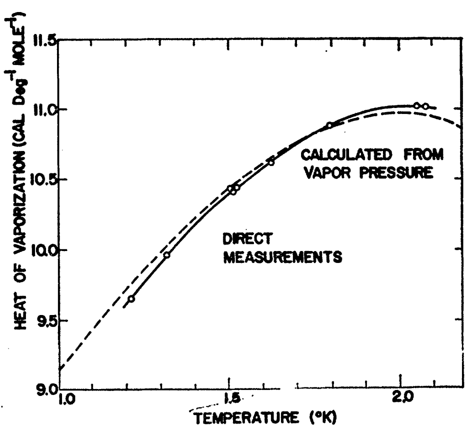

FIG. 4. Latent heat of evaporation[54-57] of liquid He^3.

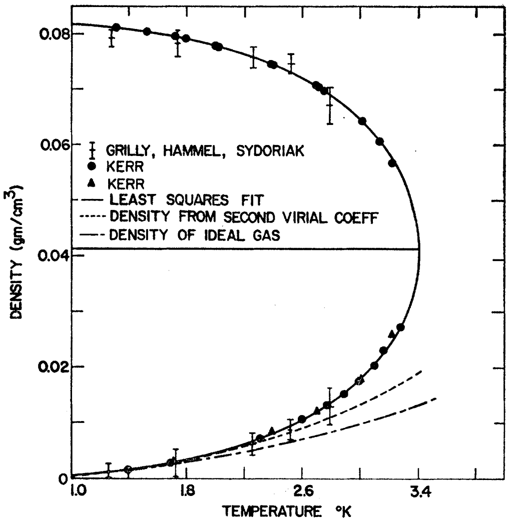

FIG. 5. Vapor and liquid densities above 1°K.

Other investigations have been carried out by Sherman and Edeskuty[59] and by Lee and Fairbank.[60,61] The former have made an extensive investigation of the PVT relations of the liquid up to the melting pressure between 0.98° and 3.32°K, from which they also calculated expansion coefficients, compressibilities, and changes in entropy and specific heat on compression. It should be noted that these authors have made a redetermination of their liquid cell volume, which necessitates a decrease in the published values of molar volumes and entropies by 0.3% and an increase in the expansion coefficients and compressibilities by 0.3%. Lee, Fairbank, and Walker[62] evaluated the density from measurements of the dielectric constant at various pressures, and Walters and Fairbank[63] measured the relative densities at 1.2°K by measurement of the nuclear susceptibility as a function of pressure. The above measurements of molar volumes near 1°K are in good agreement with each other, generally within 1%.

The density of the liquid is discussed further in the sections on the compressibility and on the thermal-expansion coefficient.

4. Thermal Expansion Coefficient

Interest in the molar volumes of liquid He^3 below 1°K was stimulated by the possibility of a negative expansion coefficient at low enough temperatures. The suggestion that a density maximum might occur has been made by a number of authors, probably first by Tien Chi Chen and London.[64] Brueckner and Atkins[22] have calculated the limiting (negative) slope of the expansion coefficient as $T \rightarrow 0$, on the basis of Brueckner and Gammel's theory of He^3, and Goldstein[17] has recently evaluated the course of the expansion coefficient as a function of temperature. An experimental indication of a negative expansion coefficient near 0.5°K was

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[57] T. P. Ptukha, J. Exptl. Theoret. Phys. (U. S. S. R.) **34**, 33 (1958); Soviet Phys.—JETP **7**, 22 (1958).

[58] R. D. Taylor and E. C. Kerr, Physica **24**, S133 (1958).

[59] R. H. Sherman and F. J. Edeskuty, Ann. Phys. **9**, 522 (1960).

[60] D. M. Lee and H. A. Fairbank, Phys. Fluids **2**, 581 (1959).

[61] D. M. Lee and H. A. Fairbank, Phys. Rev. **116**, 1359 (1959).

[62] D. M. Lee, H. A. Fairbank, and E. J. Walker, Phys. Rev. Letters **5**, 276 (1960).

[63] W. M. Fairbank, and G. K. Walters, Phys. Rev. **103**, 263 (1956).

[64] T. C. Chen and F. London, Phys. Rev. **89**, 1038 (1953).

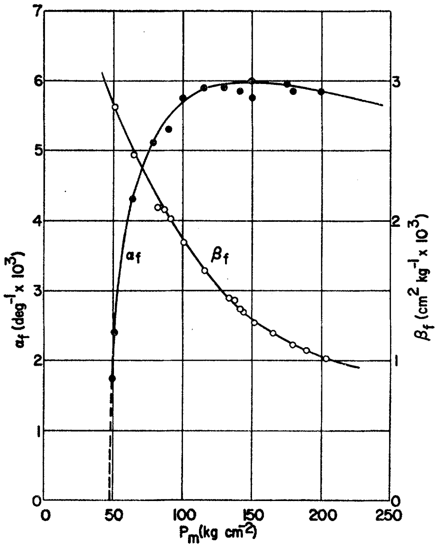

FIG. 6. Thermal expansion coefficient and compressibility of liquid He^3 at melting pressures for $p > 50$ atm.[46a]

discovered in the onset of convective heat transport observed by Lee and Fairbank[61] in thermal-conductivity measurements at low temperatures. Abraham, Osborne, and Weinstock showed by analysis and extrapolation of experimental thermal data that the expansion coefficient at constant pressure α_p should become zero at some temperature above 0.4°K. Direct confirmation of a negative expansion coefficient was found almost simultaneously in the experiments of Taylor and Kerr,[59] of Lee and Fairbank,[60] and of Brewer and Daunt,[65] the latter by measurement of the change in temperature on adiabatic expansion of the liquid at various pressures and temperatures.

Lee, Fairbank, and Walker[62] measured the dielectric constant at pressures between 0.2 and 29 atm, and from the Clausius-Mossotti equation obtained values of the density, thermal expansion coefficient, and entropy of compression. Kerr and Taylor[58] measured molar volumes directly, and found a minimum in the molar volume of 36.713 cm^3/mole at 0.506°K. This temperature should be compared with the values 0.50°K (Brewer and Daunt[65]) and 0.48°K (Lee *et al.*[62]) obtained by indirect methods. Recently, Rives and Meyer[66,67] measured the thermal expansion coefficient α_p down to 0.045°K and for pressures up to 28 atm. At 0.18 atm and below 0.1°K, their results can be expressed by $\alpha_p = -(0.12 \pm 0.02)T$, in qualitative agreement with theoretical calculations.[22]

At higher pressures, the thermal expansion coefficient becomes zero at temperatures which increase with pressure. There is a fair agreement between the results from different groups[59,62,65]; they show that the temperature where the maximum density occurs increases from about 0.5°K at zero pressure to 1.3°K at the melting pressure $[P_m(1.35°\text{K}) = 49 \text{ atm}]$.

From this discussion, it follows that the thermal expansion coefficient becomes negative below 0.5°K at zero pressure, and below higher temperatures at higher pressures (below 1.3°K at 50 atm). The experiments of Brewer and Daunt[65] also show that below 22 atm the expansion coefficient goes through a minimum at about 0.2°K at all pressures,[65] in agreement with the thermodynamic requirement that the minimum should occur above the temperature of crossover of the C_p vs T isobars (0.16°K, see Fig. 12). Goldstein,[17] using the concept of spin and nonspin entropies (Sec. II.4), has derived values of the spin expansion coefficient which follow quite closely the low-temperature experimental values in particular showing a minimum at about 0.2°K.

In the region where the specific heat and entropy vary linearly with temperature, α_p is, to a good approximation, also a linear function of T, in accordance with the relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$. The limiting value of α_p at zero pressure has been calculated by Brueckner and Atkins[22] who found $\alpha_p = -0.076T°\text{K}^{-1}$. The measurements by Brewer and Daunt[65] give $\alpha_p = -(0.1 \pm 0.02)T°\text{K}^{-1}$, those by Anderson *et al.*,[68] $-0.08T°\text{K}^{-1}$, and those by Rives and Meyer[66] give $\alpha_p = -(0.12 \pm 0.02)T°\text{K}^{-1}$.

Above 50 atm, the expansion coefficient is always positive,[46a] as shown in Fig. 6. Sherman and Edeskuty[59] measured α_p between 1° and 2.1°K for pressures up to the melting pressures (35 and 80 atm, respectively). Grilly, Sydoriak, and Mills[69] extended the measurements along the melting curve to temperatures as low as 0.4°K. Their results are shown in Fig. 7, which also includes computed values of α_p for the solid. At melting

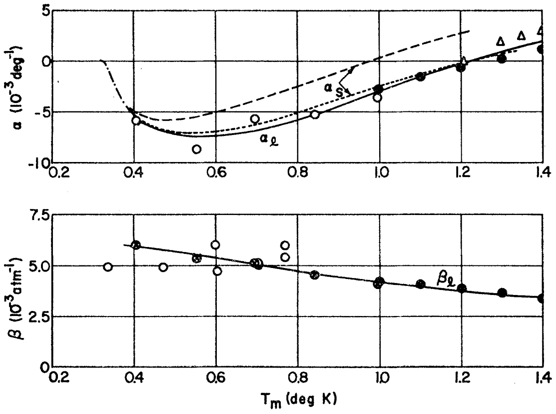

FIG. 7. Thermal expansion coefficient and compressibility of liquid and solid He^3 at melting pressures.[59,69]

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[65] D. F. Brewer and J. G. Daunt, Phys. Rev. **115**, 843 (1959).

[66] J. E. Rives and H. Meyer, Phys. Rev. Letters **7**, 217 (1961).

[67] Notice that their results above 15 atm give $\alpha_p > 0$ for $T < 0.05°\text{K}$, in disagreement with the results of Brewer and Keyston. (See reference 82 below.)

[68] A. C. Anderson, G. L. Salinger, W. A. Steyert, and J. C. Wheatley, Phys. Rev. Letters **7**, 295 (1961).

[69] S. G. Sydoriak, R. L. Mills, and E. R. Grilly, Phys. Rev. Letters **4**, 495 (1960).

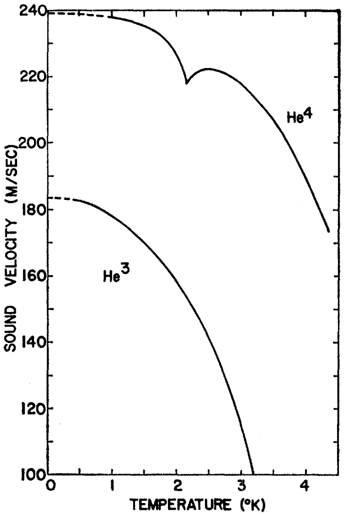

FIG. 8. Velocity of sound[70,71] in liquid He^3 and He^4 at saturated vapor pressure.

pressures, the expansion coefficient exhibits the same general features as at lower pressures, in passing through zero (at a temperature of 1.2°K) and becoming negative. In detail, the behavior is somewhat different; for example, the minimum in α_p occurs at a fairly high temperature, about 0.6°K. Although the data do not extend to temperatures low enough, Sydoriak *et al.*[69] concluded that both α and $\partial\alpha/\partial T$ along the melting curve are equal to zero at 0.32°K, the temperature where the melting curve shows a minimum (see Sec. IV.4). Such behavior differs from that at lower pressures, and would imply a curious variation of the specific heat with p and T at the melting pressures. It is clearly desirable, though difficult, to continue these experimental observations to temperatures below the minimum in the melting curve.

5. Compressibility

The isothermal compressibility $K_T \equiv -V^{-1}(\partial V/\partial p)_T$ of liquid He^3 was calculated by Sherman and Edeskuty[59] from their measurements up to the melting pressure between 0.98° and 3.2°K. Peshkov's results,[53] using the optical method outlined in the foregoing, are about 10% lower than these. The adiabatic compressibility has been computed from measurements of the velocity of sound (see Sec. III.6) by Laquer, Sydoriak, and Roberts[70] (0.36 to 3.14°K) and by Atkins and Flicker[71] (1.2° to 3.2°K). The extrapolated results at zero pressure and 0°K give $K_0 \cong 4\%$ atm^{-1}, as compared with a theoretical value[8] of 5.3% atm^{-1}.

6. Velocity of Sound

Propagation of sound in liquid He^3 is particularly interesting in view of the prediction by Landau[20] that ordinary sound of a given frequency will become increasingly attenuated as the temperature is reduced, until in the Fermi-liquid region ($T < 0.05$°K) it is replaced by "zero sound" (Sec. II.4). The velocity of sound has been measured by Laquer, Sydoriak, and Roberts[70] (5 Mc/sec) at the vapor pressure between 0.34 and 3.14°K, and by Atkins and Flicker[71] (14 Mc/sec) in the range 1.2° to 3.2°K as a function of pressure, and in the gas above the critical point.

The velocity of sound at the saturation vapor pressure is plotted in Fig. 8 (from the paper of Laquer *et al.*); Atkins and Flicker agree with these results within experimental error. Comparison with the He^4 velocities in the figure shows the two curves to be roughly parallel, except for the intervention of the λ transition in He^4.

More recently, Abel, Anderson, and Wheatley[72] measured both the velocity of sound (5 and 15 Mc/sec) and the attenuation coefficient for temperatures as low as 0.02°K and pressures up to 30.9 atm. Their results, shown in Fig. 9, agree very well with the previous ones where they overlap, and at $p=0$ and $T=0$°K $v_s = 183$ m/sec.

Abel, Anderson, and Wheatley[72] observed that, for pressures up to 29.5 atm, the propagation of sound is normal. For instance, the velocity of sound below 1°K seems to be independent of temperature, and the absorption (attenuation) coefficient decreases with temperature. In this range of pressures and below 0.1°K, the measured absorption is proportional to T^{-2} and can be explained in terms of viscosity only.[72] On the other hand, when the pressure (under which the warm liquid was frozen) is changed from 29.6 atm to 30 atm, the velocity of sound increases (practically in a discontinuous fashion) by about 25%. At the same time, the attenuation coefficient increases with temperature, which is opposite to the low-pressure behavior. This anomaly, if genuine, seems to indicate the existence of a new phase of some kind.[72] It is interesting to notice that, at about this same pressure, C_V/RT or m^*/m also show a behavior[73] which may be qualified as anomalous when

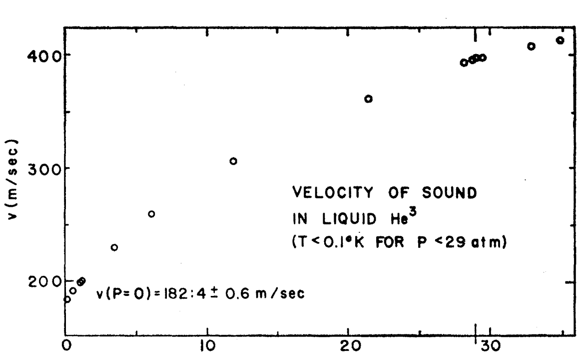

FIG. 9. Sound velocity in liquid He^3 as a function of pressure below 29 atm.[72]

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[70] H. L. Laquer, G. S. Sydoriak and T. R. Roberts, Phys. Rev. **113**, 417 (1959).

[71] K. R. Atkins and H. Flicker, Phys. Rev. **113**, 959 (1959).

[72] W. R. Abel, A. C. Anderson, and J. C. Wheatley, Phys. Rev. Letters **7**, 299 (1961).

[73] A. C. Anderson, G. L. Salinger, W. A. Steyert, and J. C. Wheatley, Phys. Rev. Letters **7**, 295 (1961).

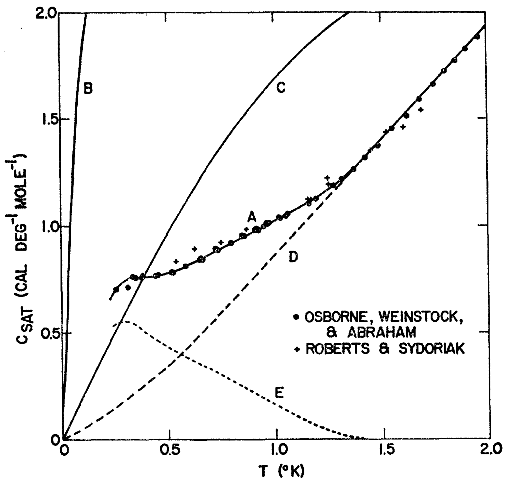

FIG. 10. Specific heat[75,76] of liquid He^3. For an explanation of curves A–D, see text.

compared to the behavior at lower pressures. The nuclear-magnetic susceptibility (Sec. 12), also shows an anomalous discontinuity at about the same pressure. It is, however, possible that all these anomalies may not be real, but only manifestations of experimental difficulties in cooling the compressed liquid. (However see the note added in proof at the end of this paper.)

7. Specific Heat

Specific-heat measurements are of particular importance for determining the nature of the thermal excitations in the liquid. In He^3, the special interest lay in determining whether the liquid behaves similarly to a perfect Fermi gas, or whether the interactions present would modify the behavior in a fundamental manner.

The first specific-heat measurements on liquid He^3 were carried out by de Vries and Daunt[74] using a very small quantity of liquid (about 19 mm^3, 96% He^3, 4% He^4) between 2.3° and 0.57°K. They were followed by Roberts and Sydoriak[75] and by Osborne, Abraham, and Weinstock[76] who reduced the temperature to 0.37 and 0.23°K, respectively, and who used larger quantities of liquid (up to 0.5 cm^3). It was concluded from the experiments that no specific-heat anomaly occurred within the range of measurement, and that the behavior could not be described by a simple Fermi-gas model. The results are shown in Fig. 10, curve A. Curve C in Fig. 10 gives C_V for a perfect Fermi-Dirac gas of the same particle mass and density as liquid He^3 (degeneracy temperature 5°K); curve B is the same calculated with a degeneracy temperature as derived from nuclear-susceptibility measurements (0.45°K, see reference 12). In an attempt to clarify the nature of the thermal excitations, Abraham *et al.*[76] divided the specific heat empirically into two contributions, one due to nuclear spins and the other due to the remaining excitations. The latter is given by curve D, an extrapolation of the high-temperature specific heat, where statistics and spin may be supposed to be unimportant. Curve E represents the "spin" specific heat which is obtained by subtracting curve D from the total specific heat, curve A. The validity of such a division into spin and nonspin contributions has been strongly criticized. However, Goldstein[17] has carried out extensive calculations of thermodynamic properties with this assumption, often agreeing closely with experiment. All the above experiments determined C_{sat}, the specific heat of the saturated liquid along the vapor pressure curve. From them, Goldstein[17] has calculated values of C_p and C_V at the saturated vapor pressure.

The general variation of the specific heat up to 1°K follows roughly that calculated by Khalatnikov and Abrikosov,[77] but does not agree in detail.

Brewer *et al.*[78] measured C_p to 0.085°K, for $p=6$–14 cm Hg, and Brewer, Daunt, and Sreedhar[79] measured C_p down to 0.07°K for pressures up to the melting pressures. The results of Brewer, Daunt, and Sreedhar, estimated to be accurate to within ±0.01 cal mole^{-1} deg^{-1}, are shown in Figs. 11 and 12. They agree satisfactorily with previous measurements above 0.23°K (also shown in Fig. 11), and showed (a) that no anomaly occurs down to 0.085°K, and (b) that below about 0.1°K the specific heat appeared to tend linearly to zero at the absolute zero with a slope of 4.00±0.1 cal mole^{-1} °K^{-2}. The linear behavior seemed to provide evidence for regarding liquid He^3 below 0.1°K as a

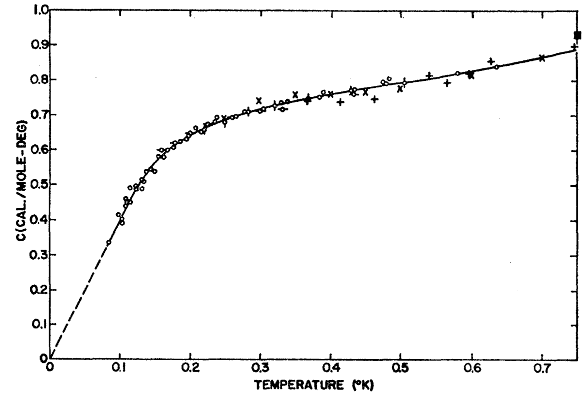

FIG. 11. Specific heat of liquid He^3 under vapor pressure.[75,76,78,79]

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[74] G. de Vries and J. G. Daunt, Phys. Rev. **92**, 1572 (1953); **93**, 631 (1954).

[75] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954); **98**, 1672 (1955).

[76] B. M. Abraham, D. W. Osborne, and B. Weinstock, Phys. Rev. **98**, 551 (1955).

[77] I. M. Khalatnikov and A. A. Abrikosov, J. Exptl. Theoret. Phys. **32**, 915 (1957) [translation, Soviet Phys.—JETP **5**, 745 (1957)].

[78] D. F. Brewer, A. K. Sreedhar, H. C. Kramers, and J. G. Daunt, Phys. Rev. **110**, 282 (1958).

[79] D. F. Brewer, J. G. Daunt, and A. K. Sreedhar, Phys. Rev. **115**, 836 (1959). D. O. Edwards, J. L. Baum, D. S. Brewer, J. G. Gaunt, and A. S. MacWilliams, reference 49, p. 126.

degenerate Fermi fluid with approximately constant effective mass, in agreement with the theories of Landau and of Brueckner and Gammel. If the ratio of effective mass to true mass is defined as $m^*/m = C/C_F$ (where C is the observed specific heat in the linear region, C_F the ideal Fermi specific heat for particles of the He^3 atomic mass m and the same density as liquid He^3), then, experimentally,[78,79] $m^*/m = 2.00 \pm 0.05$, agreeing within 7% with Brueckner and Gammel's theoretical value. The authors[79] point out that their accuracy does not rule out the possibility of a small amount of curvature remaining even at the lowest temperature of measurement, which would increase the limiting slope of the specific heat at 0°K. In fact, more-recent measurements[73,80–82] at temperatures as low as 0.005°K give a value for m^*/m as large as 2.8 ± 0.3, and hence the previous agreement with theory is partially destroyed.

Anderson *et al.*[80] measured C_V at 0.12 atm down to 0.005°K, but their temperature calibration needs correction.[73] The low-pressure results from different groups are shown in Fig. 13. It seems that C_V becomes linear only below 0.03°K. Anderson *et al.*[80] extended their C_V measurements to pressures up to the melting pressures for $T > 0.02$°K. Their results are shown in Fig. 14, and for $p < 25$ atm they can be represented within 10% by the equations

$$\lim_{T\to 0}(C/RT) = [2.8 + 0.03p]\text{-K}^{-1}, \tag{59}$$

and

$$m^*/m = [2.8 + 0.08p], \tag{60}$$

where p is the pressure in atm.

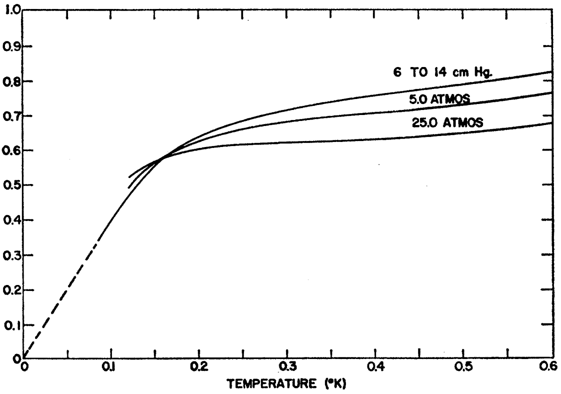

FIG. 12. Specific heat C_p of liquid He^3 as a function of temperature for different pressures.[79]

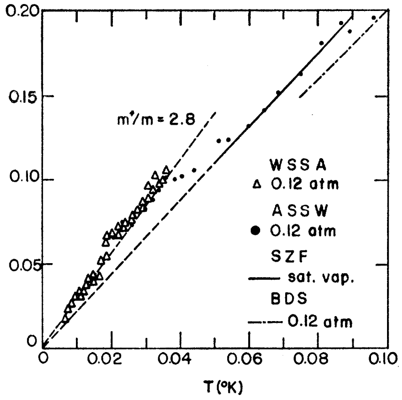

FIG. 13. Specific heat of liquid He^3 below 0.1°K.[73,79–81]

The results for $p \overset{\sim}{>} p_{\min} \cong 29$ atm appear anomalously low. For $p > 29$ atm in Fig. 14, p means the pressure to which the warm (~1°K) liquid was submitted before cooling. Since the compressed liquid will first freeze upon cooling and then melt upon further cooling, it is very difficult to assess the final mass of the liquid within the calorimeter. In the C_V data under discussion, and in all subsequent high-pressure data for discussion here, the authors have always *assumed* that the mass of liquid within the experimental cell remains constant during the cooling-freezing/cooling-melting process. The results shown in Fig. 14 for $p > 29$ atm depend on this assumption. (See note added in proof.)

8. Entropy

All of the different sets of specific-heat results above 0.1°K described in the foregoing section are in good agreement in the temperature range where they overlap (down to 0.23°K). Consequently entropy *differences* evaluated by integration of the specific heat between any two temperatures within this range also agree. Unfortunately, discrepancies occur when different methods are used to compute the *absolute* entropy. Weinstock, Abraham, and Osborne[54] accurately measured the latent heat of the liquid, $L = T(S_{\text{vap}} - S_{\text{liq}})$, calculated S_{vap} for the vapor using the Sackur-Tetrode equation with corrections for nonideality, and hence obtained S_{liq} which, at 1.5°K and saturated vapor pressure, was found equal to 2.614 ± 0.03 cal/mole°K. Roberts and Sydoriak evaluated absolute entropies from the thermodynamic vapor-pressure equation, obtaining the value 1.44 cal mole^{-1} deg^{-1} at 0.5°K. Brewer *et al.*[79] were able, by use of their linear extrapolation of the specific heat to 0°K, to derive absolute entropies directly from $S(T) = \int_0^T (C_V/T)dT$. It is found, as a result of these calculations, that the entropies of Roberts and Sydoriak and of Brewer *et al.* agree closely, but are lower by a constant amount of about 0.1 cal mole^{-1} deg^{-1} than those of Abraham *et al.* Random errors are reckoned to ± 0.01 cal mole^{-1} deg^{-1} or rather more at higher temperatures, with an additional error of ± 0.03 cal mole^{-1} deg^{-1} for Abraham *et al.*, due to possible inaccuracy in the reference vapor entropy at 1.5°K. Brewer *et al.*[79] estimate that their values may have to be increased by a maximum of 0.03 cal mole^{-1} deg^{-1} due to error in extrapolation, but, in view of the much larger values

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[80] A. C. Anderson, G. L. Salinger, W. A. Steyert, and J. C. Wheatley, Phys. Rev. Letters 6, 331 (1961).

[81] M. Strongin, G. O. Zimmerman, and H. A. Fairbank, Phys. Rev. Letters 6, 404 (1961).

[82] D. F. Brewer and J. R. G. Keyston, Nature 191, 1261 (1961).

for m^*/m and C/RT found recently, their entropies may have to be increased by an amount of the order of [Eq. (59)]

$$\frac{\delta S}{R} = \left(\frac{\delta m^*}{m}\right)\int_0^{0.04}\left(\frac{C_V}{RT}\right)dT \cong 0.4\times 2.8\times 0.04 \cong 0.05°\mathrm{K}^{-1}, \quad (61)$$

since most of the increase in m^* occurs below 0.04°K. The correction represented by Eq. (61) would remove the 0.1 cal/mole°K discrepancy.

At higher pressures, the entropy S_p can be calculated from S_0 with the equation

$$S(p,T)-S(p_0,T) = -\int_{p_0}^{p}\left(\frac{\partial V}{\partial T}\right)_p dp. \quad (62)$$

Between 1.00° and 3.30°K, the right-hand side of this equation has been evaluated by Sherman and Edeskuty[59] up to the melting pressure. Brewer and Daunt[82] evaluated it at one temperature (0.6°K) by integration of expansion coefficients under pressure, and combined the result with an integration with respect to temperature of the specific heat under pressure to obtain the entropy as a function of temperature and pressure up to 1°K and 22 atm. This procedure has also been used by Lee, Fairbank, and Walker.[62]

9. Thermal Conductivity and Thermal Boundary Resistance

It has been known since the work of Kapitza[83] that a temperature jump exists at the interface between liquid He^4 and a solid wall when heat flows across the interface. Fairbank and Lee[84] observed a similar effect in a liquid-He^3/copper interface.

As a result of this temperature jump, the observed rates of flow of heat have to be corrected for this apparent Kapitza boundary resistance. The Kapitza resistance is found to increase very rapidly[84,85] with decreasing temperatures for both He^3 and He^4.

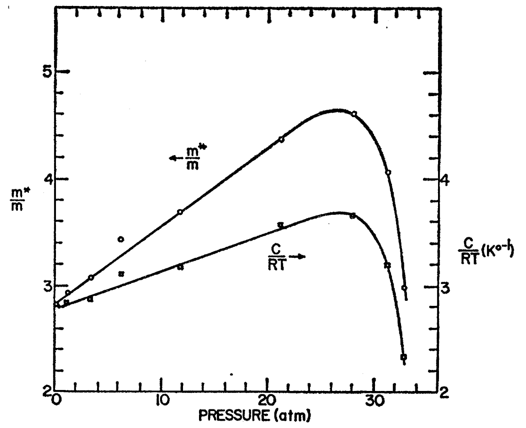

FIG. 14. C/RT and m^*/m for liquid He^3 under pressure.[80]

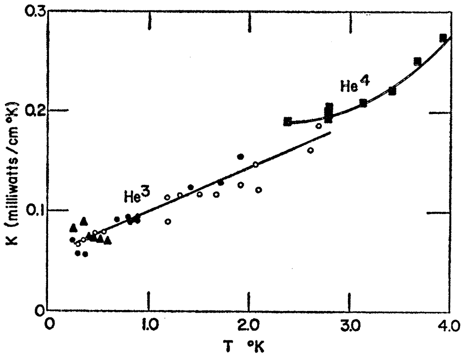

FIG. 15. Thermal conductivity of liquid He^3 above 0.24°K.[84,86]

Thermal conductivity κ data (Fig. 15) from several authors[84–86] indicated that κ *decreases* with temperature down to 0.24°K (Fig. 15), and that the uncertainty in κ is considerable due to the Kapitza-resistance corrections. Recently, Anderson, Salinger, and Wheatley[85] measured κ from 0.2°K down to 0.026°K, and they found that below 0.04°K the thermal conductivity *increases* at T^{-1} (Fig. 16) in agreement with what one expects from the Fermi-Dirac-Landau theory.[13–15] The effect of the Kapitza resistance was minimized in the experiments by Anderson, Salinger, and Wheatley[85] by placing the thermometers in direct contact with the liquid, by using surfaces with small thermal conductivity, and by increasing the total area of contact with the liquid.

Anderson[87] analyzed numerically certain corrections which, according to Jeener and Seidel,[88] should affect the published results of Lee and Fairbank[84] above 0.24°K. Anderson concluded that the corrections to the Lee and Fairbank data should not be as large as Jeener and Seidel had suggested, and, thus, that the published values[84] near 0.24°K are essentially correct. This conclusion is strengthened by the fact that the results below 0.2°K as shown in Fig. 15 join smoothly with those above 0.24°K as shown in Fig. 16.

Anderson, Salinger, and Wheatley[85] concluded from their measurements that the Kapitza resistance is proportional to T^{-3}, in agreement with a model proposed by Bekarevich and Khalatnikov.[89]

Approximate values for the relaxation time τ of the Fermi quasi-particles near the Fermi surface can be obtained from the thermal-conductivity data in the region where $\kappa \sim T^{-1}$, by means of the usual kinetic

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[83] P. L. Kapitza, J. Phys. (U. S. S. R.) 4, 182 (1941).

[84] D. M. Lee and H. A. Fairbank, Phys. Rev. **116**, 1359 (1959).

[85] A. C. Anderson, G. L. Salinger, and J. C. Wheatley, Phys. Rev. Letters **6**, 443 (1961).

[86] L. J. Challis and J. Wilks, *Proceedings of the Symposium on Liquid and Solid He³* (The Ohio State University Press, Columbus, Ohio, 1957).

[87] A. C. Anderson, Ph.D. thesis, University of Illinois, 1961 (unpublished).

[88] J. Jeener and G. Seidel, see reference 50, p. 483.

[89] I. L. Bekarevich and I. M. Khalatnikov, see reference 50, p. 480.

argument which relates κ to C_V; i.e.,

$$C_V = 3\kappa/\tau v_F^2, \tag{63}$$

where v_F is the Fermi velocity p_F/m^*. Below 0.04°K, $C_V \cong 6\times 10^6 T$ erg/cm³ °K², $m^* \cong 2.8$ m,[73] and $\kappa \cong 48T^{-1}$ erg/°K² cm sec.[85] Hence, Eq. (63) gives

$$\tau \cong 6\times 10^{-13} T^{-2} \text{ sec}, \tag{64}$$

where T is the temperature expressed in °K. The Fermi-Dirac-Landau model is expected to work only at temperatures low enough, such that $\hbar/\tau \ll kT$, which in view of Eq. (64) can be written as

$$T \ll 6k/10^{13}\hbar \cong 0.1\text{°K}, \tag{65}$$

and which indicate that even at 0.1°K the simple properties of liquid He^3 may show deviations from the Fermi-Dirac-Landau model.

10. Viscosity

The earliest flow measurements on the liquid, by Osborne, Weinstock, and Abraham,[90] were aimed principally at determining whether it became superfluid; they showed that the viscosity increases with decreasing temperature without any sign of superfluidity down to 1.05°K. Later workers used the oscillating-disk method[91] between 2.15° and 1.3°K, and the capillary-flow method[92] down to 0.35°K, the latter by means of a He^3 cryostat. They agree in confirming the temperature dependence of the viscosity found by the earlier workers, but, as shown in Fig. 17, the absolute values are different by 20% or more. Errors are assessed at about ±2% by Taylor and Dash, and at ±5% above 1°K ±10% below 1°K by Zinov'eva. Two different capillary tubes used by the latter gave essentially the same result, and the data appear rather more consistent than the quoted accuracy indicates. In any case, the discrepancy between the two methods is well outside the estimated experimental error. Both were applied to liquid He^4 above the λ point where again it appeared that the Taylor and Dash results were somewhat higher than previously found. These authors have, however, made a careful assessment of their errors.

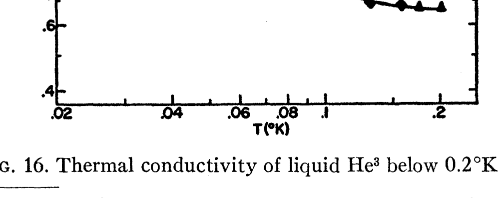

FIG. 16. Thermal conductivity of liquid He^3 below 0.2°K.[85]

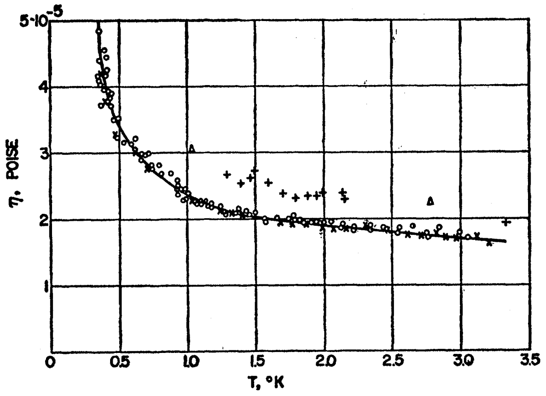

FIG. 17. Viscosity of liquid He^3 above 0.35°K.[90-92]

Direct measurements of the viscosity coefficient in the Fermi liquid region have yet to be made. However, Abel *et al.*[72] observed that the attenuation of sound below 0.06°K is due only to viscosity, and inferred that $\eta = 2.8T^{-2}$°K² μ poise, which is the temperature dependence expected from the theory.[14,15] Thus the three transport coefficients, κ, η, and D, all display temperature dependences in agreement with the Fermi liquid model below 0.05°K.

11. Surface Tension

The surface tension α of liquid He^3 has been measured using the capillary-rise method by Eselson and Bereznyak,[93] by Zinov'eva,[94] and by Lovejoy.[95] The results, given in Fig. 18, are in fairly good agreement, and show a practically linear dependence on temperature between the critical temperature $T_c = 3.33$°K and about 1.5°K. Lovejoy compares his results with the Atkins theory,[96] which considers the variation of surface tension at low temperatures to be due to the variation of the energy of surface waves. On the basis of this theory, he extrapolated his values from 1.08°K to 0°K, and obtained for the surface tension at the absolute zero $\alpha = 0.154 + 0.005$ erg/cm². The Zinov'eva data indicate that α remains constant below 0.5°K and equal to 0.152 erg/cm². By plotting α vs T/T_c for He^3 and He^4, she found that the curves are identical within experimental error. The difference in statistics between He^3

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[90] B. M. Abraham, D. W. Osborne, and B. Weinstock, Phys. Rev. **75**, 988 (1949).

[91] R. D. Taylor and J. G. Dash, Phys. Rev. **106**, 398 (1957).

[92] K. N. Zinov'eva, J. Exptl. Theoret. Phys. (U. S. S. R.) **34**, 609 (1958); Soviet Phys.—JETP **7**, 421 (1958).

[93] B. N. Eselson, N. G. Bereznyak, Doklady Akad. Nauk S. S. S. R. **99**, 365 (1954).

[94] K. N. Zinov'eva, J. Exptl. Theoret. Phys. (U. S. S. R.) **29**, 899 (1955).

[95] D. R. Lovejoy, Can. J. Phys. **33**, 49 (1955).

[96] K. R. Atkins, Can. J. Phys. **31**, 1165 (1953).

and He^4 thus has no influence on the surface tension right down to the lowest temperatures.

12. Nuclear-Magnetic Susceptibility

The nuclear-magnetic moment of an He^3 nucleus being too small, static methods are inadequate for measurements of the nuclear-magnetic susceptibility.

Fairbank and his collaborators[11,12,63,97] have made extensive use of spin-resonance techniques in order to investigate the behavior of the nuclear-spin system. Other groups have also used resonance techniques to investigate the behavior of the nuclear-spin system, as well as an indirect method of measuring the self-diffusion coefficient,[98] for instance.

The results by Fairbank *et al.*[97] are summarized in Fig. 19, in which $\chi T/C$ is plotted against T, where χ is the molar susceptibility at temperature T and C a normalizing constant. Since the linewidth due to field inhomogeneity is much greater than the natural width, the form of the observed resonance remained constant, and relative susceptibilities were given by changes in height. Absolute values could not be measured directly, and a normalizing procedure was first carried out by measuring the susceptibility in the gas at 4.2°K where its behavior would be expected to be nearly classical. The result appeared to indicate a 5% degeneracy in the liquid at 1.2°K, but the gas data were not accurate enough to be certain of this. In Fig. 19, it has in fact been assumed that the liquid degeneracy at 1.2°K is zero; i.e., all of the measurements have been normalized to unity at this temperature. This procedure was followed because the molar susceptibility appeared to be constant against change in pressure at this temperature, indicating that there was no degeneracy at 1.2°K within the accuracy of the measurements (about ±3%).

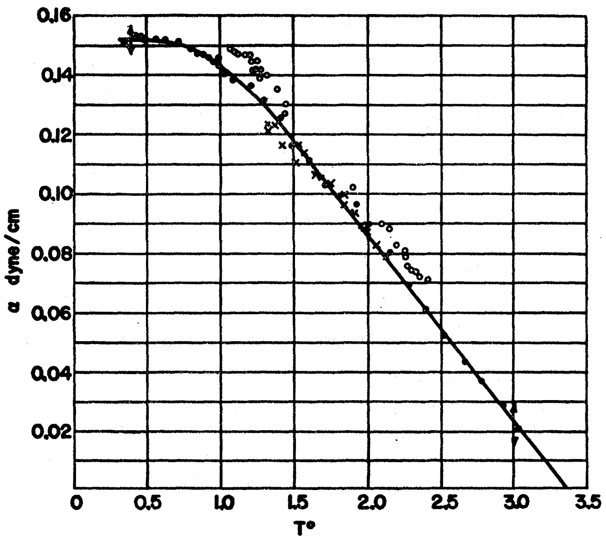

FIG. 18. Surface tension[93–95] of liquid He^3 and He^4.

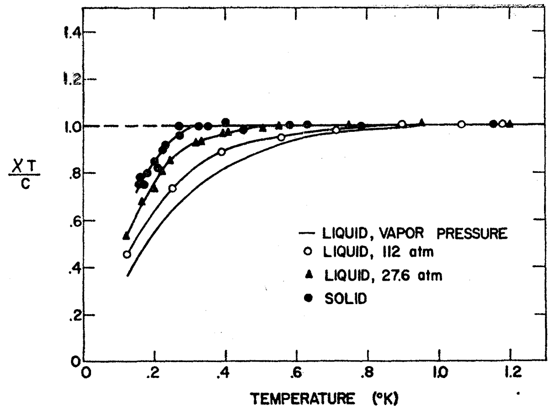

FIG. 19. Nuclear-magnetic susceptibility[97] of liquid He^3 under pressure, normalized at high temperatures (1.2°K).

In Fig. 19, a Curie law (random-spin distribution) is indicated by the horizontal line with $\chi T/C=1$. Within the accuracy of the measurements, the susceptibility at the saturated vapor pressure (lowest curve in the figure) fits that for a perfect Fermi gas with a degeneracy temperature $T=0.45$°K, an order of magnitude lower than that calculated for liquid He^3 as an ideal Fermi gas (5°K), and about four times lower than the degeneracy temperature as calculated from specific-heat data, (Sec. II.2. 3).

The data of Fig. 19 have been extended to lower temperatures,[98–100] as shown in Figs. 20–22. From these figures, one sees that the susceptibility below 0.05°K is practically independent of temperature, and that the *susceptibility per atom* below 0.05°K increases by a factor of two, when the pressure is increased from 0 to 30 atm. To a good approximation,

$$\chi_1(p=0)[1+0.03p],$$

where χ_1 is the susceptibility per atom below 0.05°K, and p is the pressure in atmospheres.

Thomson and Meyer[100] as well as Anderson *et al.*[99] observed that the susceptibility for pressures above 30 atm changes drastically within a very narrow pressure range. Figure 20 shows that the susceptibility below 0.05°K increases by a factor of almost 3 when the pressure is increased from 30.4 to 30.8 atm (curves C and Y). This behavior is similar to the behavior of the sound velocity under pressure as discussed in Sec. III.6. Figure 20 also shows that for pressures above 30.8 atm the susceptibility follows a Curie law down to 0.1°K. (See note added in proof.)

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[97] W. M. Fairband and G. K. Walters, Nuovo cimento, Suppl. 9, 297 (1958).

[98] A. C. Anderson, W. Reese, R. J. Sarwinski, and J. C. Wheatley, Phys. Rev. Letters 7, 220 (1961).

[99] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. Letters 7, 366 (1961).

[100] A. L. Thomson and H. Meyer, Bull. Am. Phys. Soc. 7, 76 (1962) and private communication. However, see note added in proof.

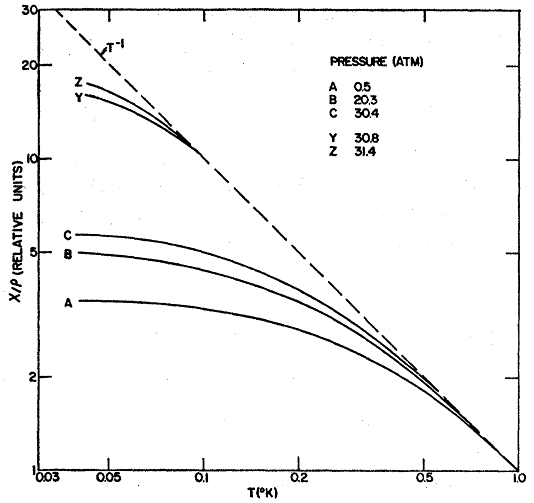

FIG. 20. Nuclear-magnetic susceptibility[100] of liquid Ne³ under pressure, normalized at 1.0°K. (See note added in proof.)

A discussion on other susceptibility data can be found in references 49 and 50.

13. Spin Relaxation

Since nuclear-spin alignment occurs in the liquid at about 0.3°K (see preceding section), there is the possibility of studying spin relaxation in He³ in a range of temperatures from the "classical" high-temperature region down to low temperatures where quantum-statistical effects become important. Experimental results for T_1 from different laboratories have given widely disparate results, but these can be explained by spurious relaxation mechanisms, and, in some cases, can be reanalyzed to give good agreement with the theory for ordinary liquids as proposed by Bloembergen, Purcell, and Pound. The best published values for T_1 seem to be those of Romer,[101] which have been confirmed by Norberg.[101] Values of T_2 do not agree with theory, but can probably be explained by the presence of bulk paramagnetic impurity.

Relaxation mechanisms giving spurious results are: (a) wall relaxation from paramagnetic impurities or adsorbed oxygen; (b) bulk relaxation from, for example, oxygen impurity or charged ions caused by decay of residual tritium in the He³; and (c) relaxation due to atomic exchange at the vapor-liquid interface. Wall relaxation was confirmed in the work of Careri *et al.*,[49] and also was investigated in detail by Walters.[49] It appears that Pyrex glass is a very poor relaxer, whereas metals are almost "black" for spin relaxation. However, even Pyrex containers can give shortened relaxation times, which are presumably due to adsorbed paramagnetic impurity, since careful cleaning of the walls increased T_1. Walters also showed experimentally[49] that the third mechanism above can be important in situations where the ratio of the free liquid surface to its volume is large. Most He³ atoms may then diffuse to the vapor-liquid interface in times comparable with or less than T_1, may become relaxed on any "black" surface in the vapor (for example, a metal), may return to the liquid, and thus may shorten the observed T_1. This mechanism, which is more effective at higher vapor pressures, is thought to account for the peaks observed by Careri *et al.*[49] Evidence for bulk-impurity relaxation is uncertain. It may have been present in the work of Low and Rorschach[49] who found a decrease in T_1 with time during some experiments, due possibly to diffusion of oxygen into the sample chamber. Walters,[49] on the other hand, found no effect even when oxygen is deliberately mixed with the He³ gas before condensing.

14. Self-Diffusion

The coefficient of self-diffusion D of liquid He³ has been measured using the spin-echo technique by Garvin and Reich[102] and by Wheatley and co-workers.[102] Garvin and Reich measured the pressure and temperature dependence in the range 2.4 to 67.0 atm between 0.45° and about 3.7°K. They found that D *increases* with temperature and decreases with pressure, and the authors consider that in this temperature range D can be understood qualitatively in terms of zero-point energy and tunneling of atoms through potential barriers.

Wheatley and co-workers[102] have measured the self-diffusion coefficient at lower temperatures below 0.5°K, and their results join smoothly with those of Garvin and Reich.[102] At lower temperatures, they found that D *decreases* with T. Below 0.04°K, their diffusion coefficients are proportional to T^{-2} in agreement with the Fermi-Dirac-Landau theory.

Thus, viscosity (Sec. 10) is the only transport property of liquid He³ which has not been measured at temperatures low enough to display a behavior characteristic of a Fermi-Dirac system.

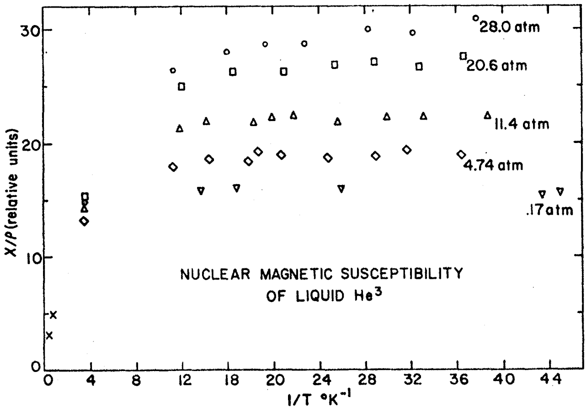

FIG. 21. Nuclear-magnetic susceptibility[98,99] of liquid He³ at very low temperatures for different pressures.

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[101] R. H. Romer, Phys. Rev. **117**, 1183 (1960); R. E. Norberg (private communication).

[102] R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959); A. C. Anderson, W. Reese, R. Sarwinski, and J. C. Wheatley, Phys. Rev. Letters **7**, 220 (1961).

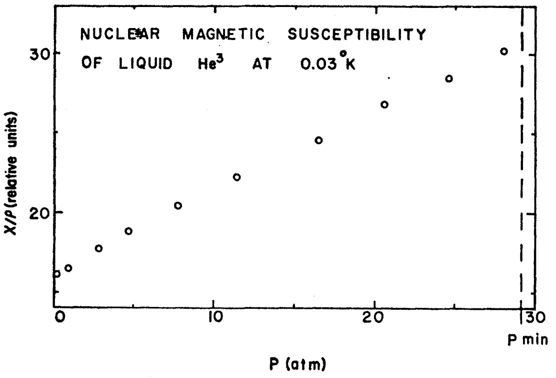

FIG. 22. Pressure dependence of the nuclear-magnetic susceptibility of liquid He^3 at very low temperatures.[98,99]

IV. SOLID PHASE: EXPERIMENTAL DATA

1. General

Little is known from experiments about the properties of solid He^3. X-ray analysis[42,43] shows that it has three different crystallographic phases (Sec. II.5).

Its cohesive energy should be about 0.5°K/atom as estimated in Sec. II.5. The density of the solid at 30 atm is known with good accuracy from the experiments of Mills and Grilly,[46a,69] which give a molar volume of 24.7 cm^3/mole. The compressibility has not been measured directly, except for some measurements of the velocity of sound v_s at some unspecified low pressure.[72] From $v_s=475$ m/sec,[72] we can infer that the compressibility $K=1/\rho v_s^2$ is equal to 3.5×10^{-3}/atm.

2. Specific Heat

The entropy of the solid may be separated into a contribution S_p from the lattice phonons and another S_s arising from the nuclear-spin system. This separation is possible since the lattice-vibration spectrum is, for all practical purposes, independent of the magnetization. At high temperatures, the spin entropy can be expanded into a power series in T^{-1},

$$S_s/R=\ln2-\alpha(T_C/T)^2+\cdots,\quad T\gg T_C, \tag{66}$$

where T_C is the exchange energy per atom and α is a numerical constant, which, for a bcc lattice, can be taken[35] equal to 3/32. On the other hand, at low temperatures a spin-wave model gives

$$S_s\cong A(T/T_C)^3,\quad T\ll T_C. \tag{67}$$

The phonon entropy may be written as

$$S_p/R=77(T/\theta)^3,\quad T\ll\theta, \tag{68}$$

where θ is the Debye temperature.

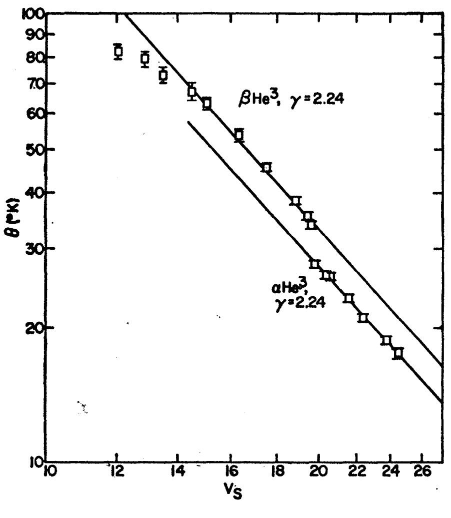

FIG. 23. Debye temperature[103] of α and β solid He^3 as functions of molar volume.

Specific-heat measurements below 0.04°K indicate that Eq. (66) is valid with $T_C\cong0.01$°K.[73]

The specific heat above 0.3°K seems to be due solely to phonons. Heltemes and Swenson[103] have measured the specific heat of both solid He^3 and He^4 for pressures up to 1800 atm. Their results are in agreement with Eq. (68), θ being a function of volume as shown in Fig. 23.[103] The values of θ and of the Grueneisen constant $\gamma=-d\ln\theta/d\ln V$ are in essential agreement with the calculations by Bernardes.[46] The experimental results may be expressed by

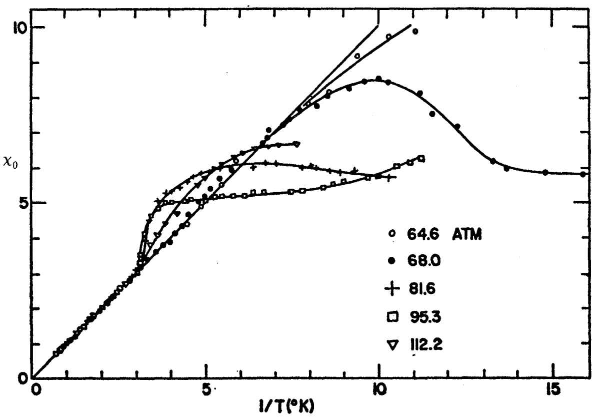

FIG. 24. Nuclear-magnetic susceptibility of solid He^3 for pressures above 60 atm.[104]

$$\theta_\alpha(°\text{K})=27(20/V)^{\gamma_\alpha},\quad V>18.6\ \text{cm}^3/\text{mole}, \tag{69}$$

$$\theta_\beta(°\text{K})=33(20/V)^{\gamma_\beta},\quad V<18.6\ \text{cm}^3/\text{mole}, \tag{70}$$

and

$$\gamma_\alpha=\gamma_\beta=2.24, \tag{71}$$

where V is the molar volume expressed in cm^3/mole.

Heltemes and Swenson[103] observed an anomaly in the low-pressure (bcc, α phase) specific heat, which can be empirically described by an Einstein specific-heat function.[103] The origin of this anomaly is not known, but it must be connected with the strong anharmonicity of the

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

lattice. In fact, if the static potential energy $U(r)$ between nearest neighbors is expanded into a power series

$$U(r)=a+br^2+cr^4, \tag{72}$$

in the deviation r from the equilibrium distance, one finds that $b<0$, $c>0$. Therefore, we may expect abnormal thermal properties for such a lattice, except at very low temperatures. The experiments of Heltemes and Swenson,[103] as well as those of Dugdale and Simon[39] for solid He^4, do indicate, however, that despite the large anharmonicity the specific heat at very low temperatures is proportional to T^3.

According to the experiments of Heltemes and Swenson, the low-pressure Debye temperatures θ_α and θ_β of the (α) bcc phase and (β) hcp phase differ by about 6°K; i.e.,

$$\theta_\beta-\theta_\alpha=6°\text{K}. \tag{73}$$

The significance of this result is discussed in Sec. IV.4.

We may conclude that the phonon entropy at 0.5°K is only about 7×10^{-4} cal/mole °K. On the other hand, at $T\cong3T_C$ the spin entropy is less than $R\ln2$ by about 10^{-2} cal/mole °K. Since T_C of Eq. (66) seems to be much smaller than 0.1°K, the total entropy of the solid between 0.1° and 0.5°K may be taken equal to $R\ln2$, within 1%.

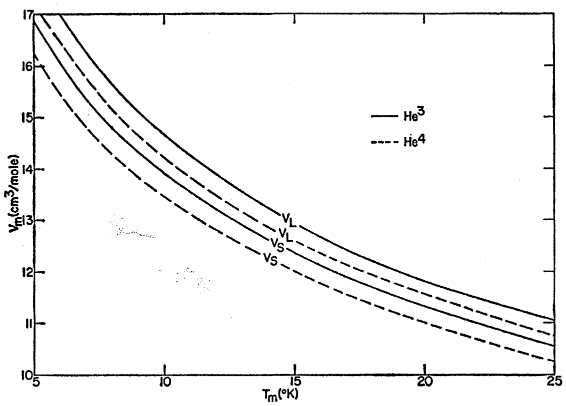

FIG. 25. Melting curve of He^3 and He^4 at high pressures.

3. Nuclear-Magnetic Susceptibility

The nuclear-magnetic susceptibility of the solid was first measured by Fairbank and Walters[97] who found large deviations from the Curie law at temperatures below 0.2°K. These experiments indicated a large value (0.1°K/atm) for the exchange energy of the order of those calculated by Bernardes and Primakoff. However, these results do not agree in detail with more-recent measurements[104] which show that, for pressures less than 60 atm the Curie law is obeyed down to 0.1°K. The susceptibility above 60 atm (Fig. 24) is quite complex. For instance, for $T\cong0.3$°K, the relative susceptibility is larger than the value given by the Curie law; this would indicate a tendency towards ferromagnetism. The reasons for this complex behavior are not understood.

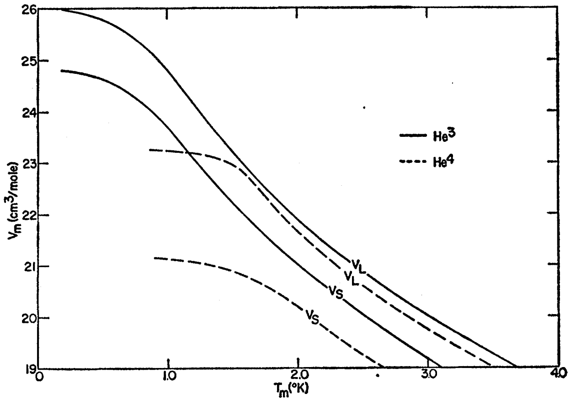

FIG. 26. Melting curve of He^3 and He^4 at low pressures.

Other spin-resonance experiments in the solid include those of Goodkind and Fairbank[105] on the relaxation times, and those of Reich[106] on the relaxation times and self-diffusion.[49,50]

4. Melting Curve

The temperature dependence of the melting pressure has been determined by several authors using the traditional blocked-capillary method[33] and, more recently, other methods.[107–110]

Even though the early measurements of Abraham, Osborne, and Weinstock[33] extended down to 0.16°K, they did not reveal the presence of the minimum in the melting curve, due to the fact that they used a blocked-capillary method. More recent experiments by Baum

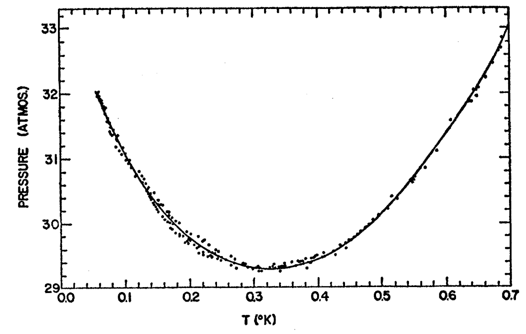

FIG. 27. Minimum in the melting curve[107] of He^3.

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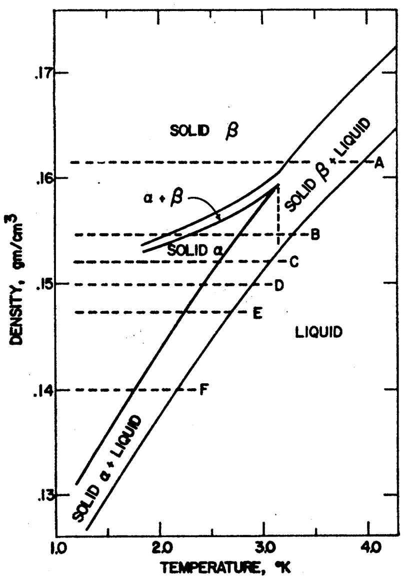

FIG. 28. Densities for thermal-conductivity data[110] (see Figs. 29 and 30).

et al.,[49,107] by Lee, Fairbank, and Walker,[108] and by Grilly, Sydoriak, and Mills[109] revealed the minimum at 0.32–0.33°K and 29.1–29.3 atm.

Mills and Grilly[46a] measured the melting pressure P_m as a function of T from 1.3°K (50 atm) to 30°K (3500 atm). They also determined the volume of the freezing liquid V_l, the volume change $\Delta V_m = V_l - V_s$, and hence, from Clapeyron's equation,

$$\frac{dP_m}{dT} = \frac{\Delta S_m}{\Delta V_m} \equiv \frac{S_l - S_s}{V_l - V_s}, \tag{74}$$

the entropy difference, $\Delta S_m = S_l - S_s$, is between liquid and solid. Their results are shown in Figs. 25 and 26, together with data at lower temperatures of Grilly, Sydoriak, and Mills.[109]

The ΔV_m measurements of Mills and Grilly[46a] revealed the existence of a phase transition near 3.1°K and 140 atm, which are discussed in the next section.

The minimum in the melting curve was detected by Baum *et al.*,[107] by Lee, Fairbank, and Walker,[108] and by Grilly, Sydoriak, and Mills.[109] The results of all these groups can be represented, within 2%, by the equation[49]

$$P_m = (29.1 \pm 0.2) + 32.2(T - 0.33)^2 \text{ atm}, \tag{75}$$

which is valid between 0.1° and 0.5°K. The results of Baum *et al.* are shown in Fig. 27.

A detailed comparison of Eq. (75) with theory is difficult. However, since the entropy of the melting solid between 0.1° and 0.5°K can be taken equal to $R \ln 2$, we may conclude that the entropy of the freezing liquid at 0.33°K is also equal to $R \ln 2$. On the other hand, the extrapolated values of S_l of Brewer and Daunt[65] give $S_l(p \cong 30 \text{ atm}) = R \ln 2$ for $T = 0.37$°K; or, in other words, the liquid entropy values of Brewer and Daunt seem to be too small by about 10%. Since their entropies at higher pressures contain the entropy at saturated vapor pressures as an additive term, one may expect this difference to arise from an invalid extrapolation to 0°K of C_V data ($m^*/m = 2$) above 0.1°K. More recent C_V data below 0.1°K give a substantially larger value for m^*/m, and hence for the liquid entropy which now seems to be $R \ln 2$ at the minimum of the melting curve (see Sec. III.8).

As discussed in Sec. II.6, the entropy of the solid at very low temperatures (below 0.1°K) should again be less than that of the liquid, and, hence, the melting curve should have a maximum below 0.1°K. The calculations of Bernardes and Primakoff[35] give 0.08°K for this temperature. But, due to the uncertainty in their exchange integral, this temperature may be as low as 0.01°K (Sec. II.6).

5. The α-β Phase Transition

The melting-curve measurements by Grilly and Mills[46a] revealed a phase transition at 3.15°K and 140 atm on the melting curve. They were able to determine the transition pressure P_t as a function of T down to 1.8°K ($P_t \cong 110$ atm), the volume change ΔV_t, and hence, from Clapeyron's equation, the entropy change ΔS_t.

Later, x-ray analysis by Schuch *et al.*[42] revealed that the low-pressure α phase has a bcc structure, whereas the high-pressure β phase has a hcp structure. An extrapolation of the experimental data to low temperatures[46a] indicates that the α-β phase transition may occur at 0°K for a pressure of the order of 100 atm.

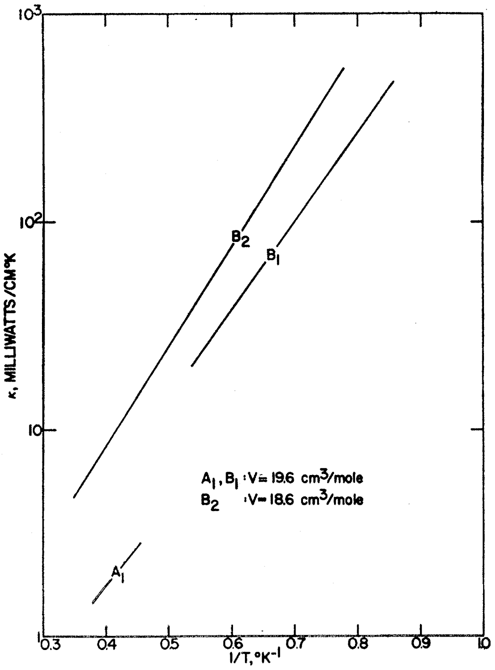

FIG. 29. Thermal conductivity[110] of α and β solid He³ for $p > 130$ atm.

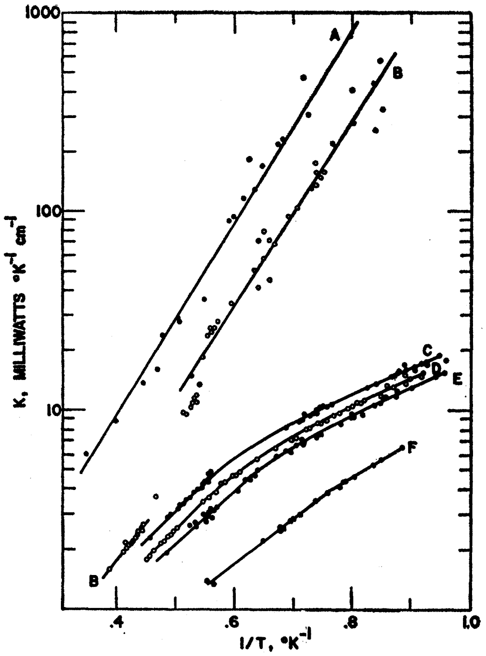

FIG. 30. Thermal conductivity[110] of α and β solid He^3. The curves are labeled according to Fig. 28.

The α-β phase transition was also observed by Fairbank and Walker[110] on the thermal conductivity of the solid under pressure, and by Heltemes and Swenson[103] on the specific heat (Sec. IV.2).

The results of Fairbank and Walker[110] for the thermal conductivity for molar volumes (Fig. 28) of 18.6 and 19.6 cm^3/mole are shown in Fig. 29. Their results for lower pressures (Figs. 28 and 30) are complex, and difficult to interpret. The results of Fig. 29 can be expressed, in mw/cm °K, by the equations,[111]

$$\kappa_\beta = 0.1\ \exp(11/T),\quad V = 18.6\ \text{cm}^3/\text{mole},\quad 1.2°\text{K} < T < 2.5°\text{K}, \tag{76}$$

$$\kappa_\beta = 0.1\ \exp(10/T),\quad V = 19.5\ \text{cm}^3/\text{mole},\quad 1.2°\text{K} < T < 2.1°\text{K}, \tag{77}$$

and

$$\kappa_\alpha = 0.05\ \exp(8.8/T),\quad V = 19.6\ \text{cm}^3/\text{mole},\quad 2.2°\text{K} < T < 2.5°\text{K}, \tag{78}$$

which are typical of insulators in a temperature range where the scattering is predominantly by umklapp.

The theory of thermal conductivity for a temperature region where umklapp processes dominate gives

$$\kappa = A\ \exp(\theta/bT), \tag{79}$$

where θ is the Debye temperature and b is a constant of the order of two.

If we assume[111] that θ in Eq. (79) is the same as given by C_V data, we may infer from the Heltemes and Swenson[103] data ($\theta_\alpha = 28°\text{K}$, $\theta_\beta = 34°\text{K}$), and from Eqs. (77) and (78) that

$$b_\alpha = 3.2, \tag{80}$$

and

$$b_\beta = 3.4, \tag{81}$$

which is reasonable. On the other hand, Eqs. (76) and (77) allow us to calculate the Grueneisen constant γ_β for the β phase,

$$\frac{11}{10} = \frac{\theta_\beta(18.6\ \text{cm}^3/\text{mole})}{\theta_\alpha(19.5\ \text{cm}^3/\text{mole})} \cong \left(\frac{19.5}{18.6}\right)^{\gamma_\beta}, \tag{82}$$

and, hence,

$$\gamma_\beta \cong 2.0, \tag{83}$$

which is in good agreement with the value obtained from C_V data,[103] Eq. (73).

An important result emerges from a comparison[111] of C_V data[103] with ΔS_t. In fact, the entropy differences[46a] ΔS_t can be represented by

$$\Delta S_t/R = (1.6 \pm 10\%) \times 10^{-3} T^3. \tag{84}$$

On the other hand, C_V data[103] show that the entropy of the solid can be described by a Debye model, for which

$$S_{\alpha,\beta}/R = 77(T/\theta_{\alpha,\beta})^3. \tag{85}$$

Hence, from C_V data, we expect

$$\Delta S_t/R = 232(\Delta\theta/\theta^4)T^3. \tag{86}$$

Since[103] $\theta_\alpha = 28°\text{K}$, $\theta_\beta = 34°\text{K}$ ($\theta = 31°\text{K}$, and $\Delta\theta = 6°\text{K}$), we may expect from C_V data alone that

$$\Delta S_t/R = 1.5 \times 10^{-3} T^3, \tag{87}$$

which is in good agreement with Eq. (84) obtained from the slope of the phase-separation line.[46a] Notice that the early ΔS_t results of Grilly and Mills,[112] which were found to be incorrect,[46a] would not give rise to such an agreement.

The analysis in the foregoing shows that the change in phonon entropy accounts for the total entropy change. Hence, it is unlikely that the crystallographic α-β transition is accompanied by a magnetic transition.[35]

We can see[111] from the following that a theoretical analysis of the relative stability of the α and β phases is very difficult. The static energies of a bcc and hcp of He^3 atoms, for volumes as large as 18 cm^3/mole, are practically the same. Hence, the energy difference at 0°K should be due to different zero-point energies E_{zp} of the two lattices. However, this zero-point energy difference ΔE_{zp} cannot be simply proportional to the difference in Debye temperatures $\Delta\theta$. In fact, from experiment,[46a] $\Delta U(0°\text{K}) \cong \Delta E_{\text{zp}} \cong 100\ \text{atm} \times 0.1\ \text{cm}^3/\text{mole} \cong 0.1°\text{K/atom}$, while $\Delta\theta = 6°\text{K}$.[103] Thus, we may conclude that, if

$$E_{\text{zp}}(\alpha) = a_\alpha \theta_\alpha$$

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[110] E. J. Walker and H. A. Fairbank, Phys. Rev. Letters **5**, 139 (1960).

[111] N. Bernardes, Phys. Rev. Letters **8**, 164 (1962).

[112] E. R. Grilly and R. L. Mills, reference 46a, p. 100.

and

$$E_{\mathrm{zp}}(\beta)=a_\beta\theta_\beta,$$

then

$$\Delta E_{\mathrm{zp}}\cong a_\alpha\theta_\alpha-\alpha_\beta\theta_\beta\cong 0.$$

Hence, $\Delta a/a\cong-\Delta\theta/\theta$. Since $a_\alpha\cong a_\beta\cong 1$ and $\Delta\theta/\theta=6/30$, we may write

$$E_{\mathrm{zp}}(\alpha)\cong 1.1\theta_\alpha, \tag{88}$$

and

$$E_{\mathrm{zp}}(\beta)\cong 0.9\theta_\beta. \tag{89}$$

This difference ($\Delta a/a\cong 20\%$) is much larger than what one expects from usual theories of lattice dynamics.[113]

Only very accurate ($\Delta E/\theta\cong 0.1/30\approx 0.3\%$) calculations will give a meaningful answer to the question of the relative stability of the α and β phases.

Above 18°K and 1800 atm ($V\cong 12$ cm^3/mole), the hcp lattice becomes unstable with respect to a fcc lattice, and a new phase transition occurs.[46] The theory of this phase transition also would be very difficult. Nevertheless, solid He^4 undergoes a similar phase transition at the same molar volume,[39] which shows[45] that this high-pressure phase transition is primarily a classical volume effect.

V. SUMMARY

We may summarize the present status of the investigations on the properties of liquid and solid He^3 by saying that the general features of liquid between 0.02° and 0.1°K are known and understood. However, the properties of the liquid below 0.3°K and above 30 atm are not too well known and should be the subject for further experiments. Also, the propagation of zero sound as well as an eventual superfluid transition in the liquid have not been detected, and experiments below 0.01°K are desirable.

On the other hand, experimental as well as theoretical results for the solid phase are meager, and much effort is still required. For instance, further magnetic-susceptibility measurements and melting-curve determinations below 0.1°K would clarify the quantum behavior of the nuclear-spin system.

Note added in proof. At the end of Sec. III.6, we mentioned the possibility that the peculiar results for the specific heat,[80] magnetic susceptibility,[100] and sound velocity[72] of the liquid above 30 atm and below 0.1 °K, as shown in Figs. 14 and 20, might not be real, and due only to experimental difficulties in cooling the compressed liquid. Recently H. A. Fairbank [Phys. Rev. Letters **8**, 49 (1962)] analyzed the pertinent data numerically, and came to the conclusion that all these peculiar results can be explained by the hypothesis that, instead of a pure liquid, one had a liquid-solid mixture. In view of this one should disregard curves Y and Z of Fig. 20, and the parts of the curves in Fig. 14 lying near and to the right of their maxima. The unpublished data of Fig. 20 was kindly provided to us by Dr. H. Meyer, who is preparing a full account of his experiments for publication.

Recent work on the properties of the liquid phase can be found in Bull. Am. Phys. Soc. **7**, 76 (1962).

ACKNOWLEDGMENT

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