

Production of Very Low Temperatures with the Dense Phases of Helium Three

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The melting anomaly of He^3 enables one to produce very low temperatures through adiabatic solidification. Exchange effects in the solid are expected to prevent the reaching of temperatures very much below the one defined by the exchange-energy parameter, where the melting anomaly should cease. Relaxation-time measurements in the solid define this parameter within the limitations of the assumed exchange-interaction scheme, as well as of those of the formalism which connects the coupling scheme with the relaxation times. With the empirical exchange parameter, the entropy of the solid at melting can be obtained down to quite low temperatures. This entropy combined with that of the liquid, available from an earlier theory of this phase, enables one to calculate the melting-pressure line, essentially from fundamentals. The agreement between the theoretical melting-pressure line and the available data at low and medium temperatures is satisfactory. The theoretical melting line has an inflection point, outside the range of measurements, due to the magnetic ordering process imposed by the assumed interaction scheme. The most promising way of verifying this prediction, at temperatures well above the ordering temperature, appears to be through the observation of the crossing of the heat-capacity curves of the liquid and solid at or near melting. The theoretical entropies of the two phases suggest that in starting with liquid He^3 at saturation and at an easily accessible temperature, adiabatic compression alone ensures, in principle, the reaching of quite low temperatures. This process is discussed in detail, and its use toward reaching temperatures in the millidegree range will be described. An analysis of the thermal anomalies of low-pressure solid He^3 due to the assumed exchange coupling will be presented. At melting these anomalies should extend up to near 0.25°K . The solid at and near melting is shown to exhibit a narrow entropy wedge over a fairly wide pressure range around the melting-line minimum. With its spin entropy being practically complete at 0.1°K , solid He^3 should have very small derivative thermal properties, expansion coefficient, and heat capacity over a fairly wide temperature and pressure range. The expansion coefficient at or near melting is estimated to vanish, and to become negative, somewhat below 0.25°K . This technically difficult region of the thermal properties extends down to a few hundredths of a degree, below which the thermal anomalies of the low-pressure solid should increase rapidly to become more accessible to observations and measurements.

1. INTRODUCTION

THE interesting prediction of the possibility of producing extremely low temperatures, below the microdegree range, through adiabatic solidification of He^3 , due to Pomeranchuk,¹ was shown to be founded² on completely neglecting exchange effects in the solid. The latter phenomenon determines the smooth spin-ordering process in the liquid phase.³ It also ensures the dominance of the nuclear-spin system in the thermal properties of the liquid at temperatures where the average thermal energy per atom is of the same order of magnitude or less than the characteristic exchange energy per atom in this nonideal nuclear paramagnetic system.⁴ In the anomalous liquid-solid transformation which would enable one to reach very low temperatures, it was assumed¹ that the solid remained an ideal nuclear paramagnet down to extremely low temperatures. This is, of course, equivalent to assuming that solid He^3 exhibits complete spin disorder down to extremely low temperatures, less than a microdegree. The persistence of the ideality of the spin system, if real, would represent an extreme statistical thermodynamic situation. Indeed, in order for it to be significant or

observable, one had to imply that there exist efficient mechanisms of energy exchange and, hence, interactions within the nuclear-spin system, as well as between this system and the degrees of freedom of the solid other than spin, for the reaching of temperature equilibrium and the measurement or verification of the predicted equilibrium magnetic properties. Simultaneously, the effective switching-off of these interactions had to be accounted for, once equilibrium has been established. And this occurs at extremely low temperatures, where the thermal energy may be of similar or even lower order of magnitude than the interaction energies responsible for the eventual reaching of equilibrium. It appeared rather difficult, to say the least, to satisfy these various and contradictory requirements imposed upon the formal description of this system. These types of problems arising in connection with the predicted¹ accessibility of extremely low temperatures have been, apparently, completely ignored.

On the other hand, the characteristic spin ordering or exchange energies have also been grossly overestimated.^{5,6} The origin of one of these estimates⁵ was connected with nuclear susceptibility data at medium temperatures which, though attributed to the solid

¹ I. Pomeranchuk, *Zh. Eksperim. i Teor. Fiz.* **20**, 1919 (1950).

² H. Primakoff, *Bull. Am. Phys. Soc.* **2**, 63 (1957).

³ L. Goldstein and M. Goldstein, *J. Chem. Phys.* **18**, 538 (1950).

⁴ L. Goldstein, *Phys. Rev.* **96**, 1455 (1954); **102**, 1205 (1956).

⁵ L. Goldstein, *Ann. Phys. (N.Y.)* **8**, 390 (1959).

⁶ N. Bernardes and H. Primakoff, *Phys. Rev. Letters* **2**, 290 (1959); **3**, 144 (1959); *Phys. Rev.* **119**, 968 (1960).

phase,⁷ referred to a liquid–solid mixture with probably very small solid content. The other estimate⁶ resulted from an attempt to calculate directly the exchange energy of pairs of atoms in the solid interacting through their mutual Van der Waals potential energy. Recent experimental determinations of nuclear spin–spin and spin–lattice relaxation times in solid He³, over a wide pressure or volume range, by two groups of workers,^{8,9} have yielded possibly fair approximations to the exchange energy. Within the limitations of the fairly complex formalism which allows one to derive from relaxation times—on the basis of an assumed exchange-coupling scheme—the exchange-energy parameter in a specified state of the solid, the thermal properties of the latter also become formally available. Subject to these limitations, the analysis of the liquid–solid equilibrium becomes formally accessible, and its use toward a detailed theoretical description of processes which may allow the reaching of very low temperature, limited though downward, becomes possible.

The thermal properties of the liquid will be described here with the help of the formalism elaborated earlier^{4,5} and the ensuing universal character of the spin system of the liquid.^{10,11} We discuss first the constant-spin-entropy transformations in the liquid phase; this is complemented by the consideration of transformations at constant total entropy which alone are observable. At low enough temperatures, the latter process is well approximated by the former. These adiabatic transformations in the liquid are of a preparatory character, since the actual production of very low temperatures involves an adiabatic solidification process in the two-phase system. The quantitative description of the adiabatic solidification phenomenon requires the knowledge of the entropy of the liquid $S_{L,M}(T)$ and of the solid $S_{s,M}(T)$ along the melting line, where these phases are in equilibrium with each other. With the empirically estimated exchange parameter of the solid, subject to the assumed interatomic coupling scheme, its thermal properties, including its entropy, can be evaluated exactly. The theory of the melting line of He³ thus acquires a solid foundation. With the start of the rapid decrease of the entropy of the solid from its asymptotic high-temperature limit, estimated with fair approximation, one locates the temperature, accessible experimentally without excessive effort, where the inflection point of the melting line determines qualitatively the

impending spin-ordering transformation in the solid and, with it, the approximate lower limit of the temperature that can be produced with He³. The assumed exchange-coupling scheme in the solid, with the empirical pressure variation of the exchange parameter, discloses the region of the thermally anomalous low-pressure solid. An additional anomaly of this solid will be shown to correspond to its having a peculiar narrow entropy wedge where both temperature and pressure variations are very small, thus ensuring very small heat capacity and expansion coefficient of the solid around its anomalous melting-pressure minimum.

2. TRANSFORMATIONS AT CONSTANT ENTROPY IN LIQUID He³

The nuclear-spin system of liquid He³ was shown to contribute the component spin-entropy^{4,5}

$$S_\sigma(T, p)/R = (\ln 2)[\chi(T, p)/\chi_0(T, p)], \quad (1)$$

to the total entropy of this liquid in the state with thermodynamic coordinates of temperature T , pressure p , and volume V , connected by the equation of state of the liquid. In (1), R is the gas constant, $\chi(T, p)$ the nuclear paramagnetic susceptibility of the liquid, and $\chi_0(T, p)$ the susceptibility it would have if it were an ideal Curie-Langevin paramagnetic system. A fundamental property of S_σ or (χ/χ_0) is their universal character,¹⁰ that is,

$$S_\sigma(T, p) = S_\sigma[T/T_0(p)], \quad (2)$$

$$\chi(T, p)/\chi_0(T, p) = r[T/T_0(p)]. \quad (3)$$

The entropy S_σ or the susceptibility ratio r are universal functions of the reduced temperature $[T/T_0(p)]$, with $T_0(p)$ being the characteristic temperature of the nuclear-spin system. As discussed earlier,^{4,5,10} the function $T_0(p)$ is available empirically from susceptibility measurements. We have made use systematically of the empirical, and hence necessarily approximate $T_0(p)$ function obtained by the Duke University workers.¹¹ As emphasized in our previous work,¹⁰ however, the accuracy of this function may improve through new and refined susceptibility measurements.

In virtue of the universal character of S_σ or (χ/χ_0) , a transformation of the liquid at constant spin-entropy, or constant susceptibility-ratio r , must leave constant the argument of S_σ or r , that is, the reduced temperature. Or, if i and f specify the initial and final states of the constant spin-entropy transformation,

$$S_\sigma[T_f/T_0(p_f)] = S_\sigma[T_i/T_0(p_i)], \quad (4)$$

or

$$T_f/T_0(p_f) = T_i/T_0(p_i). \quad (5)$$

The reduced temperature is an adiabatic invariant of the nuclear-spin system of liquid He³. Since $T_0(p)$ is a monotonically decreasing function of the pressure, it is

⁷ W. M. Fairbank and G. K. Walters, *Proceedings of the Symposium on Liquid and Solid He³* (Ohio State University Press, Columbus, Ohio, 1957), Suppl., p. 1.

⁸ R. C. Richardson, E. Hunt, and H. Meyer, *Phys. Rev.* **138**, A1326 (1965). For a correction see R. C. Richardson, A. Landesman, E. Hunt, and H. Meyer, *Phys. Rev.* **146**, 244 (1966).

⁹ H. G. Richards, J. Hatton, and R. P. Giffard, *Phys. Rev.* **139**, A91 (1965).

¹⁰ L. Goldstein, *Phys. Rev.* **133**, A52 (1964).

¹¹ A. L. Thomson, H. Meyer, and E. P. Adams, *Phys. Rev.* **128**, 509 (1962); cf. also H. T. Beal and J. Hatton, *ibid.* **139**, A1751 (1965).

seen that in a constant spin-entropy transformation through compression, $p_f > p_i$, one obtains

$$T_f = T_i [T_0(p_f)/T_0(p_i)] < T_i, \quad (6)$$

since

$$T_0(p_f) < T_0(p_i), \quad p_f > p_i. \quad (7)$$

Such a transformation is thus accompanied by cooling, which is one aspect of the fundamental thermal anomaly of the nuclear-spin system.

In a differential compression process, at constant spin-entropy, one obtains with (6), and

$$\begin{aligned} T_f &= T + \Delta T, & p_f &= p + \Delta p, & S &= S_\sigma(T, p), \\ \lim_{\Delta p \rightarrow 0} (\Delta T/\Delta p)_{S_\sigma} &= (dT/dp)_{S_\sigma} \\ &= [T/T_0(p)] [dT_0(p)/dp] < 0, \end{aligned} \quad (8)$$

because of the indicated property of $T_0(p)$, or

$$dT_0(p)/dp < 0. \quad (9)$$

With

$$\begin{aligned} dS_\sigma(T, p) &= (\partial S_\sigma/\partial T)_p dT + (\partial S_\sigma/\partial p)_T dp \\ &= 0, \end{aligned} \quad (10)$$

one obtains, at once, with (8),

$$(\partial S_\sigma/\partial p)_T > 0, \quad (11)$$

since $(\partial S_\sigma/\partial T)_p$ or $(C_{\sigma,p}/T)$, the constant-pressure spin-heat capacity is positive definite at finite T . In other words, the characteristic anomaly of the spin system given by (8) has its complementary aspect, namely isothermal compression accompanied by spin-entropy generation according to (11).

With regard to the monotonically decreasing variations of $T_0(p)$ it is to be noted that, although an early attempt at an asymptotic-type evaluation of the exchange-energy parameter^{3,4} led to a considerable overestimation of this quantity and the associated characteristic temperature, the pressure or volume dependence of the asymptotic $T_0(p)$ function did correspond qualitatively to the observed variations over the physically relevant interatomic separations in liquid He³.

The anomalous spin-entropy increase on isothermal compression expressed by (11) is compensated by the normal decrease of thermal disorder of the nonspin degrees of freedom on isothermal compression. In the present formalism of the theory of liquid He³, the total entropy of the liquid is given by

$$\begin{aligned} S(T, p) &= S_\sigma(T, p) + S_{n\sigma}(T, p) \\ &= S_\sigma[T/T_0(p)] + S_{n\sigma}(T, p). \end{aligned} \quad (12)$$

In a constant-entropy transformation, one must have

$$\begin{aligned} S_\sigma[T_i/T_0(p_i)] + S_{n\sigma}(T_i, p_i) \\ = S_\sigma[T_f/T_0(p_f)] + S_{n\sigma}(T_f, p_f), \end{aligned} \quad (13)$$

which is only an implicit relation between T_i and T_f ,

since the exact form of $S_{n\sigma}(T, p)$ is lacking at the present time. Nevertheless, we could show earlier¹² that $S_{n\sigma}(T, p)$ must be of normal pressure variation, or

$$[\partial S_{n\sigma}(T, p)/\partial p]_T < 0, \quad (14)$$

and, equivalently, one must have

$$(\partial T/\partial p)_{S_{n\sigma}} > 0. \quad (15)$$

Furthermore, we could prove recently¹³ that the nonspin entropy does not have universal character, in contrast with the spin entropy. This means that $S_{n\sigma}(T, p)$ cannot be represented by a unique function throughout the whole phase diagram of liquid He³, whereas $S_\sigma[T/T_0(p)]$ is a universal function of the reduced temperature. In an adiabatic compression process, that is, a transformation at constant total entropy which alone is accessible experimentally, one has, in virtue of the equation-of-state

$$f(S, T, p) = 0, \quad (16)$$

$$(\partial S/\partial T)_p (\partial T/\partial p)_S (\partial p/\partial S)_T = -1. \quad (17)$$

Hence, with $C_{\sigma,p}$ and $C_{n\sigma,p}$ referring to the respective components of the constant-pressure heat capacity, one has with (12)

$$\begin{aligned} (\partial T/\partial p)_S \\ = -[T/(C_{\sigma,p} + C_{n\sigma,p})] [(\partial S_\sigma/\partial p)_T + (\partial S_{n\sigma}/\partial p)_T] \\ = [TV/(C_{\sigma,p} + C_{n\sigma,p})] [\alpha_\sigma(T, p) + \alpha_{n\sigma}(T, p)], \end{aligned} \quad (18)$$

where $-(\partial S_\sigma/\partial p)_T$ and $-(\partial S_{n\sigma}/\partial p)_T$ have been replaced by $(V\alpha_\sigma)$ and $(V\alpha_{n\sigma})$, respectively. The α 's are the components of the isobaric expansion coefficients.^{4,5,12} With

$$\alpha_\sigma \leq 0, \quad \alpha_{n\sigma} \geq 0, \quad (19)$$

i.e., with the nuclear-spin system being thermally anomalous at finite temperatures and the system of degrees of freedom other than spin being normal,¹² the locus $T_\alpha(p)$, which is the root of the equation

$$\alpha_0(T, p) + \alpha_{n\sigma}(T, p) = 0, \quad (20)$$

defines two regions in the various phase diagrams. In the region $T < T_\alpha(p)$ in the (p, T) diagram, where the liquid is thermally anomalous, the thermal properties of the nuclear-spin system are dominant. In the region $T > T_\alpha(p)$ the normal nonspin degrees of freedom become dominant and the liquid exhibits normal thermal properties. Hence,

$$\begin{aligned} (\partial T/\partial p)_S \leq 0, \quad T \leq T_\alpha(p), \\ p_{\text{sat}} \leq p \leq p_M, \end{aligned} \quad (21)$$

or, the locus $T_\alpha(p)$ is also the locus of points where the temperature remains stationary on differential adiabatic compression.

¹² L. Goldstein, Phys. Rev. **112**, 1483 (1958); **117**, 375 (1960).

¹³ L. Goldstein, Phys. Rev. **148**, 108 (1966).

Using Eq. (18) the temperature variations on adiabatic compression can be represented as the linear superposition of two component processes. These are

$$(\partial T/\partial p)_{S_{\sigma}, S} = -(T/C_p)(\partial S_{\sigma}/\partial p)_T < 0,$$

and

$$(\partial T/\partial p)_{S_{n\sigma}, S} = -(T/C_p)(\partial S_{n\sigma}/\partial p)_T > 0, \quad (22)$$

where the double subscripts serve to distinguish the terms in the decomposition (18) from the effect described by (8), where the spin system is described as an autonomous subsystem representing approximately the total system as far as cooling on adiabatic compression is concerned. With the total constant-pressure heat capacity

$$C_p(T, p) = C_{\sigma, p}[T/T_0(p)] + C_{n\sigma, p}(T, p), \quad (23)$$

which appears in (18), one has with (22), for the component derivatives,

$$\begin{aligned} (\partial T/\partial p)_{S_{\sigma}, S} &= -(T/C_{\sigma, p})(\partial S_{\sigma}/\partial p)_T \\ &\quad \times [1/1 + (C_{n\sigma, p}/C_{\sigma, p})], \\ &= (\partial T/\partial p)_{S_{\sigma}} [1/1 + (C_{n\sigma, p}/C_{\sigma, p})] \\ &\quad < (\partial T/\partial p)_{S_{\sigma}}, \end{aligned} \quad (24a)$$

$$\begin{aligned} (\partial T/\partial p)_{S_{n\sigma}, S} &= (\partial T/\partial p)_{S_{n\sigma}} [1/1 + (C_{\sigma, p}/C_{n\sigma, p})] \\ &\quad < (\partial T/\partial p)_{S_{n\sigma}}. \end{aligned} \quad (24b)$$

These relations describe a situation encountered previously in the application of the theory of the nuclear-spin system to derivative thermal properties of liquid He³. Namely, the formal statistical-thermodynamic approach^{4,5,12} to the equilibrium thermal properties of liquid He³, based on the linear superposition of the component entropies of the spin system and of the system of nonspin degrees of freedom, Eq. (12), ceases to yield separable derivative thermal properties, as shown by Eqs. (24).

In the limit of low temperatures and higher pressures, one has,^{4,5} with T small referring to $T \lesssim T_0(p)$,

$$\lim_{T \text{ small, } p \gg p_{\text{sat}}} S_{\sigma}(T, p) \gg S_{n\sigma}(T, p), \quad (25)$$

and

$$\lim_{T \text{ small, } p \gg p_{\text{sat}}} C_{\sigma}(T, p) > C_{n\sigma}(T, p), \quad (26a)$$

and along the melting-pressure line $p_M(T)$,

$$\lim_{T \text{ small, } p \rightarrow p_M} C_{\sigma}(T, p) \gg C_{n\sigma}(T, p). \quad (26b)$$

Hence, by (24), one finds

$$\begin{aligned} \lim_{T \text{ small, } p \rightarrow p_M} (\partial T/\partial p)_{S_{\sigma}, S} &\rightarrow (\partial T/\partial p)_{S_{\sigma}}, \\ \lim_{T \text{ small, } p \rightarrow p_M} (\partial T/\partial p)_{S_{n\sigma}, S} &\rightarrow (\partial T/\partial p)_{S_{n\sigma}} \cdot (C_{n\sigma}/C_{\sigma}) \rightarrow 0. \end{aligned} \quad (27)$$

In these limits, the description of the liquid in terms of linearly superposed subsystems tends to become exact

for the derivatives expressing the differential temperature variations on constant-total-entropy pressure increase.

The thermal anomalies of liquid He³ have been shown to originate with its nuclear-spin system.^{4,5,12} In this system, the ensemble average of the number of spins which have escaped spin blocking or spin ordering due to the exclusion principle and the interatomic couplings, is given by⁴

$$N(T, p)/N_0 = \chi(T, p)/\chi_0(T, p), \quad (28)$$

N_0 being the total number of spins of the system. By virtue of the universal character¹² of the spin fraction (28), or the susceptibility ratio,¹² these quantities depend only on the reduced temperature $T/T_0(p)$, or $\tau(p)$, increasing monotonically with it. One has then

$$\begin{aligned} N(T, p)/N_0 &= N[T/T_0(p)]/N_0 \\ &= r[\tau(p)], \quad \tau(p) = T/T_0(p), \end{aligned} \quad (29)$$

and, on isothermal compression, using (9),

$$\begin{aligned} (\partial/\partial p)_T \{N[T/T_0(p)]/N_0\} &= (dr/dr)(\partial\tau/\partial p)_T \\ &= (-)(dr/dr) \\ &\quad \times [\tau(p)/T_0(p)] [dT_0(p)/dp] > 0. \end{aligned} \quad (30)$$

The number of spins which become free increases because the ordering energy of about $kT_0(p)$ decreases on compression. This behavior was seen to arise, over the relevant interatomic distances in the liquid, with the pressure or volume dependence of the exchange energy^{3,4} of He³ atoms, which are assumed to interact pairwise through their mutual potential. The origin of the characteristic thermal anomaly expressed by Eq. (11) goes back to Eq. (30) or to the increase of the number of free spins on isothermal compression. This fundamental property of the nuclear-spin system finds its extreme manifestation in the adiabatic solidification of liquid He³. In this process, and over a fairly wide temperature range, essentially all of the spins of the liquid become free in the paramagnetic solid, because the spin-ordering energy $kT_{0,s}$ in the solid becomes extremely small in comparison with the energy $kT_{0,L}(p_M)$ in the liquid along the melting line $p_M(T)$. Formally,

$$T_{0,L}(p_M) \gg T_{0,s}(p_M), \quad (31)$$

because of the very much reduced overlap of the localized wave functions of the assumedly pairwise-interacting atoms in the paramagnetic solid. Hence, at temperatures T such that

$$T_{0,s} \ll T \ll \Theta, \quad (32)$$

where Θ is the characteristic temperature of the phonon system of excitations associated with the simple model of the solid phase, one must have, per mole of the solid

$$\lim_{T_{0,s} \leq T \ll \Theta} S_{\sigma, s}(T_M) \simeq R \ln 2, \quad (33)$$

T_M standing for the temperature of the solid at melting, with the additional state coordinates p_M and V_M . It is to be remembered here that approximate Θ values have been obtained recently¹⁴ from heat-capacity measurements on solid He³ at moderate temperatures, $T \gtrsim 0.30^\circ\text{K}$. These measurements imply that along the melting line and over the pressure range relevant for the present work, Θ may be as low as 17–18°K. At the low temperatures of interest here, and along the melting line, the thermal excitations of the solid, and to a large extent those of the liquid also, reduce to spin excitations. At these low temperatures, the latent heat of melting in a constant-temperature and constant-pressure transformation is then the spin latent-heat. Thus

$$\begin{aligned} \lim_{T \rightarrow (T_0, L(p_M))} L_\sigma(T) \\ \simeq T(S_{\sigma, L, M} - S_{\sigma, s, M}) \\ = RT(\ln 2) \{ \chi [T/T_{0, L}(p_M)] / \chi_0(p_M) - 1 \} < 0, \end{aligned} \quad (34)$$

since the susceptibility ratio of the liquid is less than unity. The entropy of the solid $S_{\sigma, s, M}$, as given by Eq. (33), was used here. At increasing temperatures the nonspin degrees of freedom of the liquid at melting also contribute to the entropy, and (34) has to be changed to

$$\begin{aligned} L(T) &\simeq T(S_{L, M} - S_{\sigma, s, M}) \\ &= T(d p_M / d T)(V_{L, M} - V_{s, M}), \quad V_{L, M} > V_{s, M}, \end{aligned} \quad (35)$$

the second line being the Clausius-Clapeyron expression, and $V_{L, M}$ and $V_{s, M}$ standing for the molar volumes of the liquid and solid at the melting pressure $p_M(T)$. The higher-temperature heat-of-melting $L(T)$, Eq. (35), remains anomalous or negative until the melting pressure $p_M(T)$ reaches its minimum¹ at $T_{M\mu}$. Here the entropy of the liquid becomes equal to that of the solid. Approximately, because we neglect the very small phonon-entropy of the solid in comparison with its essentially complete spin-entropy, we have

$$\begin{aligned} S_L(T_{M\mu}) &\simeq S_{\sigma, s}(T_{M\mu}) \\ &= R \ln 2. \end{aligned} \quad (36)$$

In the present work we will limit ourselves essentially to temperatures $T \lesssim T_{M\mu}$. The possibility of reaching very low temperatures is connected with the exploitation of the negative latent-heat of melting.¹ Before considering the problem of the production of very low temperatures with the dense phases of He³, as well as the limitations due to spin or magnetic ordering in the solid, it seems necessary to formulate a theoretical description of solid He³. This then should allow us to give a satisfactory quantitative account of the liquid-

solid equilibrium as well as of the adiabatic solidification phenomenon leading to very low temperatures.

3. THE LIQUID-SOLID EQUILIBRIUM IN He³ AT LOW AND VERY LOW TEMPERATURES: THEORY OF THE MELTING LINE

We have noted above that the possibility of reaching quite low temperatures through adiabatic solidification of He³ required the existence of a negative latent-heat of melting. The region of the He³ phase diagram where this anomaly exists might, however, be limited at low temperatures as a consequence of spin ordering in the solid arising from the exchange interaction between near atoms of spin $\frac{1}{2}$. While direct experimental evidence for such spin ordering in solid He³ is lacking at the present time, indirect evaluation of the exchange parameter in the low-pressure solid, near or at melting, indicates that it may occur at around a few millidegrees, or at a temperature about 100 times lower than the characteristic temperature⁴ of the spin system of saturated liquid He³. The exchange spin-ordering temperature thus is still some 10^3 to 10^4 times larger than the magnetic dipole-dipole ordering temperature which was suggested originally¹ to be the only source of spin- and magnetic-moment ordering in solid He³. If the spin system started to order only around the temperature

$$\begin{aligned} T_{d-d} &\sim \mu^2 / kr \\ &\sim 10^{-8} \text{ }^\circ\text{K}, \end{aligned}$$

μ being the magnitude of the nuclear magnetic-dipole moment of He³, r the nearest-neighbor interatomic separation in the solid, and k the Boltzmann constant, then the spin system would remain completely disordered down to the vicinity of T_{d-d} . The entropy of the solid per mole would thus be

$$S_s = R \ln 2, \quad T \gtrsim T_{d-d}, \quad (37)$$

or, this solid would be an ideal spin- $\frac{1}{2}$ nuclear-paramagnet⁴ down to the vicinity of the extremely low temperature of about T_{d-d} . The incomplete character of the above reasoning, as implied already, consists, in part, of ignoring the existence of those various mechanisms of energy and momentum exchange between the various subsystems of degrees of freedom of the solid that are responsible for the establishment of thermodynamic equilibrium in the solid. Clearly, in the absence of the latter, the indicated equilibrium thermal properties, such as entropy and magnetic susceptibility, lose their meaning.

The small but finite exchange-coupling parameter is compatible with almost complete spin disorder in solid He³ down to quite low temperatures $T_{0, s}$. Also, over the interval

$$\epsilon T_{0, s} < T < T_{M\mu}, \quad \epsilon \lesssim 1, \quad (38)$$

one should have, along the melting line,

$$S_{s, M}(T) > S_{L, M}(T).$$

¹⁴E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

The characteristic temperature $T_{0,s}$ is determined by the strength of the exchange coupling. However, the exact connection between $T_{0,s}$ and the strength of the exchange parameter is not known, in general.

At equilibrium, it appears justified to write the entropy of the solid along the melting line,

$$S_{s,M}(T) = S_{\sigma,s,M}(T) + S_{\varphi,M}(T), \quad (39)$$

as the linear superposition of the entropies of the spin system and of the phonon system of excitations. Over the whole temperature range of interest in the present work, $S_{\varphi,M}$ is completely negligible in comparison with $S_{\sigma,s,M}$ and may be omitted in (39). As the region of high spin heat capacity is approached from the high-temperature side of $T_{0,s}$, (dS_{σ}/dT) becomes quite large, or the entropy of the solid starts falling at a faster rate with decreasing temperature. In an antiferromagnetic system, a hypothetical but plausible behavior of solid He³, it is then reasonable to expect⁶ that over a temperature range where spin excitations correspond approximately to spin waves, one should have, at melting,

$$S_{s,M}(T) < S_{L,M}(T), \\ T \leq T_{M\mu'}, \quad T_{M\mu'} = \epsilon T_{0,s}, \quad \epsilon \lesssim 1. \quad (40)$$

There is thus a temperature $T_{M\mu'}$ where the entropy curves of the liquid and solid cross again, as they did at $T_{M\mu}$, at the higher temperature. This second anomaly of the melting line at very low temperatures arises, in part, because of the linear decrease in temperature of the entropy of the liquid.¹³

For the low-pressure solid He³, whose structure is body-centered-cubic at melting,¹⁵ recent work on the exact high-temperature infinite series representation¹⁶ of the spin susceptibility and heat capacity of a system of exchange-coupled spins, allows one to calculate the melting-pressure line practically from first principles. In the solid, the pairwise coupling of nearest-neighbor spins according to

$$V_{i,j} = -2qJ\mathbf{s}_i \cdot \langle \mathbf{s}_j \rangle, \quad (41)$$

represents their hypothetical mutual potential energy, q being the number of nearest neighbors j of atom i , and $\langle \mathbf{s}_j \rangle$ their averaged spin vector, in units of \hbar , J standing for the exchange-energy parameter. The latter is assumed to be negative, ensuring in antiferromagnetic systems the antiparallel configuration of neighboring spins as the low-potential-energy configuration according to (41). The evaluation of the partition function of the system arising from the interactions (41) is a combinatorial problem, which was solved for high temperatures by Rushbrooke and Wood¹⁶ in various cubic structures.

The low-magnetic-field susceptibility in the above system results from the evaluation of the corresponding

¹⁵ A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. **110**, 775 (1958).

¹⁶ G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958); **6**, 409 (1963).

partition function in presence of a constant homogeneous field \mathbf{H} arising from the Hamiltonian

$$H_M = \sum_{\langle i,j \rangle} V_{i,j} - g\mu \sum_i \mathbf{s}_i \cdot \mathbf{H}, \quad (42)$$

where $\langle i, j \rangle$ refers to nearest neighbors, the i summations extending over the whole system. The field-dependent term commutes here with the direct coupling term, ($g\mu\mathbf{s}_i$) is the elementary magnetic-dipole moment vector of atom i , μ being a relevant unit moment, and g the splitting factor associated with the spins s_i . At high temperatures, $T > J/k$, in ferromagnetic systems, and at $T > |J|/k$, in antiferromagnetic systems, the exact or incomplete series representations in (J/kT) have been worked out,¹⁶ as briefly mentioned, in the three cubic structures for several spin values s , for the heat capacity and susceptibility. In simple cubic and body-centered-cubic structures, and for several spin values, the staggered or two-sublattice antiferromagnetic susceptibilities have also been obtained. The latter arise from the Hamiltonian

$$H_a = \sum_{\langle i,j \rangle} V_{i,j} - g\mu \left[\sum_i \mathbf{s}_i \cdot \mathbf{H} - \sum_j \mathbf{s}_j \cdot \mathbf{H} \right], \quad (43)$$

the i and j atoms belonging to the two sublattices into which the indicated cubic structures can be decomposed. It is to be noted that in contrast with the Hamiltonian (42), in (43) the field-dependent terms do not commute with the one term which is independent of the field.¹⁶ The high-temperature paramagnetic staggered susceptibility resembles the paramagnetic susceptibility of a ferromagnetic system. More exactly, if the Hamiltonian (42) referred to a real paramagnetic system, at large T -values one would have for its susceptibility ratio

$$\chi(T)/\chi_0(T) < 1, \quad T > |J|/k, \\ \lim_{T \text{ large}} \chi(T)/\chi_0(T) \rightarrow 1, \quad (44)$$

$\chi_0(T)$ being the limiting ideal susceptibility of that system. The susceptibility of the system described by (42) is always lower than its asymptotic ideal susceptibility. The staggered-paramagnetic-susceptibility ratio is such that

$$\chi_s(T)/\chi_0(T) > 1, \quad T > |J|/k, \\ \lim_{T \text{ large}} \chi_s(T)/\chi_0(T) \rightarrow 1, \quad (45)$$

or $\chi_s(T)$ approaches the ideal asymptotic limit from above, as does the paramagnetic susceptibility of a ferromagnet.

Inasmuch as the paramagnetic susceptibility of real antiferromagnetic systems is always less than the limiting ideal susceptibility $\chi_0(T)$, the staggered susceptibility is fictitious. It appears, however, to be useful for estimating the transition or Néel temperature of some cubic structures.¹⁶

The exact series representations,¹⁶ in ascending

powers of (J/kT) , of the susceptibility, heat capacity and of the ensuing entropy, at high temperatures, of the indicated systems can only be used quantitatively in solid He^3 if the exchange parameter J is known. As mentioned already, recent experimental investigations^{8,9} of the characteristic relaxation times in solid He^3 at $T \gtrsim 0.10^\circ\text{K}$, have yielded approximate values of the exchange parameter J at a series of densities both in the body-centered-cubic⁸ and the hexagonal-close-packed⁹ solid He^3 . However the J values are obtained through the intermediary of a fairly elaborate formalism, wherein the coupling schemes (41) and (42) are assumed at the start. If the indirectly derived J values are accepted as representing approximately the exchange parameters of solid He^3 , they enable one to evaluate various thermodynamic properties of this solid, within the limitations of the assumed Hamiltonians (41), (42), and (43). We have made use of one set of J values.⁸ These had to be extrapolated over a fair range of interatomic distances. If d_M is the characteristic nearest-neighbor separation at melting of the body-centered solid He^3 , an estimate of $J(d_M)$ was found to be

$$J(d_M)/k \simeq 1.25 \times 10^{-3} \text{ }^\circ\text{K}.$$

In view of the highly approximate value of this estimated parameter, it appeared well justified to neglect its variations over several atmospheres along the melting line.

Within the stated limitations of the derived J values, and the approximate character of $J(d_M)$, we are now prepared to evaluate the melting pressure $p_M(T)$, at the lower temperatures.

As a first step, we have to obtain the entropy $S_{L,M}(T)$ of the liquid along the melting line. It will be seen below that $S_{L,M}(T)$ can be obtained along the melting line through a rapidly converging iteration procedure. Let $S_{L,M}(T)$ be represented, according to the theory elaborated for the liquid phase, as

$$S_{L,M}(T) = S_{\sigma,L,M}(T) + S_{n\sigma,L,M}(T), \quad (46)$$

with

$$\begin{aligned} S_{\sigma,L,M}(T)/R &= (\ln 2) [\chi(T_M)/\chi_0(T_M)], \\ T_M &= T_M(p), \end{aligned} \quad (47)$$

the latter being the thermodynamic equation of the melting line. In virtue of the universal character¹⁰ of the susceptibility ratio (χ/χ_0) and of the spin entropy S_σ , one has

$$S_{\sigma,L,M}(T) = S_{\sigma,L}[T_M/T_0(p_M)], \quad (48)$$

$T_0(p_M)$ being the characteristic temperature of the spin system of the liquid at the melting pressure p_M . It is to be remembered that the $T_0(p)$ function is available empirically over most of the pressure range of interest here. By (36), one has at $T_{M\mu}$, using (46),

$$S_{\sigma,L}[T_{M\mu}/T_0(p_{M\mu})] + S_{n\sigma,L}(T_{M\mu}) = R \ln 2. \quad (49)$$

This empirical normalization determines the nonspin entropy of the liquid at the minimum $p_{M\mu}(T)$ of the melting line. One finds $S_{n\sigma,L}(T_{M\mu})$ to be about $0.11R$, or approximately 16% of the total entropy of the liquid in this state. If $S_{n\sigma,\text{sat}}(T)$ refers to the nonspin entropy of the saturated liquid, one has

$$S_{n\sigma,L}(T_{M\mu}) = \gamma S_{n\sigma,\text{sat}}(T_{M\mu}), \quad \gamma \simeq 0.72. \quad (50)$$

Thus, on compressing the liquid isothermally from the saturation pressure to the melting pressure along the isotherm $T_{M\mu}$, the normal nonspin entropy loses about 28% of its value at saturation. It will henceforth be assumed, in the absence of data on the nonspin entropy of compressed liquid He^3 , that at all temperatures $T \gtrsim T_{M\mu}$ this property of the saturated liquid is reduced by the same constant factor γ on compressing the liquid from the saturation pressure to the melting pressure. Thus, in some approximation,

$$S_{n\sigma,L,M}(T) = \gamma S_{n\sigma,\text{sat}}(T), \quad T \gtrsim T_M. \quad (51)$$

The factor γ is assumed to be independent of the temperature and pressure along the melting line over the relevant ranges of these variables, $T \lesssim 0.4^\circ\text{K}$, $p_M(T \ll T_{M\mu}) > p \sim p_{M\mu}$.

According to Eq. (35), in order to derive the melting-pressure line $p_M(T)$, we have to obtain explicitly the entropy of the solid at melting. This entropy at high temperatures $T > |J|/k$, neglecting, as noted above, the very small phonon-entropy, can be obtained from the exact heat-capacity series expansion¹⁶ in a body-centered-cubic structure of atoms of spin- $\frac{1}{2}$ coupled through the exchange potential (41). The heat capacity arising from (41) is,¹⁶

$$\begin{aligned} C_x(T)/R &= (3/\theta^2) \sum_{n=0}^{\infty} (-)^n c_n / \theta^n, \\ \theta &= kT/|J|; \quad \theta > 1. \end{aligned} \quad (52)$$

The coefficients c_n known to date are c_0 through c_5 ; these are, respectively, 1, -1, 1.75, 2.5, 5.3125, -6.4458. The exchange entropy is thus,

$$\begin{aligned} S_x(T)/R &= \int_0^T [C_x(T)/RT] dT \\ &= \left(\int_0^\infty - \int_T^\infty \right) [C_x(T)/RT] dT \\ &= \ln 2 - (3/\theta^2) \sum_{n=0}^{\infty} (-)^n c_n / (n+2)\theta^n. \end{aligned} \quad (53)$$

The entropy expressions of the liquid and solid, Eqs. (46)–(51) and (53), define the temperature derivative (dp_M/dT) of the melting-pressure line, on the relatively mild assumption that

$$\Delta V_M(T) = V_{L,M}(T) - V_{s,M}(T). \quad (54)$$

The volume change on solidification remains approxi-

mately constant below about 0.40°K, $V_{L,M}$ and $V_{s,M}$ being the molar volumes of the liquid and solid at melting. Hence, with the above expressions for the entropies, one has

$$\begin{aligned} dp_M/dT &= \Delta S_M/\Delta V_M \\ &= (\Delta V_M)^{-1} \{ S_{\sigma,L}[T/T_0(p_M)] + S_{n\sigma,L,M}(T) \\ &\quad - S_{s,M}[kT/|J(p_M)|] \}, \quad T > |J|/k, \quad (55) \end{aligned}$$

$J(p_M)$ being the exchange parameter at melting. It is seen that the unknown p_M appears in $T_0(p_M)$ as well as in $J(p_M)$. However, the empirical rates of variation of $J(p)$ with pressure turn out to be considerably smaller than those of $T_0(p_M)$ over the relevant range of p_M . The ratio of the pressure derivatives $(dT_0/dp_M)/[d(J_M/k)/dp_M]$ appears to be about 50. This, then, is the justification for completely neglecting the pressure variations of the exchange parameter (55). Actually $T_0(p_M)$ itself varies only by less than 10% from its value at $p_{M\mu}$ to the highest pressure considered here above $p_{M\mu}$, at $T < T_{M\mu}$. Hence, to a first approximation, $T_0(p_{M\mu})$ alone could be used in (55) without thereby modifying noticeably the theoretical melting pressure obtained on performing the integration of (55). Inasmuch as melting-pressure data are available down to about 0.03°K, it appeared justified to use these data in $T_0(p_M)$ appearing in $S_{\sigma,L,M}$ on the right-hand side of (55). These data thus define the initial approximate (dp_M^I/dT) -values, which in turn, on integration, yield $p_M^I(T)$, a first approximation of the theoretical melting line. When substituted into $T_0(p_M)$, these values of p_M^I yield a set of values, of dp_M^{II}/dT which in turn define $p_M^{II}(T)$. This procedure is continued until the melting pressure becomes stable under the iterations. The iteration procedure was found to converge rapidly, because of the slow variations of $T_0(p)$ over the relevant pressure range.

With the above approximate value of J_M , it was found that (dp_M/dT) exhibited a minimum at about 10.5 m deg, where its value reached -42.6 atm/°K. This inflection point of $p_M(T)$ indicates its bending over and a reduced rate of growth with the lowering of the temperature. In an earlier and quite rough analysis¹⁰ there were some indications that the melting-pressure data were compatible with the occurrence of an inflection point at temperatures higher than 0.01°K resulting from the above derivation of (dp_M/dT) . As far as the location of the inflection point $T_{M,b}$ at 10.5 m deg is concerned, it should be clearly kept in mind that this point is closely tied to the empirical and extrapolated J_M value estimated above. If an improved J_M value became available, the inflection point $T_{M,b}$ will be displaced toward higher or lower temperatures, depending on whether the more accurate J_M value is larger or smaller than the one used here. The best experimental approach toward actually

locating the inflection point of the melting line will be considered below.

It is seen that Eq. (55) could yield an analytical, if complicated, expression for the melting pressure $p_M(T)$, if the entropies inside the brackets in (55) could be integrated analytically. It is to be noted that $S_{n\sigma,sat}(T)$ has been discussed recently¹³ on the basis of an approximate analytical fit. Since $S_{\sigma,L,M}(T)$ is only available^{4,5} at the present time through asymptotic series representations for $T \ll T_0(p_M)$ and $T \gg T_0(p_M)$ with $S_{s,M}(T)$ known only at $T > |J_M|/k$, no satisfactory analytical expression can be given for $p_M(T)$. We have obtained here, numerically,

$$p_M(T) - p_{M\mu} = \int_{T < T_{M\mu}}^{T_{M\mu}} (dp_M/dT) dT,$$

and

$$p_M(T) - p_{M\mu} = \int_{T_{M\mu}}^{T > T_{M\mu}} (dp_M/dT) dT,$$

with the upper limit of the second integral taken to be 0.4°K, and the lower limit of the first integral 5 m deg or about $4(J_M/k)$, where the entropy of the solid $S_{s,M}$, Eq. (53), exhibited good convergence with the indicated coefficients c_n of its infinite series representation.

We give in Fig. 1 the calculated melting-pressure curve, using Eq. (55), with ΔV_M equal to 1.2 cm³/mole, which results from the measurements of the Los Alamos group.¹⁷ The experimental points in Fig. 1 refer to the data of the Los Alamos group¹⁷ at $T > 0.3$ °K, to those of the Ohio State University group¹⁸ as modified by the University of Illinois workers,¹⁹ and to the data of this latter group. The value of $p_{M\mu}$ was taken to be the practically coincident value of the Los Alamos¹⁷ and Illinois groups,¹⁹ namely 28.9 atm at about 0.33°K. It is seen that the theoretical melting curve does give a fairly satisfactory account of the data. It should be noted that the entropies entering into Eq. (55) are all calculated entropies, the most critical being the theoretical liquid entropy $S_{L,M}(T)$ at $T \gtrsim 0.07$ °K, that of the solid reducing at those temperatures to its full, almost constant, value of $R \ln 2$. The fair agreement between the calculated and experimental pressures indicates that the entropy of the liquid is well represented by the theory of this phase.

The insert on Fig. 1 gives the calculated (dp_M/dT) as a function of temperature between 5 and 15 mdeg. The graph displays the minimum of (dp_M/dT) , or indirectly, the inflection or bend-over point of the melting line, tied to the estimated value of the exchange

¹⁷ R. L. Mills, E. R. Grilly, and S. G. Sydorik, Ann. Phys. (N.Y.) **12**, 41 (1961).

¹⁸ D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, 1960), p. 126.

¹⁹ A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **130**, 1644 (1963).

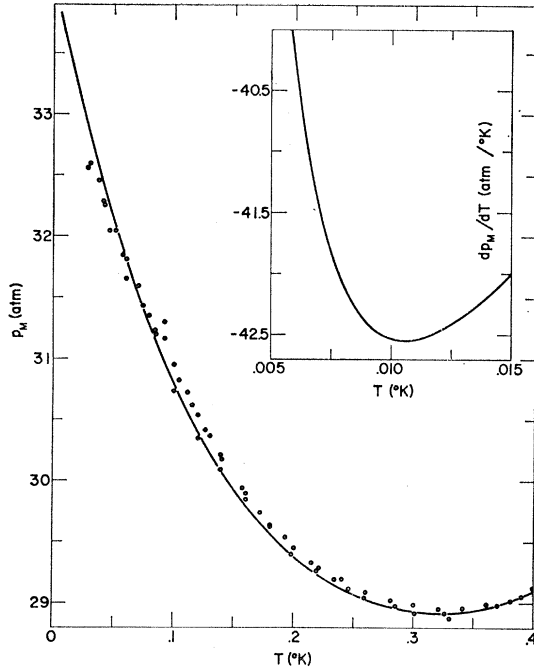


FIG. 1. The theoretical melting-pressure curve $p_M(T)$ of He^3 as a function of the temperature. The data points are from three independent sets of measurements. Insert: the temperature derivative (dp_M/dT) at very low temperatures, displaying the inflection point of the melting curve.

parameter J_M of the solid, as well as to the assumed exchange coupling (41) through the entropy (53).

To the approximation that ΔV_M is independent of the temperature, one has with (55),

$$\begin{aligned} d^2 p_M / dT^2 &= (\Delta V_M)^{-1} [d\Delta S_M(T) / dT] \\ &= (T\Delta V_M)^{-1} [C_{L,M}(T) - C_{s,M}(T)]. \end{aligned} \quad (56)$$

In this approximation of a constant ΔV_M the existence of an inflection point of the melting-pressure line is equivalent to the crossing of the heat capacities $C_{L,M}$ of the liquid, and $C_{s,M}$ of the solid, along the melting line. The limited variations of the temperature slopes dp_M/dT around the inflection point, as is apparent in Fig. 1, would make it very difficult to observe the bend-over of the melting line itself. Unless one is prepared to investigate experimentally the melting line to temperatures very much lower than $T_{M,b}$, the experimental proof of the existence of the latter point can be obtained directly through heat-capacity measurements at or near the melting line.

It should be noted that the observation of the crossing of the heat capacities $C_{L,M}$ and $C_{s,M}$ would also indicate the approach of the heat-capacity anomaly in the solid as a consequence of its increasing behavior with decreasing temperature. The latter qualitative result does not, in itself, constitute a satisfactory test of the interatomic coupling scheme, although it indicates the presence of an approaching anomaly of the solid.

We give in Fig. 2 the calculated heat capacities of the liquid and solid. The former exhibits the characteristic maximum, in common with the heat capacity of compressed liquid He^3 at pressures higher than 10-12 atm, as shown recently.¹³ The heat capacity of the liquid along the melting line results from (46) and (51), as

$$C_{s,M}(T) = C_{\sigma,L,M}(T) + \gamma C_{n\sigma,\text{sat}}(T), \quad (57)$$

and the formation of the maximum of this property was shown to result¹³ from the competition between the temperature variations of its spin and nonspin heat-capacity components. At very low temperatures, the heat capacity of the liquid tends to vanish linearly,¹³ while that of the solid decreases rapidly above its spin or magnetic-ordering temperature. The heat capacity of the solid exhibits its rapidly decreasing character with the $(1/T^2)$ factor of the exact heat-capacity series (52), valid at $T > |J_M|/k$ and above all at $T \gg |J_M|/k$. While the heat capacity of the solid given in Fig. 2 refers to Eq. (52) with the indicated value of the exchange parameter $|J_M|/k$, at the present time, as emphasized already, the latter quantity is a mere estimate, and the heat-capacity curve is mainly of qualitative interest. The indicated crossing temperature of the heat capacities is, of course, also an estimate, and even if antiferromagnetic, the correct heat-capacity curve of solid He^3 may still deviate significantly from the calculated one given in Fig. 2.

Expressions for the heat capacity and entropy arising from the interaction scheme (41), are not available at the present time near the transition temperature $T_{0,s}$, on its high-temperature side as well as throughout the region $T < T_{0,s}$. Nevertheless, a number of remarks of a semiquantitative character can be made on the expected behavior of these thermal properties as well as on the melting line $p_M(T)$ at the very low temperatures.

To start with, if the inflection point of $p_M(T)$ at

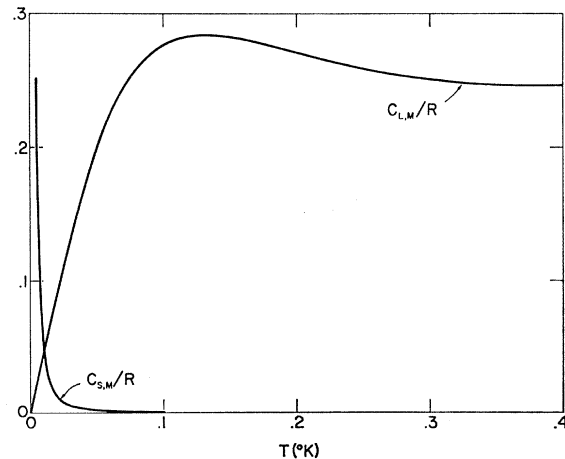


FIG. 2. The theoretical molar-heat-capacity curves of liquid and solid He^3 along the melting line.

$T_{M,b}$ is effectively located, then a maximum of $p_M(T)$ must occur at $T_{M\mu}'$, and the characteristic temperatures of the system should be in the following sequence:

$$T_{M\mu}' < T_{0,s} < T_{M,b}. \quad (58)$$

At $T_{M\mu}'$, by (55), the entropy curves $S_{L,M}$ and $S_{s,M}$ cross, as they do at $T_{M\mu}$, the minimum of the melting line at higher temperatures. On the basis of the empirically observed behavior of various antiferromagnetic systems one expects the entropy of the solid to vary or to decrease very rapidly with decreasing temperature around $T_{0,s}$, at both its high and low temperature sides. If the estimate¹⁶ of $T_{0,s}$ as

$$T_{0,s} \sim \delta |J_M|/k, \quad \delta \sim 2.9 - 3.0, \quad (59)$$

is accepted as a fair approximation for the spin or magnetic-ordering temperature of the solid, then with

$$dS_{s,M}(T)/dT = C_{s,M}(T)/T, \quad (60)$$

at $T \sim 4-5 \times 10^{-3}$ °K, one has

$$C_{s,M}(T \gtrsim T_{0,s}) \sim R, \quad (61)$$

and

$$dS_{s,M}(T \gtrsim T_{0,s})/dT \sim 200R/^\circ\text{K}, \quad (62)$$

indicating that the solid may lose essentially all its entropy over a few millidegrees of temperature around $T_{0,s}$. Hence, on the basis of the very rapid entropy loss by the solid, its entropy should fall below that of the liquid on the low-temperature side of $T_{0,s}$. The maximum of the melting line at $T_{M\mu}'$ should thus occur as indicated by (58), and it may be estimated roughly to be at about (J_M/k) or around one millidegree absolute.

Assuming tentatively $T_{M\mu}'$ to be at 1.0×10^{-3} °K, the entropy of the solid, equal to that of the liquid at this temperature, is found from the expressions (46), (48), and (50) for $S_{L,M}(T)$ to be about $(4-5) \times 10^{-3}$ R per mole. The average number of disordered spins, the fractional number of spins which have escaped the ordering effect of the coupling scheme (41), at $T < T_{0,s}$ is approximately,

$$\begin{aligned} N_{s,\sigma}(T_{M\mu}') &\sim S_{s,M}(T_{M\mu}')/k \\ &\sim (4-5)N \times 10^{-3} \\ &= 3 \times 10^{21}/\text{mole}, \end{aligned} \quad (63)$$

N being Avogadro's number. At temperatures which are low in comparison with the transition temperature, the spin-wave formalism appears to describe approximately the thermal properties of antiferromagnetic systems. If we accept this formalism as valid also, in some approximation, in solid He³ near melting and at $T \leq T_{M\mu}'$, then at the characteristic temperature T_{d-d} one has for the average number of disordered spins

$$N_{s,\sigma}(T_{d-d}) \sim N_{s,\sigma}(T_{M\mu}') (T_{d-d}/T_{M\mu}')^3, \quad (64)$$

according to the T^3 variation of the entropy of anti-

ferromagnetic systems describable with the spin-wave formalism. Actually, if $T_{M\mu}'$ is still outside the range of validity of this formalism, being too close possibly to $T_{0,s}$, then at $T_{M\mu}'$ the temperature dependence of the entropy is even stronger than T^3 , so that the right-hand side of (64) is an estimated upper limit for $N_{s,\sigma}(T_{d-d})$ at very low temperatures. With T_{d-d} taken to be about 10^{-7} °K, one has a possible upper limit, since in solid He³ near melting the nearest-neighbor distance d_M is about 3.75 Å, so that with μ equal to about 10^{-23} cgs.,

$$\mu^2/kd_M^3 \simeq 10^{-8} \text{ }^\circ\text{K}.$$

By taking 10^{-7} °K for T_{d-d} , and on the assumption of the approximate validity of the estimate (64), and using (63), one obtains

$$N_{s,\sigma}(T_{d-d}) \lesssim 10^{-12} N_{s,\sigma}(T_{M\mu}') \sim 10^9. \quad (65)$$

It is instructive to compare this estimate of the number of free or disordered spins at T_{d-d} with the normal root-mean-square fluctuations of the number of atoms in one mole of the solid at this same temperature. One obtains for this number at melting,

$$(\langle \Delta N^2 \rangle_{\text{av}})^{1/2} = [N(N/V_{s,M})kT\chi_T]^{1/2}, \quad (66a)$$

where $V_{s,M}$ is the molar volume and χ_T the isothermal compressibility of the solid. At T_{d-d} , taken to be approximately 10^{-7} °K or some ten times the temperature (μ^2/kd_M^3) , and with $V_{s,M}$ about 25 cm³/mole and χ_T estimated roughly to be about $2-4 \times 10^{-9}$ cgs from the direct measurements of Grilly²⁰ at high temperatures, one obtains

$$(\langle \Delta N^2(T_{d-d}) \rangle_{\text{av}})^{1/2} \lesssim 3 \times 10^7, \quad (66b)$$

showing that $N_{s,\sigma}(T_{d-d})$, given by (65), is uncomfortably close to the fluctuation range. Actually, with T_{d-d} taken to be μ^2/kd_M^3 , $N_{s,\sigma}(T_{d-d})$ would be entirely within the fluctuation-range estimate of (66b). In addition, it may be noted here that if the dipole-dipole transition existed, one might have expected the entropy of the solid to fall even faster with temperature at the approach of T_{d-d} than the rate estimated on the basis of the spin-wave formalism. The estimate (65) is quite conservative, and the existence of the dipole-dipole transition thereby becomes ill defined. The physical importance of the dipole-dipole ordering phenomenon tends to be reduced in view of the above estimates, which indicate that the number of magnetic dipoles available for the ordering process appears to approach the normal statistical-thermodynamic root-mean-square fluctuations of the total number of atoms in the chosen volume. The number of dipoles available for the transformation tends to lose its meaning, and, with it, the physical significance of the transformation disappears.

The problem of the existence of the dipole-dipole

²⁰ E. R. Grilly (to be published).

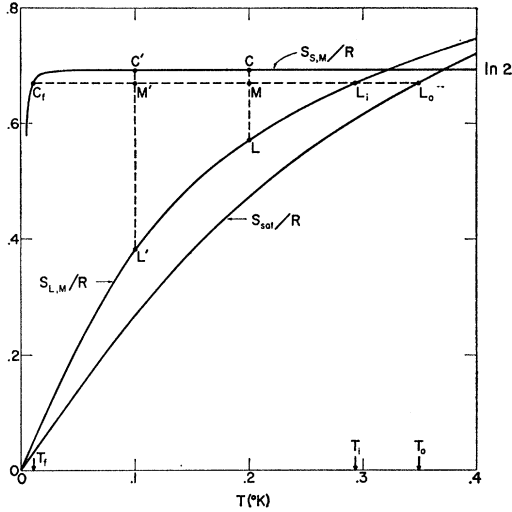


FIG. 3. The theoretical entropy curves of liquid He^3 , at saturation and along the melting line, and of solid He^3 along the melting line. The dashed lines refer to transformation paths in the two-phase system.

transition would appear in an entirely different light if solid He^3 were paramagnetic down to temperatures very much lower than $(3-4)(|J_M|/k)$, with the indicated empirical $|J_M|/k$ of about 10^{-3} °K. At the present time, the antiferromagnetic transformation of solid He^3 at $T_{0,s}$ is essentially hypothetical, and the possibility that this very loosely bound solid may exhibit nuclear paramagnetism down to extremely low temperatures cannot be ruled out. It is thus seen that experimental investigations of solid He^3 leading toward a determination of its spin-ordering properties appear to be of particular interest.

4. PRODUCTION OF VERY LOW TEMPERATURES ON ADIABATIC SOLIDIFICATION OF He^3

We gave through Eqs. (46)–(50) and (52) the expressions representing with good approximation the entropy of the liquid and the solid along the melting line, within the limitations of the assumed specific pairwise coupling (42) in the solid. These entropies determine the derivative (dp_M/dT) of the melting line, and with the help of the empirical value of the solid entropy at the point of anomaly $(T_{M\mu}, p_{M\mu})$ the melting line itself $p_M(T)$ could be evaluated. In the present section, devoted to the problem of the solidification and the production of very low temperatures, a close analysis is to be made of the separate entropies, $S_{L,M}(T)$ and $S_{s,M}(T)$. We give these in Fig. 3, together with the entropy of the saturated liquid $S_{\text{sat}}(T)$, all as a function of temperature. It is to be recalled that in the expression for the entropy of the solid, Eq. (52), we have neglected the small phonon-entropy in comparison with the very large spin-entropy.

The formal representations of $S_{\text{sat}}(T)$ and $S_{L,M}(T)$ are available, with good approximation, down to the

absolute zero, but the entropy of the solid $S_{s,M}(T)$, given by (52), is only known down to temperatures of $(4-5)(|J_M|/k)$. The limiting very-low-temperature expressions for the entropy of the liquid at saturation and at melting can be given explicitly. In a recent work¹³ we gave

$$\lim_{T \rightarrow 0^\circ\text{K}} S_{\text{sat}}(T)/R = \frac{3}{2}(\ln 2)(T/T_{0,\text{sat}}) + aT, \quad (67)$$

where $T_{0,\text{sat}}$ appears to be close to $0.43-0.45^\circ\text{K}$, and the coefficient a of the linear nonspin-entropy term was found to be approximately $0.49/^\circ\text{K}$. The limiting value of the characteristic temperature $T_{0,M}$ of the spin system of the liquid at melting can be estimated with the empirical relation^{9,10} for $T_0(p)$, within the limitations due to the relatively small pressure variations at very low temperatures. One obtains here,

$$\lim_{T \rightarrow 0^\circ\text{K}} S_{L,M}(T)/R = \frac{3}{2}(\ln 2)(T/T_{0,M}) + \gamma aT, \quad (68)$$

$$\simeq 4.58 T,$$

with the coefficient γ derived in the previous section, Eq. (50).

It is seen on Fig. 3 that the entropy of the saturated liquid $S_{\text{sat}}(T)$ crosses that of the solid at melting, $S_{s,M}(T)$, at a $T_{s,\text{sat}}$ of about 0.37°K , well above the temperature $T_{M\mu}$ of the melting-pressure minimum, where $S_{s,M}$ and $S_{L,M}$ cross. The physical significance of the crossing temperature $T_{s,\text{sat}}$ is the following: On cooling saturated liquid He^3 by evaporation below $T_{s,\text{sat}}$, this state can serve as an initial state for the adiabatic compression process to reach the melting line $p_M(T)$. The temperature of the melting line reached in this process from the state of temperature $T_\alpha < T_{s,\text{sat}}$ of the saturated liquid, is the root T_M of the equation

$$S_{L,M}(T) = S_{\text{sat}}(T_\alpha). \quad (69)$$

In terms of the component entropies, this can be written as

$$S_{\sigma,L,M}[T/T_0(p_M)] + S_{n\sigma,L,M}(T) = S_\sigma(T_\alpha/T_{0,\text{sat}}) + S_{n\sigma,\text{sat}}(T_\alpha). \quad (70)$$

It is to be noted that p_M in the argument of T_0 appearing in $S_{\sigma,L,M}$ can be replaced by its expression in T , so that the left-hand side is a unique function of T . In general, however, no analytic representation is available for the root T_M of (70). One can make good use, in this connection, of the entropy-temperature diagram of Fig. 3. Indeed, let the initial state of the liquid at saturation be represented by the point L_0 , whose coordinates are $(T_0, S_{0,\text{sat}})$. Then, on adiabatic compression as represented by the path L_0L_i , the state L_i of temperature T_i and entropy $S_{M_i} = S_{0,\text{sat}}$ is reached at melting. It is seen that, necessarily, $T_i < T_{M\mu}$. On the graph of Fig. 3, T_0 was chosen to be 0.35°K , a temperature of the saturated liquid which can be reached easily

by current forced-evaporation techniques; the temperature T_i reached then is approximately 0.29°K.

The melting anomaly of He³ can now be fully exploited toward the production of very low temperatures. For this, the initial state actually is the one of the liquid at the melting entropy line $S_{L,M}(T)$. On the path under consideration this state is represented by $L_i(T_i, S_{L,M,i})$. On adiabatic compression from this state the two-phase system is penetrated, since solidification occurs at the constant-entropy path $S_{L,M,i}$ at $T < T_{M,i}$. Consider, indeed, the two-phase system represented in the diagram of Fig. 3 by the point M , coordinates $S(M) = S_{L,M}(T_i) = S_{\text{sat}}(T_0)$, and T . This system is made up of liquid in the state L , at melting, and the solid or crystal in the state C , at melting. Let x be the fraction of the liquid in the system at M ; its complement $(1-x)$ is the fraction of the solid. Then the entropy of the system is, omitting surface effects,

$$S(x) = xS_{L,M}(T) + (1-x)S_{s,M}(T), \quad (71)$$

with

$$S(x) = S = S_{L,M}(T_i) = S_{\text{sat}}(T_0). \quad (72)$$

Or,

$$\begin{aligned} x &= x(T, S) \\ &= [S_{s,M}(T) - S] / [S_{s,M}(T) - S_{L,M}(T)] \\ &= CM/CL, \end{aligned} \quad (73)$$

where in the last relation the entropy differences are represented by the indicated segments in the entropy diagram. Clearly, at L_i ,

$$S = S_{L,M}(T_i); \quad x(T_i; S_{L,M,i}) = 1, \quad (74)$$

and the system is all liquid. At the point C_F ,

$$S = S_{L,M}(T_i) = S_{s,M}(T_f); \quad x(T_f, S_{s,m,f}) = 0, \quad (75)$$

and solidification is complete. For the particular path indicated on the diagram,

$$\begin{aligned} T_i &= 0.29_3^\circ\text{K}; & T_f &\simeq 0.010^\circ\text{K}; \\ S(T_i) &= S(T_f) = 0.670R. \end{aligned}$$

Thus, starting with the directly accessible initial temperature of 0.35°K of the saturated liquid, it is possible to reach 0.01°K after adiabatic solidification of the liquid along the indicated entropy path. With the assumed exchange coupling in the solid and the estimated coupling strength $|J_M|$, this is the lowest temperature accessible in the constant-entropy transformation indicated in the diagram, with the chosen value of the entropy of parameter S .

The lowest final temperature which can be produced in an adiabatic solidification process of entropy $S_{L,M}(T_i)$, starting from some temperature T_i of the liquid at melting, is the root T_f of

$$S_{s,M}(T) = S_{L,M}(T_i). \quad (76)$$

From (71) and (72) this lowest temperature is also $T[x=0, S_{L,M}(T_i)]$, corresponding to the completion

of the solidification process. Using (53) for $S_{s,M}(T)$, T_f , or θ_f , the latter standing for $(|J_M|/kT_f)$, is the root of

$$\ln 2 - (3/\theta^2) \sum_{n=0}^{\infty} (-)^n c_n / (n+2)\theta^n = S_{L,M}(T_i)/R. \quad (77)$$

As long as T_i is not too low, one may write approximately, using only the first term of the infinite series in $(1/\theta)$,

$$\begin{aligned} T_f &= T[x=0, S_{L,M}(T_i)] \\ &= [(|J_M|/k) \{ \frac{3}{2} [\ln 2 - (S_{L,M}(T_i)/R)] \}]^{-1/2}, \end{aligned} \quad (78)$$

and

$$T_f[x, S_{L,M}(T_i)] > T_f[x=0, S_{L,M}(T_i)].$$

The limiting relation (78) states that the lower T_i , and with it $S_{L,M}(T_i)$, the lower will be T_f . To the extent that the series in $S_{s,M}$ may be approximated by its first term, even at $S_{L,M}(T_i)/R \ll \ln 2$, one obtains,

$$\begin{aligned} \lim_{T_i \text{ small}} T_f &\simeq (|J_M|/k) (\frac{3}{2} \ln 2)^{1/2} \\ &\times [1 + \frac{1}{2} S_{L,M}(T_i)/R \ln 2 + \dots], \end{aligned} \quad (79)$$

the asymptotic lower limit of T_f being of the order of magnitude of $|J_M|/k$.

The adiabatic solidification process for the production of low temperatures refers to initial states $T_i < T_{M,\mu}$, or $S_i < S_{L,M}(T_i) < S_{M,\mu}$. This confines the $x(T, S)$, or $x(p, S)$ functions to limited regions of the (x, T) or (x, p) planes. The $x(p, S)$ functions result from the $x(T, S)$ functions on replacing T by the melting pressure p_M at T in the entropies at melting, $S_{s,M}(T)$ and $S_{L,M}(T)$, on the right-hand side of Eq. (73). While x varies between zero and unity, the temperature and pressure intervals of these functions decrease with decreasing T_i , or with decreasing values of the constant-entropy parameter S or $S_{L,M}(T_i)$. It is seen that the pressure variations of $x(p, S)$ are opposite to the temperature variations of $x(T, S)$. One has, indeed,

$$dx(T, S)/dT = \frac{x C_{L,M}(T) + (1-x) C_{s,M}(T)}{T [S_{s,M}(T) - S_{L,M}(T)]}, \quad (80a)$$

and

$$dx/dp_M = (dx/dT)/(dp_M/dT), \quad (80b)$$

where $(dp_M/dT) < 0$ in the melting-pressure region, where the anomalous cooling processes take place. At increasing x values, $x \gtrsim 0.4$, and at not too low temperatures, the second term in the numerator on the right-hand side of (80a) becomes negligible, the heat capacity $C_{s,M}$ being very small. Since $(C_{L,M}/T)$ and $(S_{s,M} - S_{C,M})$ are both of moderate variation there, (80a) practically defines $x(T)$ as an exponential function of $(T - T_i)$. At lower x values, and over the lower temperatures, the temperature variations of x become more moderate, and increase as $x \rightarrow 0$, where $C_{s,M}$ becomes rapidly varying, and the denominator on the

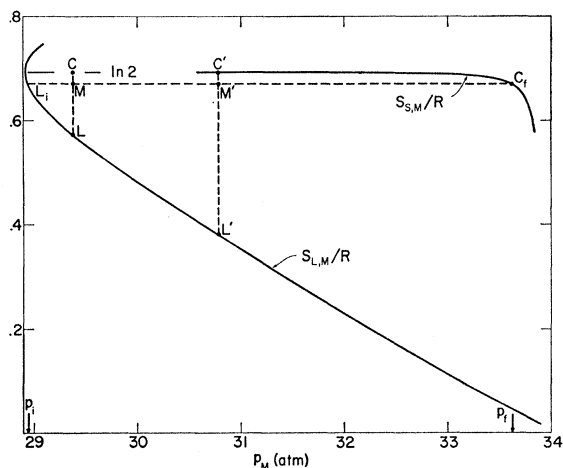


FIG. 4. The theoretical entropy curves of liquid and solid He^3 , along the melting line, as a function of pressure. The dashed lines, in the two-phase region, refer to specific transformation paths.

right-hand side of (80a) becomes smaller at an increasing rate. Since the entropy diagram of Fig. 3 enables one to calculate the $x(T, S)$ as well as the $x(p, S)$ curves, the latter with the help of the melting-pressure line of Fig. 1, they need not be displayed here.²¹

The entropy diagram shows that in order to reach temperatures in the millidegree range, the adiabatic solidification process must be initiated at the melting line at $T \lesssim 0.2^\circ\text{K}$. As pointed out to us by our colleague Dr. R. L. Mills, a two-stage or even multistage arrangement could, in principle, be used to overcome the limitations on T_f , the final accessible temperature, arising from an initial state T_i close to $T_{M\mu}$. This latter high initial temperature was imposed by the indicated method of producing the low temperatures starting with the saturated liquid cooled by forced evaporation. While the principle of the method of reaching very low temperatures through a single type of thermodynamic process, that is by adiabatic compression alone, is relatively simple, the technical problems which arise in the actual performance of producing the cooling effect, outlined schematically on the entropy diagram, are of various character. The first part, $L_0 \rightarrow L_i$, of the full process, $L_0 \rightarrow L_i \rightarrow C_f$, involves adiabatic compression over a large pressure interval Δp of about 30 atm. This first and strictly preparatory stage of the method appears to be quite complex in itself.

It is instructive both for the problem at hand and for that of the pressure anomalies of the entropy of the

²¹ Some $x(T, S)$ curves, with estimated entropy values of the liquid (presumably) have been given by Yu. D. Anufriyev, JETP Pis'ma v Redaktsiyu **1**, 155 (1965) [English transl.: JETP Letters **1**, 155 (1965)], ignoring all limitations due to exchange effects. However, several of these curves, unless wrongly labeled, carry entropy-parameter values larger than $R \ln 2$, which are excluded by the expression (73) given in the text of the present paper.

solid at melting, to display part of the entropy-pressure diagram of He^3 . This is given in Fig. 4. It is seen that, if the liquid can be prepared in an initial state represented by the point $P(p > p_{M\mu}, S < S_{M\mu})$, the compression range in the two-phase system is then alone involved in the reaching of low temperatures. This range is reduced to a few atmospheres. It may equally be noted that with an initial state of fairly low temperature T_i , and increased pressure p_i , a considerable degree of irreversibility can be tolerated in the adiabatic solidification, without thereby increasing significantly the low temperature to be reached. While the theoretical constant-entropy process is an idealization, it is likely that it can be approached fairly closely, even though the compression agent itself must undergo cooling in the course of the process, thereby causing the He^3 to be at temperatures $T > T(x, S)$, which is the ideal thermodynamic limit of the process in the state of given coordinates. Needless to say, the list of technical difficulties opposing the performance of the ideal limiting compression process mentioned briefly here is far from exhaustive. Its further consideration is, however, entirely outside the subject matter of the present work.

5. THERMAL ANOMALIES OF SOLID He^3 . CONCLUDING REMARKS

The dominance of the nuclear-spin system in determining the thermal properties of solid He^3 at low temperatures as in the case of the liquid phase,⁴ suggested already in earlier work^{5,6} the existence of thermal anomalies in the solid at the low temperatures. As mentioned, however, the overestimation of the exchange parameter J_M in the solid led to a similar overestimation of the temperature below which the solid should have become thermally anomalous.

The assumed exchange coupling (41) imposes in general the following pressure behavior

$$dJ/dp < 0, \quad (81)$$

on $J(p)$, the exchange parameter. In the particular case of liquid He^3 , and to some extent in the solid also, this behavior was discussed in early work^{4,5} on these dense phases. In the liquid phase this behavior was formulated as

$$dT_0(p)/dp < 0, \quad (82)$$

giving the qualitative pressure effect of the characteristic temperature $T_0(p)$ of the nuclear-spin system of the liquid. The qualitative pressure behavior (81) of the exchange parameter $J(p)$ is the origin of the anomalous thermal properties of the solid at low temperatures, in some similarity with the thermal anomalies of the liquid caused by the pressure dependence of $T_0(p)$.

The entropy of the exchange-coupled solid, Eq. (52), yields at once, omitting for a moment the phonon

entropy which will be taken into account subsequently,

$$\begin{aligned} [\partial S_x(T, p)/\partial p]_T &= (dS_x/d\theta)(d\theta/dJ)(dJ/dp) \\ &= (3R/\theta^2) |d \ln J/dp| \\ &\quad \times \sum_{n=0}^{\infty} (-)^n c_n/\theta^n, \end{aligned} \quad (83)$$

where use was made of the inequality (81). In the limit $\theta \gg 1$, this reduces to

$$\begin{aligned} \lim_{T \gg |J_M|/k} (-)(\partial S_x/\partial p)_T &= V_{s,M} \alpha_{x,p}(T, p) \\ &= -(3R/\theta^2) |d \ln J_M/dp|, \end{aligned} \quad (84)$$

where we reintroduce the exchange parameter at melting J_M , and where the first relation is just the thermodynamic connection between the pressure derivative of the entropy in the exchange-coupling scheme and the isobaric volume-expansion coefficient in the same interaction scheme. The exchange-coupled solid is thus thermally anomalous, the magnitude of the anomaly increasing rapidly with decreasing temperatures.

We now have to compare the exchange-coupled anomaly with the normal behavior of the solid due to phonon excitations. Here one may use the thermodynamic relation connecting the isobaric phonon expansion-coefficient $\alpha_{\varphi,p}$ with the constant-volume phonon heat capacity $C_{\varphi,v}$, and the isothermal compressibility χ_T , or

$$\alpha_{\varphi,p} = \Gamma \chi_T C_{\varphi,v} / V_s, \quad (85)$$

V_s being the molar volume of the solid and Γ the empirical Grueneisen parameter. At low enough temperatures, with the approximate experimental values of 2.5 for Γ , of 16.9°K for the characteristic temperature Θ of the solid,¹⁴ of 24.8 cm³/mole for V_s ,¹⁷ and of about 10⁻⁹ cgs, for χ_T ²⁰ one obtains⁴

$$\alpha_{\varphi,p} \simeq \epsilon_{\varphi} T^3, \quad \epsilon_{\varphi} \simeq 4 \times 10^{-4} / (^{\circ}\text{K})^4. \quad (86)$$

It should be kept in mind, however, that this component expansion coefficient as well as $\alpha_{x,p}$, are both only estimates as far as their various numerical elements are concerned. For $\alpha_{x,p}$ the data of the Duke University group⁸ yield, with dJ_M/dp estimated by us, and using the asymptotic formula (84),

$$\lim_{T \gg |J_M|/k} \alpha_{x,p} = -\epsilon_x (J_M/kT)^2; \quad \epsilon_x = (0.5-0.7) / (^{\circ}\text{K}). \quad (87)$$

With the actual isobaric expansion coefficient of the solid resulting from the representation (39) for its entropy,

$$\alpha_{M,p}(T, p) = \alpha_{x,p}(T, p) + \alpha_{\varphi,p}(T, p), \quad (88)$$

the zero of this quantity along the melting line turns out to be at

$$T_{\alpha=0}(p_M) \sim (0.25-0.3)^{\circ}\text{K}; \quad p_{\alpha=0}(T_M) \simeq 29.2 \text{ atm},$$

on the basis of the estimates (86) and (87). It is seen that, even though $|J_M|/k$ is estimated to be somewhat above one millidegree absolute, or the magnetic transition to occur¹: at a T_x of about 3 $|J_M|/k$ or around 4 mdeg, the thermal anomaly of the solid is predicted to persist over a temperature range of about 50 T_x . This approximate numerical result confirms the qualitative results of earlier work,¹⁰ according to which the thermal anomalies were shown to persist up to relatively high temperatures compared to the critical spin-ordering temperature.

In the present theory of solid He³ based on the coupling scheme (41), one is led to predict, beside the locus of the magnetic transition temperature associated with the pressure or volume variations of the exchange parameter $J(p)$, a locus $T_{\alpha}(p)$ of the zeros of the isobaric expansion coefficient $\alpha_p(T, p)$. In the body-centered-cubic solid the locus $T_{\alpha}(p)$ must extend from the melting line $p_M(T)$ up to the transition line $p_{tr}(T)$, separating the body-centered-cubic structure from the hexagonal-close-packed one. Using (84) and (85), recalling that θ stands for $kT/|J(p)|$, and with $C_{\varphi,v}$ written out explicitly in terms of $(T/\Theta(p))$, $\Theta(p)$ being the characteristic temperature of the solid at pressure p , one obtains the following equation for the locus:

$$\begin{aligned} T_{\alpha}(p) &= \{ (5/4\pi^4) [1/\Gamma \chi_T(p)] |d \ln J(p)/dp| \\ &\quad \times [\Theta(p)]^3 [J(p)/k]^2 \}^{1/5}. \end{aligned} \quad (89)$$

Let us add here that the locus of the spin or magnetic-ordering temperature $T_x(p)$ results, approximately, from $[J(p)/k]$ through

$$T_x(p) \simeq \epsilon_x [J(p)/k], \quad (90)$$

where ϵ_x may be about 3, its exact value being unknown at the present time.¹⁶ One has then

$$T_{\alpha}(p) > T_x(p), \quad (91)$$

over the pressure interval of definition of the locus $T_{\alpha}(p)$, that is, over the range $p_{\alpha,M} \leq p \leq p_{tr,\alpha}$.

For the main purposes of the present paper it was sufficient to explore the properties of the cubic solid at or near the melting line. In so doing we have been led to consider briefly the two loci $T_x(p)$ and $T_{\alpha}(p)$. Inasmuch as data⁹ exist on $J_H(p)$, and consequently on $T_{H,x}(p)$, we may mention a problem raised by this last locus. According to the data,⁹ on the starting line of $T_{H,x}(p)$ or at $p_{tr}(T)$, the solid-solid phase-transition line, $T_x(p_{tr}) > T_{H,x}(p_{tr})$, or the end point of the locus in the cubic solid is at a higher temperature than the starting point of $T_{H,x}(p_{tr})$ on the phase-separation line. Empirically, the pressure behavior of $T_{H,x}(p)$ is similar to that $T_x(p)$: they both decrease with increasing pressure. The locus in the hexagonal structure $T_{H,x}(p)$ must, however, end on a characteristic line of this solid, unless one allows for the possibility of the parameter $J_H(p)$ vanishing at some

high pressure. In the latter case the locus $T_{H,x}(p)$ would approach the pressure axis in the pressure-temperature diagram in the limit of $T \rightarrow 0^\circ\text{K}$. The nature of the characteristic line of this solid has to be determined.

Our final topic concerns the somewhat singular aspect of the entropy of solid He^3 at and around the melting-pressure minimum $(p_{M\mu}, T_{M\mu})$. In the entropy-pressure diagram, with $S_{s,M}(p)$ and $S_{L,M}(p)$, one has along the melting line

$$dS_{\lambda,M}/dp = (\partial S_{\lambda,M}/\partial p)_T + C_{p,\lambda}(T, p)/T(d\phi_M/dT),$$

$$\lambda = s, L. \quad (92)$$

The singular character of $S_{s,M}$ concerns the extreme sharpness of the vertex of the entropy at $p_{M\mu}$. We do not give in Fig. 4 the entropy curve of the solid at melting at the approaches of $p_{M\mu}$ because of the omission of the phonon entropy. Actually, only fairly rough values of the phonon entropy are available at the present time. It is justified, however, to expect that the two entropy curves, $S_{L,M}(p)$ and $S_{s,M}(p)$, being continuous, should have an internal contact at the point of anomaly $(p_{M\mu}, T_{M\mu})$, with the pressure slope of their common tangent at $p_{M\mu}$ having an infinite discontinuity across the contact. One would have here

$$\lim_{T_{M\mu}^\pm} (dS_{L,M}/dp) = \lim_{T_{M\mu}^\pm} (dS_{s,M}/dp)$$

$$= \pm \infty, \quad (93)$$

because of the vanishing of $(d\phi_M/dT)$ in the denominator of the second term on the right-hand side of (92), and where $C_{p,L}$ and $C_{p,s}$ are finite. The partial derivatives $(\partial S_{\lambda,M}/\partial p)_T$, $\lambda = L, s$, cannot be infinite either at the point of anomaly of the melting line. As a consequence of the very small phonon-entropy, in comparison with the practically complete spin-entropy of the solid of $R \ln 2$, it is seen that the singular behavior of the entropy of the solid corresponds, with its extremely sharp vortex, to the very narrow wedge formed by its two branches on both sides of $S_{M\mu}$, the entropy vertex common to the liquid and the solid. No attempt was made to represent graphically this entropy wedge of $S_{s,M}$ in Fig. 4.

The entropy-pressure diagram, even though incomplete with the upper branch of $S_{s,M}$ omitted, can be used to derive the qualitative pressure behavior of the locus $T_\alpha(p)$ of the solid. It is clear that, if the exact pressure dependence of $\chi_T(p)$ and $\Theta(p)$ in the expression (84) of $T_\alpha(p)$ were known, then $T_\alpha(p)$ would be fully defined, assuming knowledge of the function $J(p)$. This is not the case at the present time. Now, the locus $T_\alpha(p)$ is also the locus of the pressure maxima of the entropy along isotherms. We have shown above that the solid was thermally anomalous on the low temperature side of $T_\alpha(p)$, or along a sub-

family of isotherms

$$[\partial S_s(p, T)/\partial p]_T \geq 0, \quad T \leq T_\alpha(p), \quad (94a)$$

and normal along the higher-temperature isotherms

$$(\partial S_s/\partial p)_T \leq 0, \quad T \geq T_\alpha(p). \quad (94b)$$

The entropy diagrams in the (S, T) and (S, p) planes, Figs. 3 and 4, each have two isotherms drawn up in the two-phase region. In this region, these finite isotherm segments are also isobaric segments. For instance, the segment $L'C'$ in the (S, p) plane represents the isotherm of 0.10°K as well as the isobar of pressure close to 30.8 atm. While omitted in the diagram, the isotherm of this temperature in the liquid phase, the area of the diagram on the low-entropy and low-pressure side of $S_{L,M}(p)$, must reach the latter entropy curve at L' . The liquid phase being completely anomalous at low temperatures, these low-temperature isotherms originate on the saturated-liquid entropy-line and increase monotonically with pressure reaching the melting-entropy curve $S_{L,M}(p)$ with a positive pressure slope. The 0.10°K isotherm of the liquid increases from low pressures to reach $S_{L,M}$ in the state represented by L' . At C' this isotherm penetrates the solid phase. We have shown above that $T_\alpha(p_M)$, the starting temperature of the locus of vanishing expansion coefficients, is somewhat higher than 0.2°K . Hence, the 0.1°K isotherm must be anomalous in the solid and leave C' with a positive pressure slope. However, with the upper branch of the entropy wedge being very close to the lower branch, the only branch indicated approximately on the diagram, the pressure slope of this isotherm must be very small, and the entropy maximum must also be very flat. As a consequence of the very narrow entropy wedge, over a temperature range around the temperature of the vertex $T_{M\mu}$, whether normal or anomalous, the isotherms must have very small negative or positive pressure slopes. The expansion coefficient of the solid, whether normal or anomalous, must be very small in the indicated temperature range. A glance on the entropy-temperature diagram, Fig. 3, shows that the heat capacity of the solid must also become quite small over the same range. Even though very flat, these entropy maxima must develop inside the entropy wedge for the relevant isotherms. Since the entropy isotherms cannot cross, it is seen that the maxima of successive isotherms of decreasing temperature will have to appear at increasing pressures. Indeed, if the entropy isotherm T developed its pressure maximum at a pressure lower than the isotherm $(T+\Delta T)$, then the former, beyond its maximum, would start to diverge from the latter, the entropy falling with increasing pressure while the $(T+\Delta T)$ isotherm would still be increasing toward its maximum. This situation is, however, excluded, since these isotherms cover the entropy-pressure plane densely, and there is always one and only one isotherm that passes through each point of the physically sig-

nificant region of the (S, p) -plane. Hence, one must have

$$dT_{\alpha}(p)/dp < 0, \quad (95)$$

while, simultaneously,

$$S_s(p, T + \Delta T) > S_s(p, T), \quad (96)$$

since the constant-pressure heat-capacity or the ratio (C_p/T) , which is $(\partial S/\partial T)_p$, is positive definite at finite temperatures.

The region of the thermal anomalies of the cubic solid may be said to extend at least over the region between the two loci $T_x(p)$ and $T_{\alpha}(p)$. The possible modifications which may arise in the properties of the solid at very low temperatures $T < T_x(p)$, where the melting anomaly may disappear, as discussed in Sect. 2 above, could be studied more profitably once experimental evidence became available on the correct if approximate nature of the exchange-coupling scheme used here.

In concluding, it may be said that we have explored various problems arising from the liquid-solid equilibrium of He³ at low temperatures. The solid was assumed to be subject to an exchange-coupling scheme which appears compatible with, though not imposed by, recent data on the characteristic relaxation times associated with its spin and lattice degrees of freedom. The coupling scheme requires the solid to undergo spin or magnetic ordering in the range of a few millidegrees absolute. As a consequence, the anomalous melting-pressure line must have an inflection or bend-over point, which was estimated to be around 10 mdeg. Its observation, which would confirm the impending spin-ordering phenomenon, would be feasible only through measurements of the heat capacity of the liquid and solid at or near melting at temperatures well above the ordering temperature. The melting or entropy anomaly of the solid enables one to produce very low temperatures through a single thermodynamic process, that is through adiabatic compression, starting at saturation and at an easily accessible temperature. The lowest temperature obtainable is limited downward by the spin- or magnetic-ordering temperature arising from the assumed exchange coupling. The solid is thermally anomalous, its anomalies at or near melting extending

approximately up to temperatures somewhat above 0.2°K. The temperature locus of its vanishing expansion coefficient, or that of the pressure maxima of its entropy isotherms, starts at the indicated temperature at the melting line, decreases with increasing pressures toward lower temperatures to end on the phase-separation line of the low-pressure body-centered-cubic solid and the high-pressure hexagonal solid. The latter is expected to be thermally anomalous also.

The low-pressure solid at melting has a very narrow entropy wedge as a function of the pressure. As a consequence, the expansion coefficient of this solid becomes very small over a significant pressure and temperature range. Since over a wide temperature interval the entropy too remains almost constant, the solid heat capacity becomes very small there. In this region of the phase diagram of the solid the phonon excitations alone determine the thermal properties of the solid. Significant variations in the thermal properties occur only at temperatures in the range of a few hundredths of a degree absolute, where the thermally anomalous spin-excitations tend to become large and dominant.

The consideration of the specific equilibrium magnetic properties of the solid was not within the scope of the present paper. It is clear, however, that paramagnetic susceptibility measurements would be of particular interest for deciding the presence and location of the expected magnetic transformation. These measurements should be made, however, in the range of a few hundredths of a degree, still well above the expected transition temperature. The susceptibilities are accessible through nuclear-magnetic-resonance techniques where, necessarily, the spin and nonspin subsystems of degrees of freedom are separated and become autonomous. This raises difficulties connected with the possibly inordinately long time intervals needed for the subsystems to reach equilibrium to ensure the measurement of the correct susceptibilities at the indicated very low temperatures. This problem of the equilibrium times, while present, may be less acute in thermal measurements, where an extreme specification of the subsystems of degrees of freedom is avoided.

It may be hoped that experimental investigations of the problems studied in this paper leading toward a clarification of the qualitative characteristics of solid He³ will be forthcoming in a not too distant future.