

## Paramagnetism of Liquid Helium Three

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The object of the present paper is the elaboration of a theoretical model describing the paramagnetic properties of liquid  $\text{He}^3$  throughout the region of existence of this phase. The model is based on a molecular field theoretical type of approach. The ratios of the actual paramagnetic susceptibility of liquid  $\text{He}^3$  to the one it would have if it were an ideal paramagnet are predicted to be representable through a unique function depending on the reduced temperature variable. The latter contains the characteristic temperature of the nuclear spin system, which, at the present time, is only available empirically through the susceptibility ratio data. In the susceptibility ratio-reduced temperature representation all susceptibility ratios of liquid  $\text{He}^3$  fall on a single curve. This theoretical ratio curve describes very closely the experimental ratios, available through the work of the Duke University investigators, up to values of the reduced temperature of 0.90–1.0. Beyond this range the experimental susceptibility ratios become systematically larger than the calculated ratios, the differences between them being small. Quantitative arguments will be advanced which appear to explain satisfactorily these discrepancies and to indicate that the theory should be valid throughout the whole range of the natural reduced temperature variable. The spin entropy-spin susceptibility relation, established and used previously, yields, with the theoretical paramagnetism model, rigorous lower limits of the entropy, heat capacity and expansion coefficient of the liquid throughout the region of existence of this phase. With the recent extension of the melting pressure data to quite low temperatures by the University of Illinois investigators, the rigorous spin entropy of the liquid along the melting line allows one to estimate the entropy of the solid along the melting line and at low temperatures. Here the solid entropy turns out to be less than  $R \ln 2$ , per mole, yielding the temperature of its heat capacity anomaly to be below one hundredth of a degree Kelvin. The discussion of the liquid  $\text{He}^3$ -solid  $\text{He}^3$  equilibrium, on the basis of the above results, seems to render questionable any analysis of the thermal properties of the solid which ignores the existence of its nuclear spin system even at medium temperatures. Finally, a semiquantitative description of the entropy-pressure diagram of  $\text{He}^3$  discloses various singular characteristics of the liquid entropy along the melting line in its pressure dependence, as well as the peculiar features of the solid entropy at and around the melting pressure anomaly.

### 1. INTRODUCTION

IN previous work<sup>1</sup> on the properties of liquid  $\text{He}^3$  we have attempted to develop a statistical thermodynamic formalism of its nuclear spin system based on the spin entropy-spin susceptibility theorem established for a class of paramagnetics. In the various characterizations of these paramagnetics we have emphasized<sup>1,2</sup> that the particular model-like description of these systems was strictly auxiliary for the proof of the theorem. This, of course, is as it should be to insure the statistical thermodynamic nature of the spin entropy-spin-susceptibility relation in the specified systems at hand. Stated more precisely, the spin entropy-susceptibility relation being of sufficient generality, the formalism of the susceptibility law could be dispensed with essentially, as long as it was possible to verify that the conditions of validity of the above relation were safely satisfied.

Recent extensive and systematic experimental investigations<sup>3,4</sup> of the nuclear paramagnetic susceptibility of liquid  $\text{He}^3$  over wide temperature and pressure ranges opened up new ways of gaining a deeper insight into the underlying formalism of the nuclear spin

system within the limitations of a phenomenological approach. The close approximation provided by the antisymmetric ideal fluid susceptibility formula, with an empirical parameter, to the description of the observed saturated liquid  $\text{He}^3$  susceptibility law,<sup>5</sup> as well as the fair approximation with which the theoretical formula, always with an empirical parameter, appeared to represent the first compressed liquid  $\text{He}^3$  susceptibility data,<sup>6</sup> seemed to justify the use of the antisymmetric fluid formalism with the empirical parameter as an analytical tool. The strictly approximate and indirect character of the above formalism has been always emphasized<sup>1,2</sup> and the empirical parameter  $T_0(p)$ , the characteristic temperature of the nuclear spin system,<sup>7</sup> offered alone a challenging problem through its numerical values as well as through its remarkable behavior as a function of the macroscopic coordinates such as the pressure  $p$  or volume  $V$ . The above approximate analytical formalism led first to recognize the large numerical value of the partial volume expansion coefficient arising with the spin system of saturated liquid  $\text{He}^3$ , as well as to a semiquantitative description of the partial thermal excitations and volume anomaly

<sup>1</sup> L. Goldstein, Phys. Rev. **96**, 1455 (1954); Ann. Phys. (N. Y.) **15**, 141 (1961).

<sup>2</sup> L. Goldstein, Ann. Phys. (N. Y.) **8**, 390 (1959).

<sup>3</sup> A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **127**, 671 (1962).

<sup>4</sup> A. L. Thomson, H. Meyer, and E. D. Adams, Phys. Rev. **128**, 509 (1962).

<sup>5</sup> W. M. Fairbank, W. B. Ard, and G. K. Walters, Phys. Rev. **95**, 566 (1954).

<sup>6</sup> W. M. Fairbank and G. K. Walters, in *Proceedings of the Symposium on Liquid and Solid  $\text{He}^3$*  (Ohio State University Press, Columbus, Ohio, 1958), p. 1 of the Supplement.

<sup>7</sup> L. Goldstein and M. Goldstein, J. Chem. Phys. **18**, 538 (1950).

of the liquid over essentially the whole region of existence of this phase.<sup>8</sup>

In the present paper we will derive a phenomenological model for the observed susceptibility law of liquid He<sup>3</sup> valid throughout the extension of its phase diagram, the phase transformation lines included. The model thus predicts the universal character of the susceptibility ratio formula according to which the latter depends uniquely on the reduced temperature  $\tau(p)$  or  $[T/T_0(p)]$ ,  $T_0(p)$  being the empirically determined parameter of the theory. The susceptibility ratio  $[\chi(T,p)/\chi_0(T,p)]$ , at temperature  $T$  and pressure  $p$ , with  $\chi$  the actual susceptibility and  $\chi_0$  the asymptotic ideal susceptibility which the system would have if it were a Curie-Langevin paramagnet, being a unique function of  $\tau(p)$ , all susceptibility ratio values of liquid He<sup>3</sup> over the whole region of existence of its phase diagram must fall on a single curve in the  $[\chi/\chi_0, \tau(p)]$  representative plane.

Within the limitations of the phenomenological susceptibility-ratio law, the spin entropy-spin susceptibility relation defines rigorously all the partial thermal properties of the liquid arising with its nuclear spin system. The formalism is then applied to a new evaluation of the partial spin isobaric volume expansion coefficients of the liquid, which should approximate closely the total volume expansion coefficients at very low temperatures and at high pressures, the melting pressure included. There appears to be fair agreement between the theoretical and the recent indirect experimental determinations of the isobaric expansion coefficient of the liquid<sup>9</sup> at very low temperatures and high pressures.

To within the limitations of the above formalism, and the approximations of the empirical  $T_0(p)$  function<sup>4</sup> and of the melting pressure line  $p_M(T)$  extended<sup>9</sup> down to about 0.03°K, the analysis of the liquid-solid transformation yields indications on a substantial deficit of the entropy of the solid along the phase transition line and at  $T \lesssim 0.05^\circ\text{K}$  from its maximum value of  $R \ln 2$ , per mole. This suggests that the spectacular heat capacity anomalies of solid He<sup>3</sup> might appear at temperatures  $T \sim 0.010\text{--}0.005^\circ\text{K}$ , a region which remained inaccessible to experimentation so far.

With the calculated liquid and solid lower limit entropies, we also discuss various aspects of the problem of the equilibrium between the thermally anomalous liquid He<sup>3</sup> and solid He<sup>3</sup>.

The paper ends with a semiquantitative discussion of the entropy-pressure diagram of the dense phases of He<sup>3</sup>. The singular character of the two phases along the phase separation line emerges here again, with addi-

tional aspects of the thermal behavior of the solid at low temperatures.

## 2. THEORY OF THE NUCLEAR PARAMAGNETIC SUSCEPTIBILITY OF LIQUID He<sup>3</sup>

The nuclear paramagnetism of liquid He<sup>3</sup> throughout the whole range of the variables of state of this phase renders this liquid similar to a Weiss type of paramagnetic system.<sup>10</sup> The latter is a nonideal paramagnet as a consequence of the interactions between the carriers of the elementary magnetic dipoles. Consider the magnetic equation of state in the form

$$M = f(H/T, V), \quad (1)$$

giving the ensemble average of the magnetic moment  $M$ , of the system of ideal elementary magnets occupying volume  $V$ , induced by the application of a uniform constant magnetic field of strength  $H$ , at the temperature  $T$ . The latter two variables of state appear necessarily through the ratio  $(H/T)$  as imposed by the second law of thermodynamics as first shown by Langevin.<sup>11</sup> The generalization of the magnetic equation of state (1) to nonideal paramagnetic systems postulated by Weiss<sup>10</sup> consists in conserving the formal structure of the function  $f[(H/T), V]$  and replacing the applied external field  $H$  by an effective field acting within the system,

$$H_{\text{eff}} = H - h_m, \quad (2)$$

where  $h_m$ , the so-called molecular field, is a measure of the opposition developed within the system to the ordering effect of the applied external field. The molecular field  $h_m$  is assumed to arise with the interactions within the system. For magnetic dipoles of strength  $\mu$ , the classical magnetic equation of state with  $H_{\text{eff}}$  replacing  $H$  on the right-hand side of (1), there being  $N$  dipoles in volume  $V$ , is

$$M/M_0 = \coth(\mu H_{\text{eff}}/kT) - (kT/\mu H_{\text{eff}}), \quad (3)$$

$$M_0 = N\mu,$$

or the Langevin function,<sup>11</sup>  $M_0$  being the saturation moment and  $k$  Boltzmann's constant. On assuming<sup>10</sup> that the molecular field  $h_m$  is of the form

$$\begin{aligned} h_m &= nI \\ &= nM/V, \end{aligned} \quad (4)$$

where  $n$  is an empirical constant and  $I$  the magnetization, or the magnetic moment per unit volume produced by the applied uniform field of strength  $H$ , the effective field expression (2) with (4) and the equation of state (3) yield two equations for the two unknowns,  $H_{\text{eff}}$  and  $M$ . In the limit of  $\mu H_{\text{eff}} \ll kT$ , one obtains at once the susceptibility law

$$\begin{aligned} M/HV &= \chi(T, V) \\ &= \frac{1}{3}(N\mu^2/Vk)(T + \frac{1}{3}nN\mu^2/Vk)^{-1} \\ &= C/(T + \Theta), \end{aligned} \quad (5)$$

<sup>8</sup> L. Goldstein, Phys. Rev. **102**, 1205 (1956); **112**, 1465 and 1483 (1958); **117**, 375 (1960); Ann. Phys. (N. Y.) **14**, 77 (1961).

<sup>9</sup> A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **130**, 495, 1644 (1963). I wish to thank the members of this University of Illinois group for advance communication of their recent experimental data included in two preprints.

<sup>10</sup> P. Weiss, J. Phys. Radium, **6**, 661 (1907).

<sup>11</sup> P. Langevin, Ann. Chim. Phys. **5**, 70 (1905).

with the Curie constant

$$C = \frac{1}{3} N \mu^2 / V k, \quad (6)$$

and where

$$\Theta = nC,$$

is a characteristic temperature of the system arising with the interactions in the nonideal paramagnet at hand. The main feature of the preceding modification of the ideal paramagnetic equation of state consists in the formal preservation of the latter equation of state in spite of the introduction of an additional term in the response of the nonideal system to the magnetization process. This additional term arises with the nonideal character of the paramagnetic system; that is, with interactions within the system.

For an ideal collection of particles of angular momentum  $s\hbar$ , of gyromagnetic ratio  $g$ , with the natural unit  $\mu_0$  of the magnetic dipole strength, the magnetic equation of state becomes, instead of (3),

$$M/M_0 = (2s+1/2s) \coth[(2s+1/2s)(g\mu_0 H/kT)] \\ - (1/2s) \coth[(1/2s)(g\mu_0 H/kT)], \quad (7)$$

$$M_0 = N g s \mu_0,$$

as first shown by Brillouin.<sup>12</sup> The latter can be again modified to represent a nonideal paramagnet within the limitations of the molecular field hypothesis.<sup>10</sup> In the limit of low fields,

$$\mu_0 H \ll kT,$$

Eq. (7) yields the quantum-mechanical susceptibility formula,

$$\lim_{\mu H \ll kT} \chi(T, V) = N (g\mu_0)^2 (s(s+1)/3V kT) \\ = N \mu_{\text{eff}}^2 / 3V kT, \quad (8) \\ \mu_{\text{eff}}^2 = (g\mu_0)^2 s(s+1).$$

While for a Weiss paramagnet, and in the limit of validity of (5), one again recovers the latter, with the Curie constant

$$C_s = N \mu_{\text{eff}}^2 / 3V k, \quad (9)$$

and

$$\Theta_s = nC_s.$$

The molecular field approach manifests itself indirectly on the quantum-mechanical treatment of the paramagnetism of a collection of bound, and hence interacting, particles, within the approximations of the Heitler-London description of such a system. The latter corresponds to the Heisenberg model of the system.<sup>13,1</sup> At low fields and at sufficiently high temperatures the Weiss law (5) is obtained, provided that the characteristic temperature  $\Theta$  arising with the

mutual interparticle couplings is defined by

$$\Theta = E_x / 2k, \quad (10)$$

where  $E_x$  is the total exchange energy of one of the atoms with all the other atoms of the system. With the finite range of the exchange energy of pairs of atoms,  $(E_{x,i})$ , the total exchange energy  $(\sum_i E_{x,i})$  or  $E_x$  refers to the sum of pair exchange energies of neighbors. Provided that  $E_x$  be positive, paramagnetic behavior will be assured, since the energy spectrum of the above model contains a term

$$E(s) = s^2 E_x / N, \quad (11)$$

$N$  being the total number of atoms of the system, and  $s$  the total spin quantum number of the states in question; that is, the number of those spins of the system which are available for magnetization upon application of an external homogeneous magnetic field. Stated in other terms, the contribution to the magnetic moment induced by application of an external field in the above states will be proportional to  $s$ . In the ground state, then,  $s \rightarrow 0$ ; there is no spin angular momentum, nor a permanent magnetic moment. Formally, the energy term (11) resembles the molecular field energy of the Weiss model, where the field  $h_m$ , defined by (4), leads to an energy proportional to  $(I^2)$ , the square of the magnetization.

It should be noted that the quantum-mechanical approximation formalism,<sup>13,1</sup> while yielding the low field susceptibility formula (5) with  $C_s$  and  $\Theta_s$  defined by (9), has to be qualified concerning its validity at  $T < \Theta$ . However, in both the classical and quantum-mechanical approaches toward the theory of nonideal paramagnetic systems, the formal structure of the theory of ideal paramagnetics is preserved. The parameter  $\Theta$ , a characteristic temperature of the nonideal system, is some kind of a measure of the lack of ideality as manifested through the magnetic behavior of the paramagnetic system at hand.

The preceding discussion suggests that a formalism preserving approach in the theory of the magnetic properties of liquid He<sup>3</sup>, a system of bound atoms of nuclear spin angular momentum  $\hbar/2$ , might be useful for a description of the nuclear paramagnetism of this liquid. Here, the starting formalism is that of the limiting asymptotic ideal antisymmetric fluid of atoms of spin  $\frac{1}{2}$  and elementary dipole moment  $\mu$ . In presence of a constant and uniform magnetic field of strength  $H$ , the ideal system breaks up into two subsystems with the individual energies

$$\epsilon_i^\mp = \epsilon_i \mp \mu H, \quad (12)$$

the  $\epsilon_i$ 's being the individual energies in absence of the field. Their distribution functions are, respectively,  $g_i$  being the density of the levels  $\epsilon_i$ ,

$$n_i^\mp = g_i \{ \exp[\alpha + (\epsilon_i^\mp / kT)] + 1 \}^{-1}. \quad (13)$$

<sup>12</sup> L. Brillouin, *J. Phys. Radium* **8**, 74 (1927).

<sup>13</sup> W. Heisenberg, *Z. Physik*, **49**, 619 (1928). W. Pauli, in *Le Magnetisme, Proceedings of the Sixth Solvay Congress on Physics, Bruxelles, 1930* (Gauthiers-Villars, Paris, 1932), pp. 175-238.

If  $M(T, V, H)$  is the magnetic moment induced in this system, its magnetic energy is

$$-MH = \sum_i [(-\mu H)n_i^- + \mu H n_i^+], \quad (14)$$

or,

$$M = \mu \sum_i (n_i^- - n_i^+). \quad (15)$$

The parameter  $\alpha(T, V)$  or  $\alpha(T, \rho)$  or the negative Gibbs free energy per particle in units of  $kT$ , is defined through the total number of atoms of the system, that is

$$N = \sum_i (n_i^- + n_i^+). \quad (16)$$

With  $\epsilon_i$  being the free particle kinetic energies, expressed in terms of the linear momenta  $\mathbf{p}$  and mass  $m$ , the differential distribution functions, in volume  $V$ , become

$$\begin{aligned} dn^\mp(\mathbf{p}, T) &= dg(\mathbf{p}) \{ \dots \}_\mp^{-1} \\ &= 4\pi (V/h^3) \mathbf{p}^2 d\mathbf{p} \{ \dots \}_\mp^{-1}, \end{aligned} \quad (17)$$

where the curly brackets are the same as in (13) with  $\epsilon_i$  replaced by  $\mathbf{p}^2/2m$ . Finally, replacing the summations by integrations over  $\mathbf{p}$ , one has, with (14),

$$\begin{aligned} M(T, V, H) &= (V/h^3) (2\pi m k T)^{3/2} \mu \\ &\quad \times [F(\alpha - (\mu H/kT)) - F(\alpha + (\mu H/kT))] \end{aligned} \quad (18)$$

$$F(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{e^{z+x} + 1}.$$

Also, with (17) and (15), one has

$$N = (V/h^3) (2\pi m k T)^{3/2} \times [F(\alpha - (\mu H/kT)) + F(\alpha + (\mu H/kT))], \quad (19)$$

and, finally,

$$\frac{M(T, V, H)}{N\mu} = \frac{F(\alpha - (\mu H/kT)) - F(\alpha + (\mu H/kT))}{F(\alpha - (\mu H/kT)) + F(\alpha + (\mu H/kT))}, \quad (20)$$

a formula first derived by Stoner,<sup>14</sup> using a somewhat different approach.

With the well-known behavior of the  $F$  function, (20) is easily seen to reduce to the Brillouin function for spin  $\frac{1}{2}$  particles at high temperatures. In the limit of low fields,  $\mu H/kT \ll 1$ , one recovers the moment equation

$$\begin{aligned} \lim_{\mu H \ll kT} \frac{M(T, V, H)}{N\mu} &= (\mu H/kT) [-F'(\alpha)/F(\alpha)], \quad (21) \\ F'(\alpha) &= dF/d\alpha. \end{aligned}$$

Our main object now is the study of the modifications of the exact moment equation of an ideal antisymmetric collection of particles of spin  $\frac{1}{2}$  and actual magnetic moment  $\mu$ . It is instructive to consider first the paramagnetism of nonideal antisymmetric systems, where

the nonideality is expressed through the Weiss relations, Eqs. (2) and (4). The molecular field approximation is equivalent to the replacing of  $H$  in (20) by  $H_{\text{eff}}$  or  $(H - h_m)$ , by Eq. (2). In the limit of  $\mu H_{\text{eff}} \ll kT$ , one obtains

$$\begin{aligned} \lim_{\mu H_{\text{eff}} \ll kT} (M/N\mu) &= (\mu H_{\text{eff}}/kT) [-F'(\alpha)/F(\alpha)], \\ &= [(\mu H/kT) - \mu n M/VkT] \\ &\quad \times [-F'(\alpha)/F(\alpha)], \end{aligned} \quad (22)$$

or the nonideal paramagnetic susceptibility law

$$\begin{aligned} M/HV &= \chi_{\text{nonid}}(T, V) \\ &= \frac{C_{\frac{1}{2}} [-F'(\alpha)/F(\alpha)]}{T + \Theta_{\frac{1}{2}} [-F'(\alpha)/F(\alpha)]}, \end{aligned} \quad (23)$$

which is the molecular field generalization of the ideal susceptibility formula associated with (21), where by (9),

$$C_{\frac{1}{2}} = N\mu^2/Vk; \quad \Theta_{\frac{1}{2}} = nC_{\frac{1}{2}}. \quad (24)$$

It is of some interest to consider briefly the various limits of (23). Since in the ideal Fermi gas formalism

$$\lim_{T \ll T_0} [-F'(\alpha)/F(\alpha)] \rightarrow \frac{3}{2} T/T_0, \quad (23a)$$

where  $T_0$  is the degeneracy temperature, it is seen that at  $T \ll T_0$ ,

$$\lim_{T \ll T_0} \chi_{\text{nonid}} = (\frac{3}{2} C_{\frac{1}{2}}/T_0) (1 + \frac{3}{2} \Theta_{\frac{1}{2}}/T_0)^{-1}, \quad (25)$$

which is the limiting Pauli susceptibility<sup>15</sup> corrected by the Weiss temperature  $\Theta_{\frac{1}{2}}$ . At high temperatures

$$\lim_{T \gg T_0} [-F'(\alpha)/F(\alpha)] \rightarrow 1,$$

and the limiting Weiss paramagnetic susceptibility (5) is recovered. As a consequence of the molecular field assumption (2), in which the nonideality of the system tends to resist the ordering effect of the external field, the nonideality superposes itself to the effect of statistics which imposes a type of order opposite to that of the applied field. The susceptibility (23) is thus always less than the limiting ideal Fermi gas susceptibility. This result is, of course, similar qualitatively to the one expressed by (5), whereby the susceptibility of the limiting ideal paramagnetic system is reduced by the molecular field correction (2), and the formalism of the initial limiting system is qualitatively preserved.

As far as liquid  $\text{He}^3$  is concerned, the observations rule out the susceptibility behavior as expressed by (23). This shows that the classical modifications of the molecular field approach are not valid here, in this eminently characteristic quantum system. It is, however, possible to make use of a phenomenological ap-

<sup>14</sup> E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938).

<sup>15</sup> W. Pauli, Jr., Z. Physik **41**, 81 (1927).

proach which is more conform to the approximate quantum-mechanical picture of the molecular field method. The latter has no direct connection with the original Weiss assumption, Eq. (2), but refers to the modification of the energy spectrum of the system arising with the interactions within the system. This approach yields thus a new Gibbs free energy per atom or a new effective parameter  $\alpha_{\text{eff}}$  replacing the limiting ideal antisymmetric fluid parameter  $\alpha$  in the paramagnetic moment equation (20). Or, since

$$\alpha = -G_{id}/kT, \quad (26)$$

and the molecular field correction being  $\alpha_m$ ,

$$\begin{aligned} \alpha_{\text{eff}} &= \alpha + \alpha_m \\ &= -(G_{id}/kT) - (G_m/kT), \end{aligned} \quad (27)$$

where  $G_m$  corresponds to the average corrective free energy per atom. At low enough temperatures where the temperature-entropy product term of the free energy is small, and where in passing from  $\alpha$  to  $\alpha_{\text{eff}}$ , the  $pV$  product is kept constant, the modification of  $G_{id}$  will occur essentially in its energy term. In the present case, the main effect to be expected in  $G_m$  may reasonably be attributed to the limiting effect of the atoms in the nonideal system associated with an overall depression of the energy. This results,  $G_m$  being negative, in raising  $\alpha_{\text{eff}}$  over and above the value of the limiting ideal parameter  $\alpha$ . In order for the preceding modification to satisfy the condition of preserving the formalism of the magnetic properties of the starting ideal system, it is necessary that the functional relation

$$\alpha = \alpha(\tau), \quad \tau = T/T_0, \quad (28a)$$

remain unchanged in

$$\alpha_{\text{eff}} = \alpha(\tau_m), \quad \tau_m = T/T_m, \quad (28b)$$

where  $T_m$  represents the new characteristic temperature of the system defined through the molecular field type of average of the nonideal paramagnetic behavior of the actual system. In the limit of low fields, one obtains with (21) and (27),

$$\begin{aligned} \lim_{\mu H/kT \ll 1} M(T, V, H)/VH &= \chi_m(T, V) \\ &= (C_{\frac{1}{2}}/T) [-F'(\alpha_{\text{eff}})/F(\alpha_{\text{eff}})]. \end{aligned} \quad (29)$$

At low temperatures and within the ideal antisymmetric fluid formalism

$$\begin{aligned} \lim_{T \text{ small}} (-F'/F) &= \frac{3}{2} (-\alpha_{\text{eff}})^{-1} \\ &= \frac{3}{2} [-\alpha + |\alpha_m|]^{-1}, \end{aligned} \quad (30)$$

since  $\alpha_m$  or  $(-G_m/kT)$  is always positive if the corrective term  $G_m$  is determined by lowering the energy in correcting for the nonideality. Plausible arguments for this situation, required by the observed liquid He<sup>3</sup>

nuclear paramagnetic susceptibilities, have been advanced by us previously<sup>2</sup> on the basis of simplifying assumptions on the interactions within the system. In terms of (28), one also has

$$\begin{aligned} \lim_{T \text{ small}} \chi_m &= \frac{3}{2} (C_{\frac{1}{2}}/T) \tau_m \\ &= \frac{3}{2} C_{\frac{1}{2}}/T_m, \end{aligned} \quad (31)$$

which, with (21), (23a), and (30), requires that

$$\tau_m > \tau, \quad T_m < T_0, \quad (32)$$

where, in  $T_m$  and  $T_0$ , the macroscopic volume dependence may be changed into pressure dependence with the help of the equation of state. At high temperatures,  $\alpha_{\text{eff}} > 1$ , and the expansion of  $(-F'/F)$  proceeds according to ascending powers of  $(\tau_m^{-3/2})$ , or,

$$\lim_{T \text{ large}} \chi_m = (C_{\frac{1}{2}}/T) (1 - \nu \tau_m^{-3/2} + \dots), \quad (33)$$

where  $\nu$  is a numerical coefficient.

It should be noted here that the preceding phenomenological model imposes no limits on the numerical values of the characteristic temperatures  $T_m$ , or on their dependence on the variables of state. The inequality (32) is conform to the observations and the ensuing empirical determinations of the  $T_m(V)$  or  $T_m(p)$  functions. It is seen on (31) and (5) that the molecular field parameters  $T_m$  or  $\Theta$  are defined through the finite paramagnetic susceptibilities in the limit of the absolute zero. The classical approach leading to (25) contains both characteristic temperatures  $T_0$  and  $\Theta_{\frac{1}{2}}$ .

It will be observed that the low field nonideal paramagnetic model considered here is such that its susceptibility satisfies the inequalities

$$\chi_{id} \leq \chi_m \leq \chi_0, \quad (34)$$

where  $\chi_{id}$  refers to the susceptibility of the limiting ideal antisymmetric fluid of the same density as the actual fluid, and  $\chi_0$  stands for the asymptotic Langevin-Brillouin susceptibility, Eq. (8), which the actual fluid would exhibit if it were an ideal classical paramagnetic system. The inequalities (34) are conform to the observations<sup>3,4,6</sup> throughout the region of the phase diagram of He<sup>3</sup> reserved to the liquid phase and explored so far.

The description of the above nonideal paramagnetic system may be modified through the use of the susceptibility ratios

$$\begin{aligned} r(T, y) &= \chi_m(T, y)/\chi_0(T, y) \\ &= \chi_m T/C, \end{aligned} \quad (35)$$

$y$  standing for  $V$  or  $p$ , and  $C$  being the appropriate Curie constant associated with the actual system. Since the susceptibility ratio defines the spin entropy,<sup>1</sup> the latter together with the empirically obtained functional relations  $T_m(V)$  or  $T_m(p)$  allows a rigorous derivation

of the partial thermal properties of liquid  $\text{He}^3$  arising with its nuclear spin system.<sup>2,8</sup>

The main characteristic of the preceding model resembles that of the Weiss model of classical nonideal paramagnets. At low magnetic field strengths, the temperature dependence of the ideal Langevin paramagnetic susceptibility is modified, in the nonideal system, by substitution of the effective temperature ( $T+\Theta$ ) for the temperature  $T$ , in the susceptibility law. The over-all formalism preserving feature of the molecular field-theoretic model is an important element of this approach. In our problem posed by liquid  $\text{He}^3$ , the ideal asymptotic system is that of a Fermi gas of spin  $\frac{1}{2}$  point atoms with the effective elementary dipole moment  $\mu$ . Through the quantum-mechanical formalism of the molecular field approach, it is possible then to modify the ideal fluid formalism, preserving its over-all structure to a degree, so as to be adapted to the nonideal paramagnetic system. This is achieved formally by replacing the ideal free energy by the one including formally the average quantum-mechanical molecular field energy term. This is then equivalent to replacing the natural reduced temperature variable of the ideal system,  $T/T_0$ ,  $T_0$  being the ideal gas degeneracy temperature, by the effective reduced temperature  $T/T_m(p)$ , where  $T_m(p)$  is the empirically derived characteristic temperature of the system. This phenomenological procedure preserves the formal structure of the ideal fluid paramagnetic susceptibility theory. Inasmuch as  $T_m(p)$  can be completely different from  $T_0$ , referring to the ideal fluid of the same density as the actual system, it is seen that the possibility for a perturbation theoretical scheme allowing to derive  $T_m$  from  $T_0$  is rather remote. The preceding approach toward the nonideal paramagnetic behavior of liquid  $\text{He}^3$  does not seem to impose clear limitations on the validity of the theory as far as the length of the interval of the effective reduced temperature  $[T/T_m(p)]$  is concerned.

We turn now to the comparison of the phenomenological theory of the nonideal paramagnetic susceptibilities obtained above with the recent detailed measurements.<sup>3,4</sup>

### 3. COMPARISON OF THE THEORETICAL AND EXPERIMENTAL PARAMAGNETIC PROPERTIES OF LIQUID $\text{He}^3$

According to the phenomenological theory of the nonideal paramagnetism of systems like liquid  $\text{He}^3$  formulated above, the susceptibility ratio law

$$\chi(T,p)/\chi_0(T,p) = -F'[\alpha_{\text{eff}}(T,p)]/F[\alpha_{\text{eff}}(T,p)] \quad (36)$$

$$= -F'[\tau(p)]/F[\tau(p)],$$

through

$$\alpha_{\text{eff}}(T,p) = f[\tau(p)] = f[T/T_0(p)], \quad (37)$$

is a unique function of the reduced temperature  $\tau(p)$  or  $T/T_0(p)$  throughout the region of existence of the liquid phase of  $\text{He}^3$ . This function is identical with the

one occurring in the ideal spin one-half antisymmetric fluid formalism, with  $T_0(p)$  being though an empirically determined characteristic temperature of the spin system with its characteristic pressure dependence to be determined also by observations, at the present phenomenological stage of the theory. We shall henceforth replace the subscript  $m$  used in the preceding section by the subscript zero.

Stated in other terms, the susceptibility ratio law (36) requires that, when represented as a function of the reduced temperature  $\tau(p)$  or  $[T/T_0(p)]$ , all susceptibility ratio values in liquid  $\text{He}^3$  must fall on a single or universal curve. The latter is associated with the collection of ideal Fermi systems of particles of spin angular momentum  $\hbar/2$ . Various limiting series representations of the susceptibility ratio have been given previously by Stoner.<sup>16</sup> The exact numerical evaluation of the susceptibility ratio law over an extended range of  $\tau$  has been performed in this Laboratory by Jordan and Crandall<sup>17</sup> using electronic computers. The susceptibility ratio (36) has been given in graphical form by us,<sup>1,2</sup> to within the factor  $(\ln 2)$ , up to values of  $\tau$  equal to 5. Our task is now a close study of the experimental evidence for or against the formula (36).

As mentioned in the Introduction, there are, at the present time, two important series of liquid  $\text{He}^3$  nuclear magnetic susceptibility determinations originating at the University of Illinois<sup>3</sup> and Duke University.<sup>4</sup> The Illinois group, guided by Dr. Wheatley, with its own technique of measurements of the various thermal properties of liquid  $\text{He}^3$  down to temperatures of the order of 0.01–0.03°K, depending on the pressure applied on the liquid, limited the susceptibility determinations to temperatures  $T \lesssim 0.10^\circ\text{K}$ . This low temperature range was supplemented by susceptibility determinations at one or two higher solitary temperatures for purposes of an experimental normalization procedure. The Duke University group, led by Dr. Meyer, explored the paramagnetic behavior of liquid  $\text{He}^3$  throughout the temperature range 0.05–1.0°K, in a systematic way. The pressure interval investigated by both groups of investigators extended up to or somewhat above the minimum of the melting pressure. For purposes of judging the accuracy with which the susceptibility law (36) is capable of describing the magnetic properties of liquid  $\text{He}^3$  over the allowed range of variations of its thermodynamic state coordinates, the Illinois and Duke University data should have been combined into a single set as representing, at the present time, the observed magnetic properties of liquid  $\text{He}^3$ . This is, however, excluded for the time being because of as yet unexplained numerical differences between the two sets of experimental results. The  $T_0(p)$  values of the Illinois

<sup>16</sup> E. C. Stoner, Proc. Leeds Phil. Lit. Soc. Sci. Sec. 3, Part IV, 191 (1936) and Part VII, 403 (1938); J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. London **237**, 67 (1938).

<sup>17</sup> Th. L. Jordan, Jr., and K. R. Crandall (unpublished).

group are consistently larger than those of the Duke University workers at the lower and medium pressures. At the higher pressures these characteristic temperatures seem to agree better. As a result, the functional dependence of  $T_0$  on the pressure seems to be considerably stronger with the Illinois than with the Duke University data. An explanation of these differences may become possible in the future, when the two sets of results may be combined and, in addition, these combined data may be supplemented by susceptibility determinations in the less accessible regions, as well as with those in other regions of the phase diagram of liquid He<sup>3</sup> which remained unexplored so far.

For our immediate purposes, the systematic Duke University magnetic measurements, with their dense coverage of the extended temperature interval, recommended themselves for their analysis in connection with the susceptibility law (36). With the option of one set of data, however more complete than the other, one automatically increases the degree of the limitations on the validity of the conclusions to be drawn from the confrontation of the theoretical paramagnetic behavior and the chosen set of measurements.

The collection of the important data of the Duke workers<sup>4</sup> is included in their Table I. This gives  $[\chi(T, p)/T\chi_0(T, p)]$  or  $[\chi(T, p)/C]$ , at the pressures of 0.5, 6.8, 13.6, 20.5, 30.5 and 30.7 atm, and at a series of temperatures from 1.0°K downward, with the extrapolated limits of the above property at  $T \rightarrow 0$ . From these limits one obtains, with (31), the characteristic temperatures  $T_0(p)$ , denoted by  $T_m$  in (31). It is to be noted that the tabulated values of  $(\chi/C)$ , given by the Duke workers, result from smoothing their own experimentally determined  $(\chi/C)$  values.

In the present studies the susceptibility ratios  $(\chi/\chi_0)$  or  $(\chi T/C)$  are of cardinal interest. These ratios are essentially equivalent to the tabulated data of the Duke workers, being the product of the temperature  $T$  and the tabulated numbers. Actually, the table of susceptibility ratios would carry larger relative errors, possibly the double of the relative errors of the susceptibilities themselves. Disregarding the highest pressure data of 30.7 atm which are very close to the 30.5 atm data, the five other isobaric susceptibility ratios are described by a collection of some eighty values, each given at sixteen temperatures, omitting their vanishing values in the limit of the absolute zero. The susceptibility ratios  $[\chi(T, p)/\chi_0(T, p)]$  along isobars have been determined as a function of the temperature. In terms of the reduced temperatures  $\tau(p)$ , or  $[T/T_0(p)]$ , the temperatures of the Duke<sup>4</sup> table give rise to a number of nearly identical  $\tau(p)$  values with the attendant very close susceptibility ratios. These close agreements of the experimental susceptibility ratios at the nearly identical  $\tau(p)$  values are, of course, conform to the predicted paramagnetic behavior of liquid He<sup>3</sup> according to the molecular field type of theoretical model advanced in the present work.

In order to free the present discussion, as much as

possible, from involving subjective quantities associated with the data, it seems necessary to omit essentially all considerations relative to the estimated experimental accuracies and precisions. The analysis in depth of these aspects of the data should be, of course, always an important part of any account and description of experimental results and measurements. In the present case, the experimental uncertainties refer to those of the thermodynamic state coordinates,  $T$  and  $p$ , as well as to those of the susceptibility determinations. Actually, the problem of estimating the experimental errors in the susceptibility determinations appears to be more difficult than would be the case with techniques whose principal goal would be the direct measurement of this physical property. In the nuclear magnetic resonance techniques used in the experimental investigations of the equilibrium magnetic properties of liquid He<sup>3</sup>, resonance frequencies or periods rather than amplitudes form the principal objects of measurements. While the amplitudes are proportional to the induced paramagnetic moments and, hence, define the susceptibility of the sample investigated, the possibility of amplitude determinations appear to be more of a windfall, of secondary and reduced interest, and the ultimate physical property associated with the amplitudes is inextricably tied to the a priori inaccessible apparatus constant. In order to extract from the measured amplitudes the susceptibilities it is indispensable that the apparatus constant be determined however indirectly and with inevitable uncertainties, which, of course, will always plague the numerical values of the so derived susceptibilities. Using the early recognized approach<sup>5</sup> of the liquid He<sup>3</sup> paramagnetic susceptibility toward the asymptotic ideal Curie-Langevin limit, it is either assumed at some higher temperature,  $T \gtrsim 1.0^\circ\text{K}$ , that the ideal limit has been reached,<sup>3</sup> or one attempts to justify the reaching of this limit,<sup>4</sup> always from below, within the limits of the reduced precision of the technique in this range of highly reduced "amplitudes" or susceptibilities when compared with the low temperature amplitudes. In principle, the actual susceptibilities never reach their asymptotic ideal limit, so that, the above "normalization" procedure can never be justified rigorously. It is thus seen that the limitations inherent in the nuclear resonance techniques will raise difficulties for a detailed confrontation of the experimentally derived susceptibilities with those evaluated with the phenomenological theory of paramagnetism developed above, whose validity does not seem to be limited to finite intervals of the thermodynamic state coordinates of liquid He<sup>3</sup>.

Various difficulties of physical character result from the above normalization procedure. This requires that at some medium temperature  $T_n$ , and at  $T > T_n$ , the susceptibilities should be ideal, within the precision of the technique used. At  $T < T_n$ , the susceptibilities are manifestly nonideal. According to the theory of the spin system,<sup>1,2,8</sup> the normalization procedure is equiva-

lent to postulate that the temperature and pressure derivatives of the spin entropy  $S_\sigma(T, p)$  vanish discontinuously at  $T_n$ . Or, one should have

$$\begin{aligned} dS_\sigma/dT > 0, & \quad T \leq T_{n-}, \\ dS_\sigma/dT = 0, & \quad T \geq T_{n+}, \end{aligned}$$

and,

$$\begin{aligned} (\partial S_\sigma/\partial p)_T \neq 0, & \quad T \leq T_{n-}, \\ (\partial S_\sigma/\partial p)_T = 0, & \quad T \geq T_{n+}, \end{aligned}$$

or, in terms of the partial spin heat capacity and spin volume expansion coefficients,

$$\begin{aligned} C_\sigma > 0, & \quad T \leq T_{n-}, \\ C_\sigma = 0, & \quad T \geq T_{n+}, \\ \alpha_{\sigma, p} \neq 0, & \quad T \leq T_{n-}, \\ \alpha_{\sigma, p} = 0, & \quad T \geq T_{n+}. \end{aligned}$$

The heat capacity and expansion coefficient jumps would occur at the chosen  $T_n$  values. Heat capacity measurements,<sup>18</sup> experimental investigations of the equation of state<sup>19,20</sup> of liquid He<sup>3</sup> and volume expansion coefficients measurements<sup>21</sup> at medium temperatures rule out the above "normalization" discontinuities. Furthermore, in attributing ideal susceptibilities to the liquid at  $T \geq T_n$ , allowing this property to effectively reach its upper limit of strictly asymptotic character, should have the effect to accelerate its rate of increase at the approaches of  $T_n$  and overestimate the actual susceptibility. This modification of the susceptibilities should become less effective at lower temperatures differing increasingly from  $T_n$ .

The preceding discussion, while hardly exhaustive, indicates that the conclusions to be drawn from a detailed comparison of the theoretically obtained susceptibilities with the highly indirect experimental ones will have to be strongly qualified because of the multiple limitations of the data.

We give in our Table I the eighty experimental susceptibility ratios of the Duke University group,<sup>4</sup> grouped according to their reduced temperatures  $\tau(p)$  or  $[T/T_0(p)]$ , the characteristic temperatures  $T_0(p)$  being also empirical and having been derived by these investigators from their own data.<sup>4</sup> The  $\tau$  values of the table appear in the numerical tables of the calculated ratios  $[\chi(T, p)/\chi_0(T, p)]$  or  $(\chi T/C)$ , obtained by Jordan and Crandall,<sup>17</sup> which accounts for their carrying more decimal figures than warranted by any experimentally determined reduced temperatures. The second column gives the experimental susceptibility ratios, the third contains the calculated ratios, the fourth represent their relative deviations, the fifth and sixth give the liquid temperatures and pressures. Clearly, part of this

Table I giving  $(\chi T/C)_{\text{calc}}$  as a function of  $\tau$  in the range  $0.0 \leq \tau \leq 5.0$ , is, of course, an exact table of the theoretical ratios. There are no data over  $\tau$  ranges at  $\tau \leq 0.10$ , and at  $\tau \geq 4.0$ . We also give in Fig. 1 the theoretical susceptibility ratio curve at  $0 \leq \tau \leq 4.0$ , together with the eighty experimental points.

With all due reserve entailed by the various limitations of both qualitative and quantitative character of the data<sup>4</sup> accepted for the present discussions, our Table I and Fig. 1 seem to justify a first tentative conclusion. Namely, the theoretical susceptibility ratios appear to fully describe the experimental situation over a limited range of the reduced temperature  $\tau$ , extending to about 0.90–1.0. At  $\tau > 1.0$ , the systematically larger experimental ratios might suggest some positive correction term to the phenomenological theory. It is to be noted that while systematic, these deviations might be still compatible with the possibly large experimental uncertainties. From the point of view of the molecular field theoretical type of model, developed in the preceding section, its apparent breakdown at the rather large values of 0.9–1.0 of the natural independent variable of the problem,  $\tau$ , is rather unexpected, to say the least. If the theory had broken down at much smaller values of  $\tau$ , the breakdown would have suggested an asymptotic validity only of the theory, limited to a small range of  $\tau$ . In view of the tolerable values of the systematic positive relative differences between the experimental and calculated  $(\chi T/C)$  values, at  $\tau \geq 1.0$ , we would like to advance now a possibly acceptable explanation of this discrepancy.

It may be justified at the present time, to adopt tentatively a less conservative attitude in the comparison of the experimental and theoretical susceptibility ratios, provided one attributes the systematic deviations at  $\tau \geq 0.90$ –1.0, to the difficulties arising with the over all decreased experimental precisions at and above the normalization temperature  $T_n$ , leading to the above-mentioned inconsistencies arising with the adopted normalization procedure. This tends to lift the values of the susceptibilities derived from the experimentally accessible resonance amplitudes over and above their actual values. This lifting effect may reasonably be expected to become more effective beyond the vertex of susceptibility ratio curve where this curve has curvatures distinctly below its maximum curvature realized at its vertex. The curvature, or the reciprocal of the radius of curvature, is defined by

$$\frac{1}{\rho} = |d^2/d\tau^2(\chi T/C)|/[1+(d/d\tau(\chi T/C))^2]^{3/2}, \quad (38)$$

or, in terms of the spin entropy-susceptibility relation this may also be written as,

$$\frac{1}{\rho} = (d/d\tau)(C_\sigma(\tau)/R) - (C_\sigma/R\tau)/\tau(\ln 2)[1+[C_\sigma/R\tau(\ln 2)]^2]^{3/2}. \quad (39)$$

<sup>18</sup> T. R. Roberts and S. G. Sydorak, Phys. Rev. **98**, 1672 (1955).

<sup>19</sup> E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **8**, 1 (1959).

<sup>20</sup> R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N. Y.) **9**, 522 (1960).

<sup>21</sup> E. C. Kerr and R. D. Taylor, Ann. Phys. (N. Y.) **20**, 450 (1962).



TABLE I. Experimental and theoretical nuclear susceptibility ratios of liquid He<sup>3</sup>.

$\tau$	$\left(\frac{\chi T}{C}\right)_{\text{exp}}$	$\left(\frac{\chi T}{C}\right)_{\text{calc}}$	$\frac{\text{exp-calc}}{\text{exp}}\%$	T (°K)	P (atm)	$\tau$	$\left(\frac{\chi T}{C}\right)_{\text{exp}}$	$\left(\frac{\chi T}{C}\right)_{\text{calc}}$	$\frac{\text{exp-calc}}{\text{exp}}\%$	T (°K)	P (atm)
0.00		0.00				0.61920	0.680	0.6563	3.53	0.20	13.6
0.025		0.03748				0.62016	0.638	0.6568	-2.98	0.16	30.5
0.030		0.04497				0.62069	0.657	0.657	0.00	0.18	20.5
0.050		0.07484				0.68966	0.690	0.6905	0.00	0.20	20.5
0.060		0.08973				0.69767	0.675	0.6941	-2.81	0.18	30.5
0.070		0.1046				0.69768	0.702	0.6941	1.14	0.30	0.5
0.080		0.1194				0.77519	0.704	0.7256	-3.12	0.20	30.5
0.085		0.1267				0.80000	0.768	0.7346	4.30	0.30	6.8
0.090		0.1341				0.92879	0.825	0.7750	6.06	0.30	13.6
0.095		0.1414				0.93023	0.804	0.7754	3.61	0.40	0.5
0.10465	0.157	0.1557	1.27	0.045	0.5	1.03448	0.831	0.8014	3.61	0.30	20.5
0.12000	0.179	0.1777	0.56	0.045	6.8	1.06667	0.852	0.8084	5.16	0.40	6.8
0.13932	0.205	0.2053	0.00	0.045	13.6	1.16279	0.834	0.8274	0.84	0.50	0.5
0.13954	0.206	0.2056	0.00	0.06	0.5	1.16279	0.870	0.8274	4.94	0.30	30.5
0.15517	0.226	0.2276	-0.88	0.045	20.5	1.23839	0.908	0.8403	7.49	0.40	13.6
0.16000	0.233	0.2343	-0.43	0.06	6.8	1.33333	0.910	0.8544	6.15	0.50	6.8
0.17442	0.253	0.2541	-0.40	0.045	30.5	1.37931	0.908	0.8605	5.18	0.40	20.5
0.18576	0.267	0.2694	-0.75	0.06	13.6	1.39535	0.924	0.8626	6.60	0.60	0.5
0.18605	0.267	0.2698	-1.12	0.08	0.5	1.54799	0.950	0.8798	7.37	0.50	13.6
0.20690	0.296	0.2973	-0.34	0.06	20.5	1.55039	0.912	0.8801	3.51	0.40	30.5
0.21333	0.302	0.3056	-1.32	0.08	6.8	1.60000	0.948	0.8849	6.65	0.60	6.8
0.23256	0.322	0.3299	-2.48	0.10	0.5	1.62791	0.966	0.8875	8.18	0.70	0.5
0.23256	0.327	0.3299	-0.92	0.06	30.5	1.72414	0.955	0.8957	6.18	0.50	20.5
0.24768	0.348	0.3485	0.00	0.08	13.6	1.85759	0.978	0.9056	7.40	0.60	13.6
0.26667	0.368	0.3711	-0.82	0.10	6.8	1.86047	0.984	0.9058	7.93	0.80	0.5
0.27586	0.378	0.3817	-1.06	0.08	20.5	1.86667	0.987	0.9063	8.21	0.70	6.8
0.27907	0.374	0.3853	-2.94	0.12	0.5	1.93799	0.960	0.9109	5.10	0.50	30.5
0.30960	0.420	0.4190	0.24	0.10	13.6	2.06897	0.984	0.9185	6.71	0.60	20.5
0.31008	0.420	0.4195	0.00	0.08	30.5	2.13333	0.992	0.9218	7.06	0.80	6.8
0.32000	0.431	0.430	0.23	0.12	6.8	2.16718	0.994	0.9235	7.04	0.70	13.6
0.32558	0.420	0.4358	-3.81	0.14	0.5	2.32558	1.0	0.9306	6.90	1.00	0.5
0.34483	0.450	0.4552	-1.11	0.10	20.5	2.32558	0.990	0.9306	5.96	0.60	30.5
0.37152	0.491	0.4809	2.04	0.12	13.6	2.41379	0.994	0.9341	6.04	0.70	20.5
0.37209	0.466	0.4814	-3.22	0.16	0.5	2.47678	1.0	0.9364	6.40	0.80	13.6
0.37335	0.486	0.4825	0.62	0.14	6.8	2.66667	1.0	0.9427	5.70	1.00	6.8
0.38760	0.488	0.4956	-1.64	0.10	30.5	2.71318	1.0	0.9441	5.60	0.70	30.5
0.41379	0.510	0.5184	-1.57	0.12	20.5	2.75862	1.0	0.9454	5.50	0.80	20.5
0.41861	0.509	0.5224	-2.55	0.18	0.5	3.09598	1.0	0.9536	4.60	1.00	13.6
0.42667	0.533	0.5291	0.75	0.16	6.8	3.10078	1.0	0.9537	4.60	0.80	30.5
0.43344	0.560	0.5346	4.29	0.14	13.6	3.44828	1.0	0.9602	4.00	1.00	20.5
0.46512	0.544	0.5592	-2.76	0.20	0.5	3.87597	1.0	0.9664	3.40	1.00	30.5
0.46512	0.544	0.5592	-2.76	0.12	30.5	3.90		0.9667			
0.48000	0.574	0.5702	0.70	0.18	6.8	3.95		0.9673			
0.48276	0.566	0.5722	-1.06	0.14	20.5	4.00		0.9679			
0.49536	0.608	0.5811	4.44	0.16	13.6	4.10		0.9690			
0.53333	0.616	0.6065	1.62	0.20	6.8	4.25		0.9706			
0.54264	0.592	0.6124	-3.38	0.14	30.5	4.50		0.9730			
0.55172	0.611	0.6180	-1.15	0.16	20.5	4.75		0.9750			
0.55728	0.648	0.6214	4.17	0.18	13.6	5.00		0.9768			

One finds that the vertex is at about  $\tau$  close to 0.47, while the curvature did decrease by a factor of about two at  $\tau$  close to 0.95. It should be noted that the graph of Fig. 1 is somewhat deceptive because of the different linear scales of the ordinate and abscissa. By Table I, the normalization procedure is equivalent to force the ratio curve to reach its "asymptote" at  $\tau$  values of about 2 to 3, depending on the pressure. The asymptotic region of the experimental ratio curve is effectively eliminated and its curvature made to drop discontinuously to zero at the  $\tau$  value of about 2. This is a likely explanation of the systematic though fairly small excess values of the experimental susceptibility ratios over the calculated ones at increasing  $\tau$  values beyond about  $\tau \geq 0.90-1.0$ . A verification of this tentative con-

clusion might be possible by renouncing the normalization procedure used so far, and, above all, by increasing the experimental precision so as to increase the normalization temperature  $T_n$  or the normalization  $\tau_n$  values. In this way, the condition imposed upon the experimental susceptibilities to become ideal at these elevated  $T_n$  or  $\tau_n$  values will have a more moderate effect of deformation, and the possible agreement between the experimental and theoretical susceptibilities may extend over a wider range of  $\tau$  values than realized at the present time.

If this second less conservative attitude advanced here is given up for the first more cautious one, then, as stated already, within the various limitations mentioned in the course of this analysis, the theory appears.

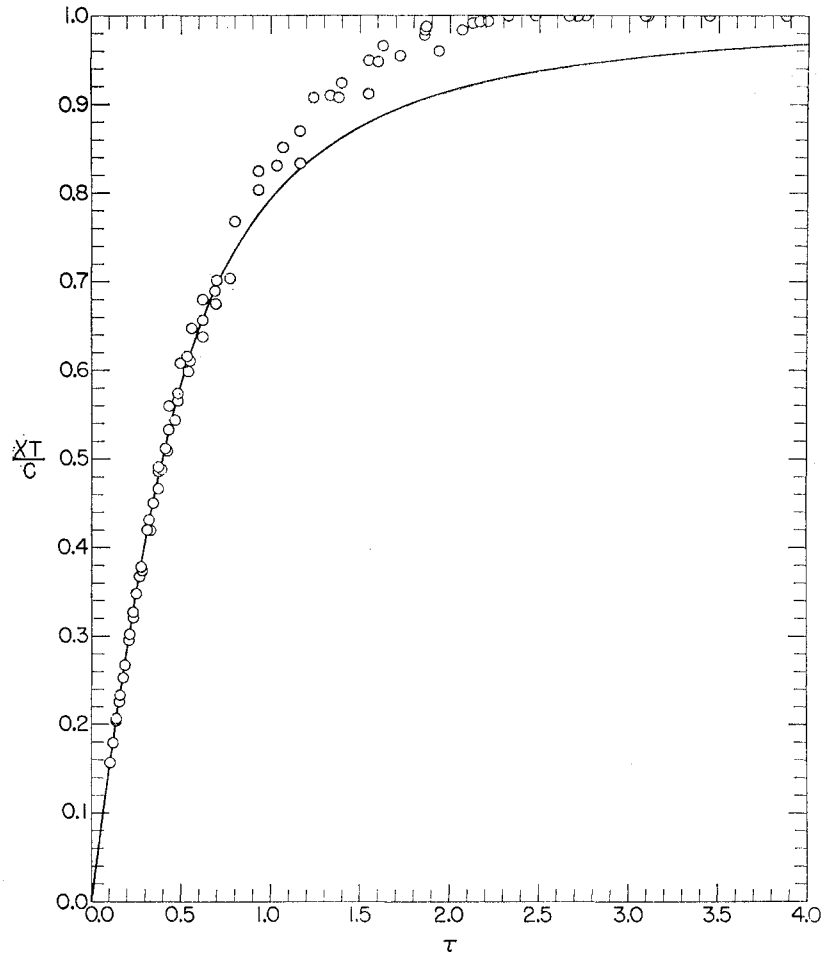


FIG. 1. The liquid He<sup>3</sup> theoretical paramagnetic susceptibility ratio curve ( $\chi T/C$ ), as a function of the reduced temperature  $\tau$ , and the experimental data obtained by the Duke University investigators, Ref. 4.

to describe satisfactorily the data over the range  $0 \leq \tau \leq 0.9$ . This in turn would justify the use of the susceptibility formalism based on the molecular field theoretical type approach as a basis for the theory of the thermal properties of the nuclear spin system of liquid He<sup>3</sup> over a limited range of  $\tau$ , but throughout the pressure range of existence of this phase. As mentioned, the formalism is to be completed by the empirical connection between the characteristic temperatures  $T_0$  of the spin system and the pressure  $p$ .

To resume then, as required by the theory advanced here, all susceptibility ratios  $\chi(T, p)/\chi_0(T, p)$ , or  $[\chi(T, p)T/C]$ , of liquid He<sup>3</sup> fall on a unique curve when represented as a function of the reduced temperature  $\tau(p)$  or  $[T/T_0(p)]$ , up to about  $\tau \sim 0.9-1.0$ .

We turn now to various applications of the theory of the spin system advanced here.

#### 4. THERMAL PROPERTIES OF THE NUCLEAR SPIN SYSTEM

By the spin-entropy-spin-susceptibility relation,<sup>1</sup> the entropy of the nuclear spin system is

$$S_\sigma(T, p)/R = (\ln 2)[\chi(T, p)/\chi_0(T, p)], \quad (40)$$

or, since the right-hand side depends only on the reduced temperature  $\tau(p)$ , the spin entropy  $S_\sigma(T, p)$  is also a function of this natural variable. We have used this property of  $S_\sigma$  previously<sup>2,8</sup> on explicitly assuming that the ideal antisymmetric fluid formalism may be used as an analytical approximation in the description of the nuclear spin system. The molecular field theoretic type approach followed in the preceding sections removes the necessity of this assumption, and when it is used in conjunction with the pressure law of the characteristic temperature  $T_0(p)$  of the spin system, the equation of state of the latter becomes fully determined. This then is the basis of a rigorous statistical-thermodynamic formalism of the partial thermal properties of liquid He<sup>3</sup> arising with its nuclear-spin system. It yields a rigorous lower limit of all those thermal properties of this liquid which can be represented additively in terms of those of the spin system and those arising with the degrees of freedom other than spin. The limitations of this statistical-thermodynamic formalism are determined by those of the theory of paramagnetism discussed above, to which one has to add the uncertainties arising with the empirically de-

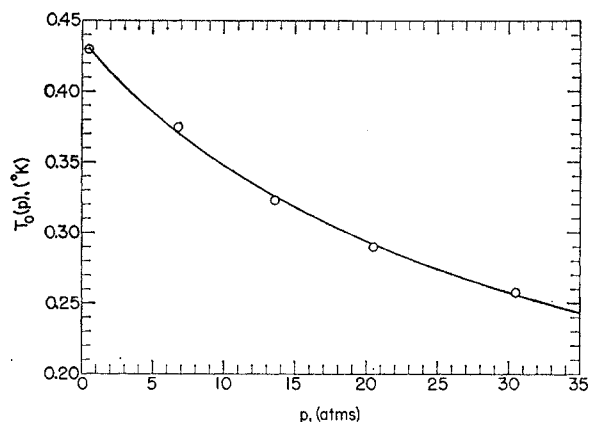


FIG. 2. The analytical fit to the empirically derived characteristic temperatures of the nuclear spin system of liquid  $\text{He}^3$  as a function of the pressure  $T_0(p)$ , with the data points.

rived functional connection  $T_0(p)$ . By thermodynamics, the constant pressure heat capacity of the spin system is

$$\begin{aligned} C_{\sigma,p}(T,p)/R &= (T/R)[\partial S_\sigma(T,p)/\partial T]_p \\ &= [\tau(p)/R](d/d\tau)[S_\sigma(\tau)] \\ &= \frac{3}{2}(\ln 2)[F''(\alpha_{\text{eff}})/F'(\alpha_{\text{eff}}) - F'(\alpha_{\text{eff}})/F(\alpha_{\text{eff}})], \end{aligned} \quad (41)$$

where use was made of the relation (36) and (37), as well as of those of the ideal antisymmetric fluid formalism<sup>1,2</sup> valid to the extent of its intervention in the theory of the nonideal spin paramagnetism developed here. The universal character of  $(\chi/\chi_0)$ ,  $S_\sigma(\tau)$  and  $C_\sigma(\tau)$  clearly emerges here through the reduction of these thermal properties to their sole dependence on the reduced temperature  $\tau$ . The dependence of these thermal properties on one of the other coordinates of

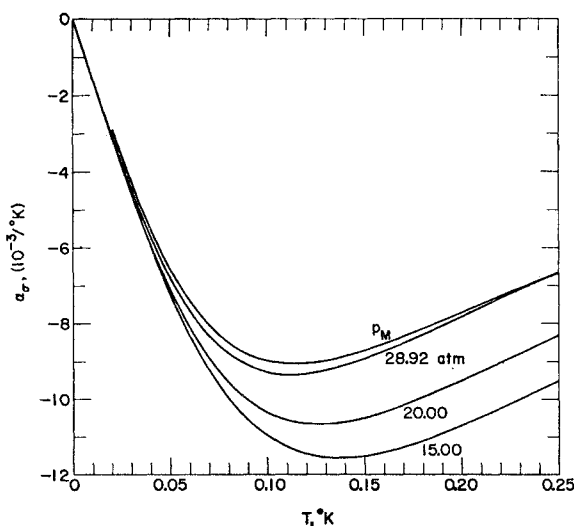


FIG. 3. The partial spin expansion coefficients  $\alpha_\sigma$  of liquid  $\text{He}^3$  along the indicated isobars and the melting pressure  $p_M$  as a function of the temperature.

state,  $p$  or  $V$ , is included in the implicit dependence of  $\tau$  on either one of these coordinates.

The spin-heat capacity has been discussed previously<sup>1,2,8</sup> and will not be considered here any further, since its functional form is identical with the one assumed in earlier work.

The partial isobaric spin expansion coefficient  $\alpha_\sigma(T,p)$  or the product  $\alpha_{\sigma,p}(T,p)V(T,p)$ , that is, by (41) and the definition of  $\tau(p)$ ,

$$\begin{aligned} \alpha_{\sigma,p}(T,p)V(T,p) &= -[\partial S_\sigma(T,p)/\partial p]_T \\ &= -[\partial S_\sigma(\tau)/\partial \tau]_p(d\tau/dp) \\ &= [C_{\sigma,p}(\tau)/T_0(p)][dT_0(p)/dp], \end{aligned} \quad (42)$$

is, however, of great interest inasmuch as this quantity is now rigorously expressed formally with the help of the empirical function  $T_0(p)$ . The limitations involved in the previous evaluation of this property<sup>2,8</sup> have now been lifted. The estimation and assessment of the precision of the numerically evaluated spin expansion coefficients through the rigorous relation (41) presents a difficult problem at the present time. The errors in  $V(T,p)$  are likely to be quite small,<sup>20</sup> those in  $C_{\sigma,p}(\tau)$  involve the errors in the numerical values of  $T_0(p)$ , while the precision of the derivatives  $[dT_0(p)/dp]$  depends critically on the empirical  $T_0(p)$  relation.

The  $T_0(p)$  function resulting from the Duke University data is given in Fig. 2 as the drawn curve, which is a least square fit with a hyperbola type function with three parameters, to the data points given on the graph. The  $T_0(p)$  function has been extrapolated beyond the last highest pressure data point over a limited pressure interval.

Using the empirical<sup>4</sup>  $T_0(p)$  function, we have obtained in Fig. 3, several  $\alpha_{\sigma,p}(T,p)$  curves, along the indicated isobars, together with  $\alpha_{\sigma,p_M}$ , or the spin-expansion coefficients along the melting pressure line  $p_M(T)$ . The temperature interval extends only to 0.25°K, so that these calculated spin-expansion coefficients although lower limits of the total volume-expansion coefficients  $\alpha_p(T,p)$ , may be fair approximations to the latter over the above restricted temperature range. Actually, the approximation achieved by  $\alpha_{\sigma,p}$  on  $\alpha_p$  improves as the temperature decreases, so that  $\alpha_\sigma$  should be fairly close to the exact total expansion coefficients at  $T \lesssim 0.10^\circ\text{K}$ . Although similar to the  $\alpha_\sigma$ 's obtained in the previous calculation of considerably poorer approximation, the new values are larger numerically than the earlier ones.<sup>8</sup> As to the  $\alpha_{\sigma,p_M}$  values along the melting pressure line, these are based on a slight extrapolation of the empirical  $T_0(p)$  function from 30.5 to about 33 atm. This extrapolation is performed in terms of the analytical least-square fit of the empirical  $T_0(p)$  data.

At the present time, an approximate evaluation of the additive positive partial nonspin expansion coefficient represented by the thermodynamic relation<sup>2,8</sup>

$$\alpha_{n\sigma,p}(T,p) = \frac{2}{3}\epsilon_{n\sigma}(T,p)\chi_T(T,p)C_{n\sigma,p}(T,p)/V(T,p), \quad (43)$$

is hardly feasible. Here,  $\epsilon_{n\sigma}$  is a parametric function,  $\chi_T$  is the isothermal compressibility and  $C_{n\sigma,p}$  the constant pressure nonspin heat capacity. Values of the latter are not available, while the parameter  $\epsilon_{n\sigma}$  can only be reached through the subtraction of the theoretical  $\alpha_\sigma$ 's from the experimental  $\alpha_p$ 's.

A glance at the  $\alpha_\sigma$ -curves of Fig. 3 shows that below about 0.06°K, or so, where these spin expansion coefficients should be close to the observed total expansion coefficients of the liquid, experimental discrimination of the expansion coefficients along isobars  $p \gtrsim 10$ –15 atm may hardly succeed. At increasing temperatures, with  $\alpha_{n\sigma}$  becoming more significant a narrowing of the band of the actual expansion coefficient curves may be expected on the following grounds. In (43), the nonspin heat capacity  $C_{n\sigma,p}$  and compressibility  $\chi_T$  factors, with their decrease on increasing pressure, overtake the increase in  $[1/V(T,p)]$ . With the rate of decrease of  $\alpha_{n\sigma,p}$  being likely the largest at the lower pressures, and the smallest at the higher pressures, the lowest pressure  $\alpha_\sigma$ 's will be raised the most by their complement of  $\alpha_{n\sigma}$ , the highest pressure  $\alpha_\sigma$ 's will be raised the least. Hence, the differences between the various total  $\alpha_p$ 's, at the same temperature, will be minimized as compared with the differences between the  $\alpha_{\sigma,p}$  values at the various pressures. As shown by us previously<sup>2,8</sup> the family of  $\alpha_{\sigma,p}$  curves, are modified by the positive  $\alpha_{n\sigma,p}$ 's so as to insure the lower pressure  $\alpha_p$ 's to reach their zero first, and the higher pressure  $\alpha_p$ 's to reach their zero at increasingly higher temperatures. This interval of the zeros of  $\alpha_p$  extends from about 0.50°K, at saturation pressure, to about 1.25°K, at 47 atm, approximately. The complete coalescing of the total expansion coefficient curves along the various isobars is hard to contemplate at  $T \gtrsim 0.10^\circ\text{K}$ , although their differentiation above 15 atm may become quite laborious experimentally, within the expected, possibly fairly large, experimental errors, at  $T \lesssim 0.25$ – $0.30^\circ\text{K}$ . Qualitatively, this may account for the recent indirect determinations of  $\alpha_p$  in compressed liquid He<sup>3</sup> by the University of Illinois investigators.<sup>9</sup> These workers could not truly discriminate between the isobaric expansion coefficients at the same temperature, along isobars in the pressure range  $14 \leq p \leq 29$  atm. Within the experimental uncertainties, the indirectly obtained  $\alpha_p$ 's seemed to be distributed along a single curve in the  $(\alpha_p, T)$  representative plane, at  $T \lesssim 0.25$ – $0.30^\circ\text{K}$ . A cursory comparison of these experimental determinations of  $\alpha_p$  with the calculated  $\alpha_{\sigma,p}$ 's of Fig. 3 indicates only qualitative agreement. More than this could not be expected because of the lack of discrimination of the  $\alpha_p$  data over the indicated pressure range as well as the lower limit character of the calculated  $\alpha_{\sigma,p}$  values.

It may be hoped that direct measurements of the expansion coefficients  $\alpha_p$  of liquid He<sup>3</sup> will be performed allowing a more extensive analysis of the partial spin-expansion coefficients, at the low temperatures where they should be good approximations to the actual ex-

pansion coefficients of the liquid. Similar comparisons of  $\alpha_{\sigma,p}$  or of  $[-V(T,p)\alpha_{\sigma,p}]$  or  $(\partial S_\sigma/\partial p)_T$  could be made with the pressure derivative of the liquid entropies at the low temperatures, when they become available.

## 5. LIQUID AND SOLID He<sup>3</sup> ALONG THE PHASE SEPARATION LINE

### 5.1. Some Thermal Properties of the Dense Phases at Equilibrium with Each Other at Very Low Temperatures

With the rigorous formalism of the nuclear spin system of liquid He<sup>3</sup> throughout the whole region of existence of this phase, it becomes possible to obtain a first outline of the entropy diagram of He<sup>3</sup>. This sketch of the entropy diagram is based partly on the approximate entropies of the liquid and solid in equilibrium along the phase boundary line at the lowest temperatures. At the present time, the diagram still has a wide gap at and around the temperature of anomaly  $T_a$  of the melting pressure minimum. Beyond about 1.0°K or 40 atm, the entropies of the dense phases at the phase separation line are available with good approximation through the work of Grilly and Mills<sup>19</sup> and that of Sherman and Edeskuty.<sup>20</sup>

Our main object now is the evaluation of the approximate entropy values of solid He<sup>3</sup> along the phase separation line, relying on the corresponding approximate entropies of the liquid in equilibrium with the solid. In thermodynamic equilibrium, the total entropy of the liquid is, in terms of the theory of the nuclear spin system,

$$S_L(T,p) = S_\sigma^{(L)}[\tau(p)] + S_{n\sigma}^{(L)}(T,p), \quad (44)$$

the degrees of freedom of spin of the nonideal paramagnetic system and the degrees of freedom other than spin forming two subsystems which allow the representation (44) of the total entropy.<sup>1</sup> Since at  $T > 0$ , partial or component entropies are positive definite quantities, one has, with (44),

$$\liminf S_L(T,p) = S_\sigma^{(L)}[\tau(p)], \quad (45)$$

or the partial spin entropy is a lower limit of the total entropy. At low enough temperatures,

$$S_\sigma^{(L)}[\tau(p)] \gg S_{n\sigma}^{(L)}(T,p), \quad T \ll T_0(p), \quad (46)$$

and, at low pressures, at saturation or somewhat above saturation, the ratio  $[S_\sigma^{(L)}/S_{n\sigma}^{(L)}]_{T \ll T_0(p)}$  has been estimated by us<sup>8</sup> to be about 5 to 5.5. At increasing pressures, we have shown<sup>8</sup> that the low temperature partial entropy ratios may reasonably be expected to increase as a consequence of the spin entropy increase and the normal but small decrease of the nonspin entropy. The entropy change on solidification is, from thermodynamics,

$$\begin{aligned} \Delta S(T) &= S_L(T) - S_s(T) \\ &= [V_L(T) - V_s(T)](dp_M/dT), \end{aligned} \quad (47)$$

$S_s$  and  $V_s$  standing, respectively, for the entropy and volume of the solid. A lower limit of the solid entropy along the melting line is then given by

$$\begin{aligned} \liminf S_s(T) &= \liminf S_L(T) - \Delta S(T) \\ &= S_{\sigma}^{(L)}[\tau(\phi)] - \Delta S(T), \end{aligned} \quad (48)$$

where  $\Delta S(T)$  is an empirically determined quantity. The partial spin entropy  $S_{\sigma}^{(L)}[\tau(\phi_M)]$  along the melting line is fully determined by the formalism of the spin system derived above. The  $T_0(\phi)$  relation has to be used here to pressures of about 33 atm which necessitates the extrapolation of the empirical  $T_0(\phi)$  law<sup>4</sup> from about 30.5 atm. In (47), the volume difference ( $V_L - V_s$ ) may reasonably be expected to change only very little at  $T \lesssim 0.32-0.33^\circ\text{K}$ , at which temperature there is a measurement of this volume change due to Mills, Grilly and Sydoriak.<sup>22</sup>

The experimental melting pressure values have been studied through various types of analytical least square fits by Dr. R. K. Zeigler and E. A. Perego, of this Laboratory. The various analytical  $\phi_M(T)$  functions have been obtained under the constraint that they reduce to a vertical osculating parabola in the  $(\phi, T)$  plane, in the neighborhood of the vertex of the melting line. The data fitted analytically over the temperature range  $0.03-0.40^\circ\text{K}$  are a composite of various melting pressure measurements of the Illinois group,<sup>9</sup> the Los Alamos<sup>22</sup> and Ohio State University<sup>23</sup> workers. The results of the latter group were known to be higher systematically than those of the Los Alamos group,<sup>22</sup> and the Illinois workers<sup>9</sup> could reconcile them with their own data and with those of the Los Alamos group on reducing them uniformly by a constant pressure  $\Delta\phi$ . Over the above temperature range, with the large number of data points, the various analytical expressions approximated the melting pressure data with rather good accuracy. This happens whether imposing upon the analytical fit the coordinates of the vertex or letting the latter to be determined also by the fitting process. They also yielded the derivatives ( $d\phi_M/dT$ ) which differed by a few percent at most with the various fits and over most of the temperature range. The class of analytical fits which carried no constraints as far as their behavior was concerned in the limit of the absolute zero became invalid physically in this limit, and they were used only down to about  $0.02^\circ\text{K}$ . It is worth mentioning, although no use was made of it at all, that some of these analytical  $\phi_M(T)$  approximations indicated the existence of an inflection point at somewhat above the beginning of the range,  $T \sim 0.04^\circ\text{K}$ , or somewhat below it,  $T \sim 0.025^\circ\text{K}$ .

The analytical approximations having yielded similar  $\Delta S$ -values, it appeared justified to assume tentatively that in the lower limit of the solid entropy  $S_s$ , in (48),

<sup>22</sup> R. L. Mills, E. R. Grilly, and S. G. Sydoriak, *Ann. Phys. (N. Y.)* **12**, 41 (1961).

<sup>23</sup> D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 126.

TABLE II. Calculated lower limits of the liquid He<sup>3</sup> entropy and heat capacity and of the solid He<sup>3</sup> entropy along the melting line.

T (°K)	$\phi_M$ (atm)	$S_{L,M}/R$	$\Delta S/R$	$S_{s,M}/R$	$C_{L,M}/R$
0.020	32.91	0.083	-0.448	0.531	0.082
0.025	32.76	0.104	-0.438	0.542	0.102
0.030	32.61	0.123	-0.427	0.550	0.120
0.035	32.47	0.143	-0.417	0.560	0.137
0.040	32.33	0.162	-0.407	0.569	0.153
0.045	32.19	0.181	-0.397	0.578	0.168
0.050	32.06	0.199	-0.387	0.586	0.181
0.055	31.93	0.216	-0.377	0.593	0.193
0.060	31.80	0.233	-0.367	0.600	0.203
0.065	31.67	0.249	-0.357	0.606	0.212
0.070	31.55	0.265	-0.348	0.613	0.219
0.075	31.44	0.281	-0.338	0.619	0.226
0.080	31.32	0.294	-0.329	0.623	0.231
0.085	31.21	0.308	-0.320	0.628	0.235
0.090	31.10	0.322	-0.311	0.633	0.238
0.095	31.00	0.335	-0.302	0.637	0.240
0.100	30.90	0.347	-0.293	0.640	0.242

$\Delta S(T)$  was rather well determined. The spin entropy  $S_{\sigma}^{(L)}[\tau(\phi_M)]$  is fully tied to the paramagnetic susceptibility of the liquid along the melting line and its theoretical description, which we saw above to be quite satisfactory at  $\tau(\phi) \lesssim 0.90-1.0$ . With the approximations stated one obtains, in a straightforward way, the lower limits of the solid entropy along the phase separation line. They are included in Table II, which also gives the melting pressure  $\phi_M(T)$ , calculated with a particular analytical fit, the lower limit of the liquid entropy  $S_{L,M}$ , through its spin entropy  $S_{\sigma,M}^{(L)}$ , and the approximate entropy changes on solidification  $\Delta S(T)$ . The last column gives the lower limit of the liquid heat capacity  $C_{L,M}$ , that is, its spin heat capacity  $C_{\sigma,M}^{(L)}$ . All entropies and heat capacities are in molar units.

Within the limits of validity of Table II, at the lowest temperatures, the lower limit of the solid entropy  $S_s$  falls considerably below the limiting asymptotic spin entropy of  $R \ln 2$ . Even with the extreme assumption, which attributes to the nonspin entropy a value equal to the spin entropy, it is only at about  $0.035^\circ\text{K}$  that the solid entropy could reach the full spin entropy value. Actually, it is rather difficult to see how the nonspin entropy of the liquid can reach, at the low temperatures of Table II, values larger than about  $(0.20-0.25)S_{\sigma}^{(L)}$ . If the latter situation prevailed, the solid entropy would become  $R \ln 2$  at about  $0.08-0.085^\circ\text{K}$ .

It is also possible to use a relation similar to (48) to obtain approximate lower limits of the solid He<sup>3</sup> heat capacities along the melting line. One has here

$$\liminf C_{s,M}(T) = C_{\sigma}^{(L)}[\tau(\phi_M)] - \Delta C(T), \quad (49)$$

with  $\Delta C(T)$  standing for  $(C_{L,M} - C_{s,M})$ . This heat capacity difference along the phase boundary line is

$$\begin{aligned} \Delta C &= T(d/dT)\Delta S(T) \\ &= T(V_L - V_s)(d^2\phi_M/dT^2), \end{aligned} \quad (50)$$

on the assumption that  $(d/dT)(V_L - V_s)$  is very small at the lowest temperatures and the term,  $T(d\phi_M/dT) \times (d/dT)(V_L - V_s)$ , may be omitted in comparison with the term retained on the right-hand side of (50). The lower limit solid heat capacities are, of course, also available through the lower limit solid entropies  $S_{s,M}$  of Table II. One finds that these lower limit solid heat capacities vary between  $0.04R$  and  $0.08R$  over the temperature range  $(0.02-0.10)^\circ\text{K}$ , with a hump at about  $0.06-0.07^\circ\text{K}$ . The latter may be spurious, and at the present time the order of magnitude of the lower limit solid  $\text{He}^3$  heat capacities is of significance as another aspect of the solid  $\text{He}^3$  entropy being below  $R \ln 2$ , within the limitations of the approximate Table II. The thermodynamic entropy and heat capacity differences, (47) and (49), include of course the contributions of all degrees of freedom. It is hoped that experimentalists may soon investigate the interesting magnetic and thermal properties of the dense phases of  $\text{He}^3$  at and in the vicinity of the melting line.

### 5.2. Some Points of the Liquid $\text{He}^3$ -Solid $\text{He}^3$ Equilibrium

The earliest observation on the susceptibility of solid  $\text{He}^3$  appeared to suggest<sup>8</sup> that the solid susceptibility ratios belonged to an extension of the family of susceptibility ratio curves of the liquid. This in turn seemed to justify<sup>8,2</sup> the discussion of the thermal properties of the solid arising with its nuclear spin system, whereby the latter, according to the observations,<sup>6</sup> exhibited a fairly large characteristic temperature even though smaller than in the highly compressed liquid. The discussions of the thermal properties of the solid were tied to the early susceptibility observations.<sup>6</sup> In the light of the approximate solid entropy value of about  $(0.53-0.58)R$  at  $0.02^\circ\text{K}$ , derived above, the heat capacity anomaly arising with its spin system must occur at  $T < 0.02^\circ\text{K}$ , or the characteristic temperature of the spin system of the solid must be considerably smaller than indicated by the early susceptibility measurements<sup>6</sup> which have not been substantiated so far. The discussion of the thermal properties of solid  $\text{He}^3$  along the melting line<sup>2</sup> have to be qualified accordingly. Namely, the suggested thermal anomaly of the solid extending to medium temperatures may now be unjustified because of the highly reduced characteristic temperature of the spin system of the solid according to the just calculated approximate solid entropies. In pursuing the earlier suggestion advanced by us<sup>3</sup> on the basis of the first susceptibility observations in the solid,<sup>6</sup> the Los Alamos group<sup>22</sup> used a strictly thermodynamic analysis of their liquid  $\text{He}^3$ -solid  $\text{He}^3$  equilibrium data. On adopting the not too unjustified attitude that the elastic behavior of the solid is normal, requiring its isothermal compressibility  $\chi_{s,T}(\phi_M)$  to be smaller than, or at most equal to, that of the liquid in equilibrium with it,  $\chi_{L,T}(\phi_M)$ , the analysis showed that the solid should

exhibit anomalous thermal properties below about  $0.95-1.0^\circ\text{K}$ . It should be noted in this connection that Bridgman<sup>24</sup> called attention to the situation that in a liquid-solid transformation the elastic anomaly of the solid in the form just stated,  $\chi_{s,T}(\phi_M) \geq \chi_{L,T}(\phi_M)$ , could not be ruled out. On postulating that solid  $\text{He}^3$  must have normal thermal properties at medium temperatures, the liquid  $\text{He}^3$ -solid  $\text{He}^3$  equilibrium data<sup>22</sup> tend to impose elastic anomaly upon the solid. Recently, Heltemes and Swenson<sup>25</sup> have made heat capacity measurements at constant volume on compressed solid  $\text{He}^3$ , that is away from the boundary line, although the latter might have been approached. Since the solid temperature was  $T \gtrsim 0.3^\circ\text{K}$ , where even the early "solid" susceptibility observations claimed the reaching of the ideal paramagnetic susceptibility limit, all contributions of the nuclear spin system of the solid to its heat capacity at these temperatures have been neglected *ab uovo*.<sup>25</sup> The measured heat capacities could be analyzed in terms of a Debye and an Einstein heat capacity, both of which appeared to yield through the volume variations of their respective characteristic temperatures, fairly constant Grüneisen parameters. The constancy of the latter parameters suggested the use of the Debye-Einstein solid model, corrected by these empirical parameters, in evaluating the isobaric expansion coefficient. Clearly, the above model in its form used by Heltemes and Swenson<sup>25</sup> could not but yield positive isobaric expansion coefficients for the solid. These then combined with the Los Alamos liquid  $\text{He}^3$ -solid  $\text{He}^3$  equilibrium data<sup>22</sup> could not but yield isothermal compressibilities  $\chi_{s,T}$  of the solid which had to be larger or at least equal to the isothermal compressibility  $\chi_{L,T}$  of the liquid in equilibrium with the solid along the melting line at  $T > 0.30^\circ\text{K}$ .

The analysis<sup>25</sup> of the thermal properties of solid  $\text{He}^3$  based on the model equation of state which allows only Debye and Einstein excitations to determine the thermal properties at  $T > 0.30^\circ\text{K}$  needs additional justification to be satisfactory. Indeed, we have already attempted to point out in the preceding sections that if the paramagnetic susceptibility of a system was actually shown to be nonideal over a finite range of some state coordinates, such as the temperature for instance, that system cannot become an ideal paramagnetic at finite temperatures, unless it exhibits a magnetic transition process which imposes ideal behavior on it in a discontinuous fashion. If such a transition did not exist, as is the case in the liquid phase according to data available there at the present time, then the ideal limiting behavior of the spin system is an asymptotic one, or, the spin entropy in the solid phase  $S_{s,\sigma}(T,\phi)$  might be expected to be of the same type as  $S_{\sigma^L}[\tau(\phi)]$ , the liquid entropy, at higher temperatures. Hence,

$$S_{s,\sigma}(T,\phi)/R = (\ln 2) \{1 - \sigma[\Theta(\phi)/T]\}, \quad T \gg \Theta, \quad (51)$$

<sup>24</sup> P. W. Bridgman, in *Physics of High Pressure* (G. Bell and Sons, Ltd. London, 1952), p. 215.

<sup>25</sup> E. C. Heltemes and C. A. Swenson, *Phys. Rev.* **128**, 1512 (1962).

where  $\sigma(x)$  is some function of the temperature and another variable of state, through the parameter  $\Theta$ , and  $\sigma$  is such that

$$\lim_{x \text{ small}} \sigma(x) \rightarrow 0. \quad (51a)$$

It should be noted that the dependence of  $\sigma$  on  $T$  and  $p$ , through  $\Theta/T$  in (51) is strictly illustrative inasmuch as the actual high temperature behavior of  $S_{s,\sigma}$  is unknown at the present time. On the basis of (51), it is of course possible that, to a fair degree of approximation, at some value of  $T$ ,  $T \gg \Theta$ ,  $S_{s,\sigma}$  may be close to  $R \ln 2$ , the approach being necessarily from below. However, it is seen that along an isobar,

$$C_{\sigma,p}^{(s)}(T,p)/R = (\ln 2)(\Theta/T)\sigma'(\Theta/T), \quad (52)$$

$$\sigma'(x) = d\sigma/dx > 0,$$

and along an isotherm,

$$\begin{aligned} (\partial S_{s,\sigma}/\partial p)_T &= -(R \ln 2)T^{-1}\sigma'(\Theta/T)(\partial\Theta/\partial p)_T \\ &= (-)(C_{\sigma,p}^{(s)}(\Theta/T)/\Theta)(\partial\Theta/\partial p)_T. \end{aligned} \quad (53)$$

Hence, the spin heat capacity and spin expansion coefficient, the latter proportional to  $(-)(\partial S_{s,\sigma}/\partial p)_T$ , may not have approached their limiting vanishing values close enough. If the heat capacity and expansion coefficient arising with the degrees of freedom other than spin are quite small, which appears to be the case over a range of temperatures even at  $T > 0.30^\circ\text{K}$ , the contributions of the type (52) and (53) of the spin system to the thermal properties of the solid cannot be ignored. Stated in other terms, the analysis of Heltemes and Swenson<sup>25</sup> is based on the implicit assumption that the derivatives of an asymptote may be substituted for the asymptotes of the derivatives, an assumption which needs to be closely justified to be acceptable in the case of the spin system of solid  $\text{He}^3$ . It would seem then that the preceding considerations, while essentially qualitative, tend to set aside, at the present time, the tentative conclusions reached<sup>25</sup> on the thermal properties of solid  $\text{He}^3$  resulting from an analysis which totally ignores the possible intervention of the nuclear spin system even at  $T \gtrsim 0.30^\circ\text{K}$ . Unless and until satisfactory proof is provided for the justified omission of the effects of the spin system on the thermal properties of solid  $\text{He}^3$ , the problem posed by the latter remains more widely open than it ever was.

It should equally be noted that at  $T \geq 1.0^\circ\text{K}$ , the apparent solid compressibilities

$$\chi_{s,M} = -V_s^{-1}(dV_s/dp_M),$$

with the derivatives taken along the phase boundary line, and resulting from the Grilly, Mills and Sydorik work<sup>19,22</sup> on phase equilibrium, have not been confronted with the liquid isothermal compressibility determinations of Sherman and Edeskuty.<sup>20</sup> The extensive liquid  $\text{He}^3$  equation of state data of these workers at  $T \geq 1.0^\circ\text{K}$ , up to and including the melting line, must

have escaped, we presume, the attention of Heltemes and Swenson.<sup>25</sup> Actually, the Sherman-Edeskuty isothermal compressibilities of the liquid along the melting line, at  $T \geq 1.0^\circ\text{K}$ , are larger or at least equal to the solid compressibilities indicated by Heltemes and Swenson.<sup>25</sup> Clearly, an assessment of the precision of these compressibilities appears to be quite difficult. Also, as shown recently with Dr. Mills,<sup>26</sup> the derivative  $(dV_s/dp_M)$  is singular at  $T_a$ , and the problem of the thermal properties of the solid at and around the melting curve minimum are far from being settled. It is equally worth noting that Grilly and Mills<sup>19</sup> were the first to point out that at melting pressures,  $p_M \geq 50$  atm, there were indications of the extreme closeness of the liquid and solid  $\text{He}^3$  isothermal compressibilities along the phase separation line.

The preceding studies clearly suggest the importance of direct measurements of the solid  $\text{He}^3$  expansion coefficients and compressibilities along the melting line. These should be helpful toward an understanding of the equilibrium between solid  $\text{He}^3$  and the thermally anomalous liquid  $\text{He}^3$ , a problem which was stated in fairly general terms by us recently<sup>27</sup> in connection with  $\text{He}^4$ .

### 5.3. The Entropy Diagram of $\text{He}^3$

With the approximate liquid and solid entropies derived above at the low temperatures, and the entropies of these phases at  $T \geq 1.0^\circ\text{K}$  which became available some time ago through the saturated liquid entropy,<sup>18</sup> the entropies of compression<sup>20</sup> and the entropy changes on solidification,<sup>19,22</sup> it is possible to sketch the principal lines of the entropy diagram of  $\text{He}^3$ . We will limit ourselves here to the entropy-pressure or  $(S,p)$  diagram.

One of the simplest lines of this diagram refers to the entropy of the saturated liquid,  $S_L(p_s)$  which has as its tangent at the origin of the diagram the  $S$  axis itself. The singularity of the pressure slope  $dS_L(p_s)/dp_s$  is imposed essentially by the nuclear spin system. Indeed, one has

$$\begin{aligned} dS_L/dp_s &= (\partial S_L/\partial p)_T + (\partial S_L/\partial T)_p / (dp_s/dT) \\ &= -V_{L,s}\alpha_{L,p} + C_{L,p}/T(d p_s/dT), \end{aligned} \quad (54)$$

where  $p_s$  refers to the saturation vapor pressure,  $V_{L,s}$  the liquid volume,  $\alpha_{L,p}$  its isobaric expansion coefficient and  $C_{L,p}$  its constant pressure heat capacity at the saturation line. By the Nernst theorem,

$$\lim_{T \rightarrow 0} \alpha_{L,p} \rightarrow 0, \quad \lim_{T \rightarrow 0} (dp_s/dT) \rightarrow 0, \quad (55)$$

while, the theory of the spin system requires that

$$\lim_{T \rightarrow 0} (C_{L,p}/T) \rightarrow \text{const}. \quad (56)$$

<sup>26</sup> L. Goldstein and R. L. Mills, Phys. Rev. **128**, 2479 (1962).

<sup>27</sup> L. Goldstein, Phys. Rev. **122**, 726 (1961); **128**, 1520 (1962).

Hence, (51) yields

$$\lim_{T \rightarrow 0} (dS_L/dp_s) \rightarrow +\infty. \quad (57)$$

The  $S_L(p_s)$  curve rises thus steeply and increases monotonically to some finite large value, around  $2R$ , at the critical pressure,  $p_c \sim 1.15$  atm.

An interesting if auxiliary line of this  $(S, p)$  diagram is the straight line  $p = p_M(T_a)$ , which is tangent to the entropy curve of the liquid  $S_L(p_M)$  along the melting line  $P_M(T)$  at the minimum melting pressure  $p_M(T_a)$ . Using again the thermodynamic relation equivalent to (54), along the melting line,

$$dS_{L,M}(p)/dp = -V_L(p_M)\alpha_{L,p}(p_M) + C_{L,p}/T(dp_M/dT), \quad (58)$$

one has, with  $\alpha_{L,p}$  and  $C_{L,p}$  being finite at  $p_M(T_a)$ ,

$$\begin{aligned} \lim_{p \rightarrow p_M(T_a+)} (dS_{L,M}/dp_M) &\rightarrow +\infty, \\ \lim_{p \rightarrow p_M(T_a-)} (dS_{L,M}/dp_M) &\rightarrow -\infty, \end{aligned} \quad (59)$$

or the pressure slope of  $S_{L,M}$  has an infinite jump at  $p_M(T_a)$ ,

$$\Delta(dS_{L,M}/dp_M)_{T_a} = (dS_{L,M}/dp_M)_{T_a+} - (dS_{L,M}/dp_M)_{T_a-} \rightarrow \infty. \quad (60)$$

This shows how the melting line anomaly carries over into the entropy diagram through the singularities (59) of the pressure derivatives of  $S_{L,M}$  at  $p_M(T_a)$ . The  $S_{L,M}$  or  $S_L(p_M)$  curve has a vertex with a vertical tangent at  $p_M(T_a)$ .

The  $S_{L,M}$  line resembles a wide mouthed parabolic curve whose upper branch at  $S_{L,M} > S_L[p_M(T_a)]$  decreases uniformly with pressure toward its vertex. The entropy  $S_L[p_M(T_a)]$  is still somewhat uncertain. Estimates based on entropies of the compressed liquid evaluated with incomplete constant pressure heat capacities of still exploratory character<sup>28,9</sup> locate  $S_L[p_M(T_a)]$  at values close to  $R \ln 2$ , within rather generous limits ( $\pm \delta S$ ). At any rate, the osculating parabola of  $S_{L,M}(p)$  at its vertex is

$$S_{L,M}^2(p) - S_{L,M}^2[p_M(T_a)] = \bar{\omega}[p - p_M(T_a)], \quad (61)$$

$\bar{\omega}$  standing for a constant.

It is seen in Table II that at about  $0.02^\circ\text{K}$  the melting pressure reaches some 33 atm, approximately, and the entropy of the liquid has decreased from about  $0.4R$ , at  $0.10^\circ\text{K}$  or 31 atm to about  $0.1R$  at  $0.02^\circ\text{K}$  or 33 atm, or by a factor of about four over a pressure interval of 2 atm. Now, whether the melting line  $p_M(T)$  has contortions or not at  $T < 0.02^\circ\text{K}$ , the nuclear spin system of the liquid imposes again a singular behavior on the

<sup>28</sup> M. Strongin, G. O. Zimmerman, and H. A. Fairbank, in *Proceedings of the Eighth International Conference on Low Temperature Physics and Chemistry, London, 1962* (Butterworths Scientific Publications, Ltd., London, to be published).

pressure slope ( $dS_{L,M}/dp$ ) in the limit of the absolute zero. Using (58), the first term on the right-hand side may be omitted because of the vanishing of  $\alpha_{L,p}(p_M)$  at  $T \rightarrow 0$ . In the second term, with  $C_{L,p}$  being the sum of the two positive definite partial heat capacities  $C_{\sigma,p}^{(L)}$  and  $C_{n\sigma,p}^{(L)}$ , the term with the spin heat capacity yields

$$\lim_{T \rightarrow 0} (C_{\sigma,p}^{(L)}/T) \rightarrow \text{const.},$$

and with it

$$\lim_{T \rightarrow 0} (dS_{L,M}/dp) \rightarrow -\infty, \quad (62a)$$

if  $p_M(T)$  approaches  $p_M(0)$  monotonically from below, while

$$\lim_{T \rightarrow 0} (dS_{L,M}/dp) \rightarrow +\infty, \quad (62b)$$

if  $p_M(T)$  approaches  $p_M(0)$  from above. The branch of  $S_L(p_M)$  at  $S_{L,M} \leq S_L[p_M(T_a)]$  decreases monotonically in case (62a), inside the pressure interval  $p_M(T_a) \leq p \leq p_M(0)$ , with vertical tangents at both ends of this interval. If  $S_{L,M}$  did not decrease monotonically in this pressure interval, its derivative must have at least one singularity inside it, in addition to those at the limits of the interval.

The region reserved to the liquid phase of the  $(S, p)$  plane is thus included between the finite  $S(p_s)$  arc, the pressure axis and the  $S_{L,M}(p)$  curve. The interesting family of entropy lines of this region is that of the isotherms  $S_L(p, T)$ . These isotherms form three groups. Those of the lowest temperature, group I, are anomalous throughout the length of their finite arcs. They start at  $S(p_s)$  to increase monotonically until they reach the  $S_{L,M}(p)$  line. If  $T_a(p_s)$  is the temperature at which the locus of vanishing isobaric expansion coefficients reaches the saturation line, the group I isotherms are such that

$$(\partial S_L/\partial p)_{T \leq T_a(p_s)} \geq 0; \quad \alpha_{L,p}(T, p) \leq 0, \quad T \leq T_a(p_s). \quad (63a)$$

The isotherms of group II are normal over part of their finite arcs, and anomalous over the rest of their arcs. These isotherms have as their limiting curve the one which starts out at  $p_s(T_a)$  with a vanishing tangent; those of  $T > T_a(p_s)$  leave  $S_L(p_s)$  with normal or negative slopes. The latter increase toward zero to become positive and stay positive until they reach the  $S_{L,M}(p)$  line. These are such that

$$\begin{aligned} (\partial S_L/\partial p)_{T=T_a(p_s)} &= 0; \quad (\partial S_L/\partial p)_T < 0, \\ T_a(p_s) \leq T \leq T_a(p), \quad (\partial S_L/\partial p)_T &> 0, \\ T_a(p) \leq T \leq T_a(p_M), \end{aligned} \quad (63b)$$

where  $T_a(p)$  is the locus of vanishing  $\alpha$ 's or that of the minimas of  $S_L(p)$ , at  $p_s(T_a) \leq p \leq p_M(T_a)$ . While the first member of this group leaves  $S_L(p_s)$  with vanishing pressure slope, its last member reaches  $S_{L,M}(p)$  with a vanishing slope. These isotherms are those of  $0.50$  and  $1.25^\circ\text{K}$  with  $p_s(T_a)$  and  $p_M(T_a)$  being, respectively,



almost vanishing and about 47.5 atm. Finally, the isotherms of  $T \gtrsim 1.25^\circ\text{K}$ , group III, all decrease monotonically to end on  $S_{L,M}(p)$ , at  $T > 1.25^\circ\text{K}$ ,  $p_M > 47.5$  atm.

In contrast with the region of the  $(S,p)$  plane reserved to the liquid phase, the region associated with the solid phase is as yet essentially unexplored. As was the case with  $S_{L,M}(p)$ ,  $S_{s,M}(p)$  is only known over finite arcs. We have in Table II the approximate lower limit entropies of the solid along the melting line over the intervals of  $0.02$ – $0.10^\circ\text{K}$ , and the pressure range of  $30.9$  to about  $32.9$  atm. At  $0.10^\circ\text{K}$ ,  $S_{s,M}(p)$  may be in the range of  $0.66$ – $0.68R$ , and at  $0.02^\circ\text{K}$ , this entropy has decreased to about  $0.53$ – $0.55R$ . The entropy branch of the solid at  $S_{s,M} < S_{s,M}[p_M(T_a)]$ , between  $0.10^\circ\text{K}$  and  $0.32$ – $0.33^\circ\text{K}$ , or  $T_a$ , and over the pressure interval of about  $2$  atm, increases from  $0.66$ – $0.68R$  to  $S_{L,M}[p_M(T_a)]$ , which may be close to  $R \ln 2$ , or  $0.69R$ , a very small change indeed. At the present time, the Los Alamos equation of state data<sup>18–20,22</sup> yield  $S_{s,M}(p)$  values between  $1.0$  and  $2.0^\circ\text{K}$  varying from about  $0.71R$  to  $0.75R$ , approximately. Assuming here that the spin entropy is close to its asymptotic limit, the nonspin entropy of  $0.02R$  to  $0.06R$  appears to be compatible with phonon entropy if due account is taken of the expected increase of the characteristic temperature of the phonons over the above temperature range, or the pressure range from  $39$  to about  $76$  atm, or the volume interval of  $23.5$  to  $21.0$  cm<sup>3</sup>/mole, approximately, according to the Los Alamos data.<sup>19,20,22</sup> The upper branch of the solid entropy  $S_{s,M}(p)$  will have to decrease from about  $0.71R$ , at  $1.0^\circ\text{K}$ , to the value of  $S_{L,M}[p_M(T_a)]$ , the entropy at the vertex of  $S_{L,M}(p)$  at  $T_a$ . If the latter is close to  $R \ln 2$ , it is seen that over the rather wide temperature range ( $1.0$ – $0.33^\circ\text{K}$ ), and the pressure interval, between  $39$  and  $29$  atm, the entropy change is quite small. In the  $(S,p)$  diagram then the approach of the lower and upper branches of  $S_{s,M}$  toward the vertex  $S_{L,M}[p_M(T_a)]$ , as well as the way these two branches of the solid entropy join remains undetermined at the present time.

The upper and lower branches of  $S_{s,M}$  form the boundary of a very narrow strip of the  $(S,p)$  plane on both sides of  $S_L = S_M[p_M(T_a)]$ , and over the indicated temperature and pressure ranges. If they joined smoothly at the vertex at  $p_M(T_a)$ , the  $S_{L,M}$  and  $S_{s,M}$  curves would have a first order contact at the common vertex. To the extent that one defines, in this affine plane, a curvature or radius of curvature, through the

use of homogeneous coordinates possibly, the smooth joining of the two branches of  $S_{s,M}$  would be accompanied by a very large curvature at the vertex. If these two branches did not join smoothly, then with Eq. (58) written for the solid,

$$dS_{s,M}(p)/dp = (\partial S_{s,M}/\partial p)_T + C_{s,p}/T(dp_M/dT), \quad (58a)$$

it is seen that with finite derivatives,

$$(dS_{s,M}/dp)_{p_M(T_{a\pm})} \geq 0, \quad (59)$$

at  $p_M(T_{a+})$  and  $p_M(T_{a-})$ , the constant pressure heat capacity should be such that the second term on the right-hand side be finite, its denominator vanishing at  $p_M(T_a)$ . It is assumed here that the expansion coefficient of the solid is finite at  $T_a$ . This then raises the problem of the behavior of the constant pressure heat capacity of the solid, or of that of its isobaric expansion coefficient at  $p_M(T_a)$ . Strictly speaking, at  $T_a$  and  $p_M(T_a)$  the constant pressure heat capacity of the solid cannot be defined directly, since at the isobar of  $p_M(T_a)$  the solid exists only at a single point of state coordinates  $[p_M(T_a), V_M(T_a), T_a]$ . As discussed by us recently<sup>29</sup> the constant pressure heat capacity at  $p_M(T_a)$  could be defined through a limiting process. The same problem arises with  $(\partial S_{s,M}/\partial p)_T$  at  $p_M(T_a)$ . If the latter is finite,  $C_{s,p}$  would have to vanish at  $p_M(T_a)$ , a situation difficult to contemplate since  $C_{s,p}$  at  $V_M(T_a)$  seems to be finite, the  $V_M(T_a)$  isochore being a finite arc.<sup>26</sup> With the expansion coefficient or  $(\partial S_{s,M}/\partial p)_T$  being finite, the needle shaped  $S_{s,M}$  curve at the approach of the vertex  $S_{L,M}(T_a)$  with (59), or with a cusp of vanishing slope at the vertex, appears unlikely at the present time.

These discussions emphasized the importance of experimental investigations of the low pressure solid He<sup>3</sup> in the vicinity of the melting line over a wide temperature range. A clarification of the solid entropy curve in the pathological region of the melting pressure minimum appears to be of particular interest.

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<sup>29</sup> L. Goldstein, Ann. Phys. (N. Y.) **16**, 205 (1961).