

Theory of Solid He⁴†

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Using a phenomenological approach, it is shown first that solid He⁴ in equilibrium with liquid He⁴ II along the phase separation line, as well as at pressures somewhat above the melting pressure, should have anomalous thermal properties over a finite temperature range or, at least, at isolated temperatures. Such a behavior of the solid results from a correlation of thermodynamic character of its thermal properties with those of the anomalous liquid. The predicted anomalies of the solid will then be effectively verified in terms of rigorous thermodynamics and somewhat incomplete data available on liquid and solid He⁴ along the melting line over a finite temperature interval. A specific anomaly of the melting pressure consisting in a shallow temperature minimum will be predicted at low temperatures, where both the liquid and solid phases are assumed to exhibit normal static thermal properties. The persistence of the anomalous equilibrium properties of liquid He⁴ II on solidification will be discussed qualitatively as suggesting a similar origin of these anomalies in both phases, such a situation having been shown previously to exist with respect to the thermal anomalies of liquid and solid He³.

1. INTRODUCTION

IN recent work on the dense phases of the lighter He isotope He³, we have studied¹ the liquid-solid phase transformation from the point of view of the statistical thermodynamics of the nuclear spin systems of these phases. Observations² seemed to indicate that the nuclear spin paramagnetism of the compressed liquid was preserved in the solid phase or that this important physical property was invariant under the phase transformation. On the basis of this interpretation of the nuclear magnetic properties of these phases, we have analyzed, in a semiquantitative way, the pathological character³ of the liquid-solid transformation. This has led us to predict the anomalous thermal properties of the solid¹ at or near the phase transition line. These anomalous thermal properties were shown to originate with the anomalous partial thermal properties of the nuclear spin system of the solid. The spin system was shown⁴⁻⁶ previously to be responsible for all the anomalous thermal properties of the liquid phase, over a limited region of the state surface associated with the liquid, the boundaries of the region included. Actually, these dense phases of He³ have at least two competing groups of thermal excitations localized, respectively, on the system of spin degrees of freedom and on that of the degrees of freedom other than spin.^{4-6,7}

The dense phases of the He isotopes, as collections of neutral atoms, represent systems where the pertinent quantum statistics, with the interatomic forces, would be expected to lead to specific distinctive thermal

properties. The fundamental differences between the flow properties of the two liquid isotopes notwithstanding, there appeared to be also peculiar similarities between some of their static equilibrium thermal properties. We had the opportunity recently⁸ to call attention briefly to such similarities. In liquid He⁴, as is the case⁴ with liquid He³, the anomalous static equilibrium properties can be accounted for in terms of the competition between at least two groups of thermal excitations, one giving rise to normal, the other to anomalous partial thermal properties. In that region of the thermodynamic state surface of He⁴, reserved to its liquid phase, where the anomalous group of thermal excitations is dominant, the liquid is anomalous. In those regions of the state surface of the liquid, where the group of thermal excitations of normal partial thermal properties is dominant, the liquid must be normal. We could predict in this way⁹ that at lower temperatures where the dominant thermal excitations of liquid He⁴ have been shown to be phonons¹⁰ associated with the compressional elastic modes of motion of the liquid, the static thermal properties of the latter must become normal, contrasting with their anomalous behavior at higher temperatures^{11,12} over a finite temperature range.

The anomalies of solid He³ as predicted¹ from those of liquid He³ and indirectly verified experimentally,¹³ raise the following problem in He⁴: Does solid He⁴, in equilibrium with the anomalous liquid along the phase separation line or somewhat above the latter, exhibit

† A short communication on this paper has appeared in *Phys. Rev. Letters* **5**, 104 (1960).

¹ L. Goldstein, *Ann. Phys.* **8**, 390 (1959).

² W. M. Fairbank and G. K. Walters, *Symposium on Liquid and Solid He³* (Ohio State University Press, Columbus, 1958), page 1 of the Supplement.

³ This anomaly was first conjectured by I. Pomeranchuk, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **20**, 919 (1950).

⁴ L. Goldstein, *Phys. Rev.* **96**, 1455 (1954); **112**, 1465 (1958).

⁵ L. Goldstein, *Phys. Rev.* **102**, 1205 (1956).

⁶ L. Goldstein, *Phys. Rev.* **112**, 1483 (1958).

⁷ L. Goldstein, *Phys. Rev.* **117**, 375 (1960).

⁸ L. Goldstein, *Ann. Phys.* (to be published).

⁹ L. Goldstein, *Phys. Rev.* **89**, 597 (1953).

¹⁰ H. C. Kramers, J. D. Wasscher, and C. J. Gorter, *Physica* **18**, 329 (1952); J. Wiebes, C. G. Niels-Hakkenberg, and H. C. Kramers, *Physica* **23**, 625 (1957); A. H. Markham, D. C. Pearce, R. G. Netzel, and J. R. Dillinger, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press Madison, Wisconsin, 1958), p. 45.

¹¹ L. Tisza, *J. phys. radium* **1**, 164, 350 (1940).

¹² W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942), pp. 186-254.

¹³ S. G. Sydorak, R. L. Mills, and E. R. Grilly, *Phys. Rev. Letters* **4**, 495 (1960); *Ann. Phys.* **12**, 41 (1961).

also thermal anomalies or not? If the answer were affirmative, as was the case in He³, it would point toward the existence in solid He⁴ of at least two groups of thermal excitations, as in liquid He⁴ as well as in liquid and solid He³. It would raise in solid He⁴ the important problem of the extent of the anomalies, since the peculiar liquid-liquid transformation would be expected to be restrained. At any rate, the partially or completely anomalous solid He⁴, as a collection of interacting atoms subject to symmetrical statistics, would raise the problem of the existence of a possibly mild transformation-like process in this phase. These problems may also shed, indirectly, additional light on the phase transformation of liquid He⁴, whose nature has not been explained satisfactorily either.

The object of the present paper is to give an account of various studies into several aspects of the above-stated problems in He⁴.

II. LIQUID-SOLID TRANSFORMATION IN He⁴

II.1. Anomalous Region of Liquid He⁴ II Near the Melting Line

The first group of problems which will concern us refers to the anomalous liquid He⁴ II at temperatures $T \lesssim 1.8^\circ\text{K}$. Above this temperature, it was shown experimentally¹⁴ that both liquid and solid He⁴, along the phase separation line, have normal thermal properties. The anomalous thermal properties of liquid He⁴ II along the phase separation line are characterized by a set of interdependent thermodynamic relations. When needed, we shall make use of the subscripts l and s to refer to some property of the liquid or of the solid. In the liquid phase, one has, V denoting its volume, S its entropy, C_p and C_v its constant pressure and constant volume heat capacities,

$$\begin{aligned}\alpha_p(p, T) &= (V(p, T))^{-1}(\partial V / \partial T)_p \\ &= -(V(p, T))^{-1}(\partial S / \partial p)_T \\ &= [C_p(p, T) / TV(p, T)](\partial T / \partial p)_s \leq 0,\end{aligned}\quad (1a)$$

and,

$$\begin{aligned}(\partial p / \partial T)_V &= (\partial S / \partial V)_T \\ &= -[C_v(V, T) / T](\partial T / \partial V)_s \leq 0.\end{aligned}\quad (1b)$$

By virtue of the equation of state,

$$(\partial p / \partial T)_V = \alpha_p(p, T) / \kappa_T(p, T), \quad (2)$$

where

$$\kappa_T(p, T) = -[V(p, T)]^{-1}(\partial V / \partial p)_T > 0, \quad (2a)$$

is the positive-definite isothermal compressibility, the discussion of the anomalous thermal properties of any system requires the consideration of a single property entering into (1a) and (1b). The anomalous thermal properties refer to the negative isobaric volume expansion coefficient, $\alpha_p(p, T)$, or the increase of entropy on isothermal compression, or the cooling on adiabatic

compression, since

$$C_p(p, T) \geq 0, \quad C_v(V, T) \geq 0, \quad (3)$$

these heat capacities being semidefinite positive quantities. The relations (1b) are equivalent to the relations (1a). They express the anomalous thermal properties through the negative temperature coefficient of the pressure, the entropy decrease on isothermal expansion, or the temperature increase on adiabatic expansion.

These characteristic anomalies of the thermal properties of liquid He⁴ exist over a limited region of its equation of state surface reserved to the liquid phase. In a cartesian coordinate system of the variables of state (p, V, T) , the anomalous domain of the liquid region of the state surface, when projected onto the (p, T) plane, is limited by four lines. Two of these correspond to the phase separation lines between vapor and liquid, $p_{\text{sat}}(T)$, and liquid and solid, $p_m(T)$, respectively. The anomalous thermal properties of the liquid extend over finite arcs of these lines. These finite arcs of the saturation and melting lines, $p_{\text{sat}}(T)$ and $p_m(T)$, result from their intersections by the two loci,

$$T_I = T_\alpha(p)_I, \quad T_{II} = T_\alpha(p)_{II}, \quad (4)$$

of vanishing expansion coefficients in the liquid He⁴ I and He⁴ II regions. The anomalies of the static thermal properties along these loci are given by the set of relations (1a) and (1b) with vanishing right-hand sides. The temperature coordinates of the four intersection points of the four lines, $p_{\text{sat}}(T)$, $p_m(T)$, $T_\alpha(p)_I$, and $T_\alpha(p)_{II}$ are thus, respectively:

$$T_\alpha(p_{\text{sat}})_{II}, \quad T_\alpha(p_m)_{II}, \quad T_\alpha(p_{\text{sat}})_I, \quad T_\alpha(p_m)_I.$$

We have to consider now the two loci $T_\alpha(p)_I$ and $T_\alpha(p)_{II}$ somewhat in detail since the latter, in particular, has not even been studied so far, while the former is being currently investigated experimentally and has been located approximately.¹⁵

As briefly mentioned in the Introduction, we have been led to predict⁹ the change in sign of the anomalous negative isobaric expansion coefficient of liquid He⁴ II in the low-temperature region where the thermal excitations of the liquid are phonons predominantly. Let $S(p, T)$ denote the total entropy of the liquid. At a precise temperature, in a state of thermodynamic equilibrium of the liquid, the atoms involved in the two groups of thermal excitation, associated with low- and high-energy states, may be said to form independent subsystems within the liquid, the total multiplicity of the states involving the two independent subsystems being

$$P_t = P_\varphi P_h,$$

in a state (p, V, T) of the liquid, the total entropy is, by Boltzmann's theorem,

$$S(p, T) = S_\varphi(p, T) + S_h(p, T), \quad (5)$$

¹⁴ E. R. Grilly and R. L. Mills, Ann. Phys. 8, 1 (1959).

¹⁵ O. V. Lounasmaa and L. Kaunisto, Bull. Am. Phys. Soc. 5, 290 (1960); Ann. Acad. Sci. Fennicae Ser. A, VI, No. 59 (1960).

where S_φ and S_h refer to the partial entropies arising from the excitation of the phonons and of the higher energy states, respectively. Taking negative partial derivatives with respect to the pressure on both sides of (5) and dividing by the total volume $V(p, T)$, one obtains, by (1a),

$$\alpha_p(p, T) = \alpha_{p,\varphi}(p, T) + \alpha_{p,h}(p, T). \quad (6)$$

The total isobaric volume expansion coefficient $\alpha_p(p, T)$ is the sum of the partial expansion coefficient arising with the thermal excitations of the phonons, $\alpha_{p,\varphi}$, and with those of higher energy $\alpha_{p,h}$. Observations indicate¹² that in liquid He⁴,

$$\begin{aligned} \alpha_p(p, T) &\leq 0, \quad (\partial p / \partial T)_v \leq 0, \\ T_\alpha(p)_{\text{II}} \leq T \leq T_\alpha(p)_{\text{I}}, \quad p_m(T) &\geq p \geq p_{\text{sat}}(T), \end{aligned} \quad (7)$$

and since

$$\alpha_{p,\varphi} \geq 0, \quad (8)$$

the phonon expansion coefficient being semidefinite positive, one finds, with (6) and (7),

$$\alpha_{p,h}(p, T) \leq 0, \quad (\partial S_h / \partial p)_T \geq 0, \quad (9)$$

over the temperature and pressure intervals given in (7). The equal signs in (8) and (9) would only apply at the absolute zero.

In the phonon system, the pressure arising with the excitations is

$$p_\varphi(V, T) = \frac{1}{3} E_\varphi(V, T) / V, \quad (10)$$

E_φ being the total energy of phonon excitations. In the system of high-energy excitations, the pressure may be written as

$$p_h(V, T) = \frac{2}{3} \epsilon_h(V, T) E_h(V, T) / V, \quad (11)$$

where the parametric function $\epsilon_h(V, T)$ describes the nonideal character of these excitations of higher energy $E_h(V, T)$. Within the formalism of thermodynamics, one is led to show^{5,6} that

$$\alpha_{p,\varphi}(p, T) = \frac{1}{3} (\kappa_T(p, T) / V) C_{v,\varphi}(V, T), \quad (12)$$

and

$$\alpha_{p,h}(V, T) = \frac{2}{3} (\kappa_T(p, T) / V) \epsilon_h(V, T) C_{v,h}(V, T), \quad (13)$$

provided that the parametric function $\epsilon_h(V, T)$ varies far less rapidly with temperature than does $E_h(V, T)$. By (6),

$$\alpha_p(p, T) = \frac{1}{3} (\kappa_T(p, T) / V) [C_{v,\varphi} + 2\epsilon_h(V, T) C_{v,h}]. \quad (14)$$

In order for α_p to be positive at low temperatures and negative at high temperatures, it is necessary that throughout the range of validity of (11) and (13),

$$p_h(V, T) < 0, \quad \epsilon_h(V, T) < 0, \quad (15)$$

since $E_h(V, T)$, the energy of the associated thermal excitations must be semi-definite positive.

Experimental determination of α_p , κ_T , V , and the prior evaluation of $C_{v,\varphi}$ and $C_{v,h}$, the latter through $C_v(V, T)$, the total heat capacity, yields the parametric

function $\epsilon_h(V, T)$, to the approximation of (13). As mentioned, this is equivalent to neglecting the temperature variations of $\epsilon_h(V, T)$ in comparison with those of $E_h(V, T)$.

The preceding analysis of the contributions to the total isobaric expansion coefficient of the two groups of thermal excitations, (φ) and (h), leads one to assign the characteristic thermal anomalies to those arising with the group (h). This result is, of course, imposed by the empirical findings according to which, in the completely anomalous region of liquid He⁴ II, the partial thermal properties associated with the group of excitations (h) completely dominate the thermal properties of the liquid.

It is equally advantageous and important, in an analysis of the thermal anomalies of the system, to study the total parametric function $\epsilon_t(V, T)$ associated with the thermal excitations of the system as a whole. This is defined through the representation of the total pressure due to the thermal excitations as

$$p_t(V, T) = \frac{2}{3} \epsilon_t(V, T) E(V, T) / V, \quad (16)$$

where $E(V, T)$ is the total energy of thermal excitations. It is seen that the numerical coefficient $\frac{2}{3}$, on the right-hand sides of (11) or (16), corresponds to a normalization of the pressures p_h or p_t so as to insure their reduction to the ideal limit as ϵ_h or $\epsilon_t \rightarrow 1$. Equation (16) leads then,^{5,6} under the assumption of not too rapid temperature variations of $\epsilon_t(V, T)$, to

$$\alpha_p(p, T) = \frac{2}{3} (\kappa_T(p, T) / V) \epsilon_t(V, T) C_v(V, T), \quad (17)$$

which allows one to evaluate $\epsilon_t(V, T)$ in terms of the thermal properties entering into (17). We have thus used previously⁷ (17) in connection with liquid He³ and water. Clearly, in anomalous systems, where $\alpha_p(p, T)$ changes sign, $\epsilon_t(V, T)$ will also change sign, its zero being common with that of $\alpha_p(p, T)$.

Recent experimental work on saturated liquid He⁴ by Kerr and Taylor¹⁶ locates the zero of $\alpha_{\text{sat}}(T)$, that is, the expansion coefficient along the saturation line $p_{\text{sat}}(T)$ at about 1.17°K. Since

$$\alpha_{\text{sat}}(T) = \alpha_p(p_{\text{sat}}) - \kappa_T(p, T) (dp_{\text{sat}} / dT), \quad (18)$$

and since

$$\kappa_T dp_{\text{sat}} / dT \geq 0, \quad (19)$$

the zero of α_p is displaced toward a temperature at which α_{sat} is already negative or which is somewhat higher than the zero of α_{sat} . For all practical purposes, however, the above low temperature zero of α_{sat} may be taken to be the same as that of $\alpha_p(p_{\text{sat}})$. The intersection of the locus $T_\alpha(p)_{\text{II}}$ with the saturation line at $T_\alpha(p_{\text{sat}})_{\text{II}}$ at 1.17°K occurs at about the value of 0.54 of the reduced temperature ($T / T_\lambda(p_{\text{sat}})$) where the transition temperature $T_\lambda(p_{\text{sat}})$ is about 2.17°K. If, in some approxima-

¹⁶ E. C. Kerr and R. D. Taylor (to be published). The zero of $\alpha_{\text{sat}}(T)$ was estimated earlier to be at 1.15–1.16°K by K. R. Atkins and M. H. Edwards, Phys. Rev. **96**, 551 (1954).

tion, the locus intersected the melting line $p_m(T)$ at about the same value of the reduced temperature $T/T_\lambda(p_m)$, one would find $T_\alpha(p_m)_{II}$ to be about 0.95°K. The locus temperature $T_\alpha(p)_{II}$ would thus be decreasing with increasing pressure, as is the case with the locus of the lambda points $T_\lambda(p)$, the lambda point $T_\lambda(p_m)$ being taken to be 1.76°K approximately.^{15,17} There is a recent indirect determination of the temperature $T_\alpha(p)_{II}$ of this locus in the liquid at a pressure close to 25 atm due to Grilly and Mills.¹⁴ The temperature $T_\alpha(p=25 \text{ atm})$ obtained by graphical extrapolation is at about 1.05–1.10°K. Since the melting pressure at about 1.0°K is somewhat higher than 25 atm, one would have to conclude that $T_\alpha(p_m)_{II} \leq 1.1^\circ\text{K}$, confirming thus the negative pressure slope of the locus $T_\alpha(p)_{II}$.

The high-temperature locus $T_\alpha(p)_I$ is entirely in the liquid He⁴ I region.^{15,16} The existence of this locus is qualitatively in accord with the observation¹⁸ that C_{sat} , the saturated liquid heat capacity, appears to have a sharp peak at the lambda temperature and not a finite discontinuity as older measurements seemed to suggest.¹² The existence of a heat capacity peak at the transition temperature was shown¹⁹ to impose the continuity across the transition point of the latent heat of vaporization, $L(T)$, with an inflection point of this property at the transition temperature. It was also shown that whether the tangent (dL/dT) , at the transition point $T_\lambda(p_{\text{sat}})$, had a finite, though large, negative slope or whether this slope tended to become negatively infinite, depended on the finite or infinite height of the heat capacity peak. At any rate, if the existence of a heat capacity peak were confirmed, the locus of transition temperatures, $T_\lambda(p)$, instead of being a locus of discontinuities of the first derivatives of the variables of state, could become associated with second derivatives of these variables which would thus exhibit changes in sign of their curvatures at the crossing of the transition point $T_\lambda(p_{\text{sat}})$ or, more generally, the transition line $T_\lambda(p)$. With the existence of a heat capacity peak instead of an actual discontinuity in the heat capacity, the liquid-liquid transition stopped to be a lambda transition and became a transformation of milder character.

It is instructive to recall here that in our previous discussion¹⁹ of the liquid He⁴ II \rightarrow liquid He⁴ I transformation, we made use of older density measurements which implied that the transition coincided with the onset of both the thermal and transport anomalies of liquid He⁴. The implications of the heat capacity measurements, through the appearance of a heat capacity peak, led to attribute a cusp or a double point to the liquid density or volume at the transition tempera-

ture. The temperature derivatives of the latter had to be such that

$$\lim_{T \rightarrow T_{\lambda-}} dV_-/dT \rightarrow -\infty, \text{ or large and negative,}$$

$$\lim_{T \rightarrow T_{\lambda+}} dV_+/dT \rightarrow +\infty, \text{ or large and positive,}$$

according as the heat capacity peak tended toward infinity or only toward a finite though large value at T_λ . The former case would have required

$$\lim_{T \rightarrow T_{\lambda-}} (d^2V_-/dT^2) \rightarrow -\infty, \text{ or large and negative.}$$

Inasmuch as (d^2V_+/dT^2) appeared to be still $(-\infty)$ or large and negative at T_λ and since it had to change rapidly to become positive at $T_\lambda + \tau$, τ being a small temperature interval, because $V_+(T)$ becoming concave upward at $T > T_\lambda$, the latter volume branch had to have an inflection point close to T_λ .

Recent Los Alamos measurements¹⁶ seem to show that, under saturation condition, both the liquid volume and its temperature derivative are continuous at T_λ . The volume continues to decrease at $T > T_\lambda$ or the thermal anomalies extend into the liquid He⁴ I region in contrast with the implications of older volume measurements. The onset of the thermal anomalies is thus at the locus $T_\alpha(p)_I$ beyond the locus $T_\lambda(p)$ of the transformation temperatures. The locus $T_\alpha(p)_I$ is a locus of volume minimas. But the volume is concave toward smaller volumes at $T < T_\lambda$; hence there must be a change in sign of the volume curvature at $T < T_\alpha(p)_I$. On the basis of the Kerr and Taylor measurements,¹⁶ one is led to expect that the vanishing of (d^2V/dT^2) , under saturation, might occur at $T_\lambda(p_{\text{sat}})$. Along isobars, one would expect

$$\begin{aligned} (\partial^2 V_- / \partial T^2)_p &< 0, & T < T_\lambda(p), \\ (\partial^2 V_+ / \partial T^2)_p &> 0, & T > T_\lambda(p), \\ (\partial^2 V_- / \partial T^2)_p &= (\partial^2 V_+ / \partial T^2)_p = 0, & T = T_\lambda(p). \end{aligned} \quad (20)$$

The first direct measurements of $(\partial p / \partial T)_v$, due to Lounasmaa and Kaunisto,¹⁵ seem to suggest a similar situation. Here the qualitative results may correspond, with due regard to the determinations¹⁵ of isochores $p(T)_v$ across $T_\lambda(p)$, to

$$\begin{aligned} (\partial^2 p_- / \partial T^2)_v &< 0, & T < T_\lambda(p), \\ (\partial^2 p_+ / \partial T^2)_v &> 0, & T \geq T_\lambda(p), \end{aligned} \quad (21a)$$

and, possibly,

$$(\partial^2 p_- / \partial T^2)_v = (\partial^2 p_+ / \partial T^2)_v = 0, \quad T = T_\lambda(p). \quad (21b)$$

So far, a satisfactory experimental verification of the rigorous equality of $(\partial p_- / \partial T)_v$ and $(\partial p_+ / \partial T)_v$ at $T_\lambda(p)$ is lacking. Also, the occurrence of the inflection point of the isobars $p(T)_v$ at the transition line is conjectural, although the volume measurements¹⁶ tend to favor such

¹⁷ C. A. Swenson, Phys. Rev. **79**, 626 (1950); **86**, 870 (1952); **89**, 538 (1953).

¹⁸ W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 50.

¹⁹ L. Goldstein, Ann. Phys. **2**, 177 (1957).

a behavior.^{20,21} It should be noted that the isochores¹⁵ seem to suggest also the continuity of $p(T)_v$ and $(\partial p/\partial T)_v$ across the transition point. Considering the $(\partial p/\partial T)_v$ values alone, these are given¹⁵ as having a cusp-like behavior at $T_\lambda(p)$ with an attendant discontinuity of $(\partial^2 p/\partial T^2)_v$ at $T_\lambda(p)$. It will be necessary to reconcile the latter behavior, if confirmed, with the shape of the isochores $p(T)_v$ themselves, which could have an inflection point at $T_\lambda(p)$, as seems to be the case with the $V(T)$ curve of Kerr and Taylor¹⁶ along the saturation line.

We should like to invoke here an argument of geometric character on the qualitative behavior of the isochores $p(T)_v$ around the transition line. In the (p, T) representative diagram, the locus of transition temperatures $T_\lambda(p)$ decreases monotonically with increasing pressure; the inverse function $p_\lambda(T)$ decreases monotonically with increasing temperatures. The isochores $p(T)_v$ are also monotonically decreasing functions of the temperature at $T \geq T_{\alpha}(p)_{II}$. The isochores of the liquid cannot reach the He⁴ I region unless they cross the locus of transition points $p_\lambda(T)$. The latter is such that

$$\begin{aligned} dp_\lambda/dT < 0, \quad (d^2 p_\lambda/dT^2) < 0, \\ T_\lambda(p_m) \leq T \leq T_\lambda(p_{sat}). \end{aligned} \quad (22)$$

In order for $p(T)_v$ to cross $p_\lambda(T)$, it is necessary that, with

$$\begin{aligned} (\partial p_-/\partial T)_v < 0, \\ T_\alpha(p)_{II} \leq T \leq T_\alpha(p)_I, \end{aligned} \quad (23)$$

one should have

$$0 > \lim_{T \rightarrow T_\lambda} (\partial p_-/\partial T)_v \geq (dp_\lambda/dT), \quad V = V_\lambda, \quad (24)$$

since

$$\begin{aligned} p_-(T)_v &> p_\lambda(T), \\ T &< T_\lambda(p), \quad V = V_\lambda. \end{aligned} \quad (25)$$

It is an empirically established fact¹² that (dp_λ/dT) is finite along the major part of the transition arc $p_\lambda(T)$. Hence, with (23) and (24), $(\partial p_-/\partial T)_v$ must be finite over the transition arc, where (dp_λ/dT) is finite.

Before considering the behavior of (dp_λ/dT) at the approaches of saturation pressure, we would like to study briefly the consequences of the relation (24). Let us rewrite (2) in the following form:

$$\begin{aligned} -(\partial V/\partial p)_T &= \kappa_T V \\ &= (\partial V/\partial T)_p/(\partial p/\partial T)_v. \end{aligned} \quad (26)$$

We have just proved that over the major part of $p_\lambda(T)$,

²⁰ M. H. Edwards, Can. J. Phys. **36**, 884 (1958), was the first to call attention to the likely extension of the thermal anomalies into the He⁴ I region.

²¹ Indirect determinations of (dV_-/dT) , at the approach of $T_\lambda(p_{sat})$, through dielectric constant measurements seemed to have yielded finite though large negative values of this derivative, see E. Maxwell, C. E. Chase, and W. E. Millett, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), page 53.

$(\partial p/\partial T)_v$ is finite. In order for the isothermal compressibility to stay finite, it is necessary that

$$\begin{aligned} \lim_{T \rightarrow T_\lambda} (\partial V/\partial T)_p &= V_\lambda \alpha_p(p_\lambda, T_\lambda) \\ &\rightarrow \text{finite}, \end{aligned} \quad (27)$$

that is, the expansion coefficient must remain finite at $T_\lambda(p)$. At the present time, there are no empirical indications of $\kappa_T(p, T)$ becoming very large at the approach of the transition line. It should be remembered, however, that direct experimental studies on the isothermal compressibility κ_T are lacking at the present time and above all in the critical regions of vicinity of the transition line $T_\lambda(p)$. Direct experimental investigations on this property appear to be desirable.

The loci of the minimas of the isochores $p(T)_v$ and the isobars $V(T)_p$ correspond, of course, to the same temperatures. At these loci, the compressibility κ_T is finite. Its value is to be evaluated with L'Hospital's rule, or

$$\begin{aligned} \lim_{T \rightarrow T_{\alpha(p)_I}} \kappa_T(p, T_\alpha) \\ = \lim_{T \rightarrow T_{\alpha(p)_I}} (V(T_\alpha))^{-1} (\partial^2 V/\partial T^2)_p / (\partial^2 p/\partial T^2)_v, \end{aligned} \quad (28)$$

where the minimas of $V(T)_p$ and $p(T)_v$ insure the positive signs of the two second partial temperature derivatives.

The finite character of κ_T along the transition line, together with the finite values of $\alpha_p(p_\lambda, T_\lambda)$, Eq. (27), has another major consequence. Consider indeed the relation (17) of essentially statistical thermodynamic character involving the phenomenological parametric function $\epsilon_t(V, T)$. The latter is only a slowly varying function of the temperature. Equation (17) requires that with $\alpha_p(p, T)$ and $\kappa_T(p, T)$ being finite along the major part of the transition line, the heat capacity $C_v(V, T)$ must remain finite also at or in the vicinity of $T_\lambda(p)$.

The limitations of the preceding results to only a part of the transition line originates with the situation that because of the decrease of (dp_λ/dT) toward large negative values, the possibility still exists for this derivative to become very large in the limit of the saturating vapor pressure.²² This would allow, by (24), very large values for $(\partial p/\partial T)_v$ and $(\partial V/\partial T)_p$, under saturation condition, at $T_\lambda(p_{sat})$ and, in turn, this would justify C_v becoming very large also. A clarification of the actual situation under saturation condition would be very helpful indeed.

The location of the locus $T_\alpha(p)_I$ appears to be fairly well established whereby

$$\begin{aligned} T_\alpha(p)_I &> T_\lambda(p), \\ p_{sat} &\leq p \leq p_m. \end{aligned} \quad (29)$$

²² W. E. Keller and E. F. Hammel, Jr., Ann. Phys. **10**, 202 (1960).

According to the volume measurements¹⁶

$$T_\alpha(p_{\text{sat}})_I = T_\lambda(p_{\text{sat}}) + (5-8) \times 10^{-3} \text{K},$$

while at higher pressures, the vanishing of the derivatives $(\partial p_+/\partial T)_v$ occurs¹⁵ at increasingly larger values of the difference $[T_\alpha(p)_I - T_\lambda(p)]$. The latter may reach values as high as¹⁵ 0.07–0.075°K at the melting line.

The region of the state surface of the liquid where its thermal properties are anomalous as described by the relations (1a) and (1b) has now been fully specified with its boundaries formed by the four lines discussed above, the boundaries themselves belonging to the anomalous region. Geometrically, the anomalous region of the state surface or its projection on a representative plane of the variables of state is thus a closed set of states, the limiting set of states belonging to the set. The region of the anomalous thermal properties is thus divided by the locus $T_\lambda(p)$, whose subscript is already a misnomer, into two regions belonging, respectively, to the He⁴ II and He⁴ I modifications.

II.2. Solidification of the Anomalous Liquid He⁴

The object of this section is a brief discussion of the liquid-solid transformation over that temperature range where the liquid is anomalous. As shown above, this interval extends from $T_\alpha(p_m)_{II}$ to $T_\alpha(p_m)_I$, but the present discussion will be limited to a somewhat shorter interval, extending only from $T_\alpha(p_m)_{II}$ to $T_\lambda(p_m)$, or to temperatures somewhat less than $T_\lambda(p_m)$. Inasmuch as our approach is strictly phenomenological, the use of experimental data in the vicinity of $T_\lambda(p_m)$ becomes more difficult to justify as a consequence of the uncertainties involved in those data. In the range $(T_\lambda(p_m) - T_\alpha(p_m)_{II})$, the liquid may be described, to some degree of approximation, in terms of the two-fluid model¹¹ used generally for the liquid along the saturation line. According to this model, the normal fluid fraction of the liquid carries the thermal excitations and, hence, the entropy of the liquid. Its complement is formed by the group of atoms which are still in the ground state of the liquid as a whole. This model imposes certain conditions on the solidification process. In the range of temperatures of interest for us, it is observed¹⁷ that the solidification is accompanied by an entropy decrease of the liquid or,

$$\begin{aligned} S_{l,m}(T) &> S_{s,m}(T), \\ T_\alpha(p_m)_{II} &\leq T \leq T_\lambda(p_m), \end{aligned} \quad (30)$$

that is, the entropy of the liquid, in equilibrium with the solid along the phase separation line, is larger than that of the solid. Inasmuch as only the normal fluid fraction of the liquid has entropy, only this fluid fraction can lose entropy in the solidification. As a consequence, the phase transformation is determined by the normal fluid fraction, and the details of the melting line $p_m(T)$ must originate essentially with the entropy $S_{l,m}(T)$ of this normal fluid fraction.

In a first approximation, the entropy in the He⁴ II range is proportional to the number of normal fluid atoms¹¹ or, along the melting line $p_m(T)$,

$$\begin{aligned} S_l(p_m)/S_l(T_\lambda(p_m)) &\simeq N(p_m)/N \\ &= \rho_n(p_m)/\rho(p_m), \end{aligned} \quad (31)$$

$S_l(T_\lambda(p_m))$ being the entropy at the intersection of the transformation line $T_\lambda(p)$ and the melting line $p_m(T)$, N is the total number of atoms, ρ_n and ρ the densities of the normal fluid and of the liquid, respectively. Over the indicated temperature range, $\Delta S_m(T)$ or $[S_{l,m}(T) - S_{s,m}(T)]$ is positive, by (30), and the volume change on melting,

$$\Delta V_m(T) = V_{l,m}(T) - V_{s,m}(T) > 0, \quad (30a)$$

is also positive, with $\Delta V_m(T)$ being only a slowly varying function of the temperature. Hence, with (31), the Clapeyron-Clausius relation yields

$$\begin{aligned} dp_m/dT &= \Delta S_m/\Delta V_m \\ &= \{S_l(T_\lambda(p_m))[\rho_n(p_m)/\rho(p_m)] \\ &\quad - S_s(p_m)\}/\Delta V_m(T). \end{aligned} \quad (32)$$

It is remarkable that the empirically derived temperature derivative function¹⁶ of the melting line resembles closely the temperature variation of the (ρ_n/ρ) ratio in the saturated liquid. This ratio in the compressed liquid along the melting line would be expected to differ only slightly from its value under saturation. The observed shape of (dp_m/dT) indicates that $S_s(p_m)$ or $S_{s,m}(T)$, the entropy of the solid, remains generally small in comparison with that of the liquid, on the right-hand side of (32). At any rate, the determinations of dp_m/dT confirm the prominent role played by the normal fluid fraction in the solidification process.

Using in (32) the empirical values of dp_m/dT , $\Delta V_m(T)$,¹⁷ and the entropy of the liquid¹² $S_l(p_m)$, one can evaluate, to the approximation of these quantities, the entropy of the solid $S_s(p_m)$ along the melting line. We give in Fig. 1 these approximate solid entropy values as a function of the temperature. It will be seen that $S_{s,m}(T)$ is a rapidly increasing function of the temperature. It displays the characteristic behavior of the liquid entropy at the approaches of the transition temperature $T_\lambda(p_m)$. The qualitative temperature dependence of $S_s(p_m, T)$ indicates that solid He⁴ along the melting line, in equilibrium there with the thermally anomalous liquid He⁴ II, may be expected to be quite different in its overall thermal properties from the conventional or normal solids.

II.3. Thermal Properties of Solid He⁴ in Equilibrium with the Anomalous Liquid

The object of the present section is to predict qualitatively within the broad formalism of thermodynamics the thermal properties of solid He⁴ in equilibrium along the melting line with the liquid in terms of the thermal

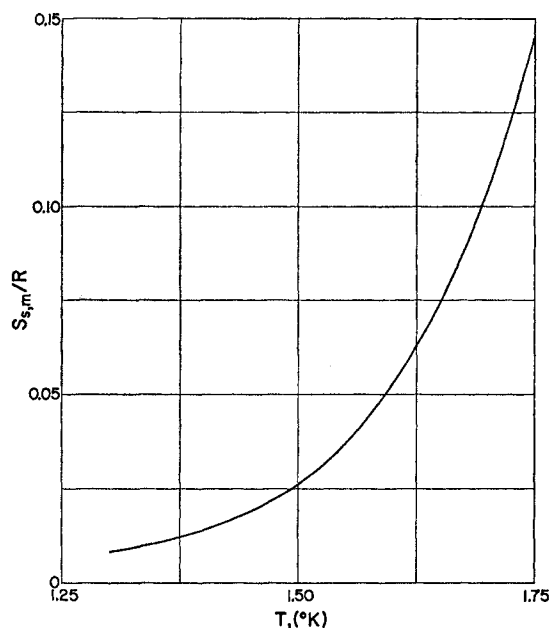


FIG. 1. Approximate molar entropy $S_{s,m}/R$ of solid He^4 along the phase separation line, as a function of the temperature ($^{\circ}\text{K}$).

properties of the latter. Before entering this main topic, it appears instructive to compare some of the thermal properties of the liquid and solid phases of normal substances, these phases being in equilibrium along the phase separation line. In these normal substances, the set of relations (1a) and (1b) are modified so as to insure the semi-definite positive character of α_p , or

$$\alpha_{p,\mu}(\phi_m) = [V_\mu(\phi_m)]^{-1}(\partial V_\mu / \partial T)_p \geq 0, \quad \mu = l, s. \quad (33)$$

In these substances and along the melting line,

$$V_l(\phi_m) > V_s(\phi_m), \quad (34)$$

at all points of $\phi_m(T)$, while the inequality

$$\alpha_{p,l}(\phi_m) \geq \alpha_{p,s}(\phi_m), \quad (35)$$

appears to be a rule of empirical foundation. Since in these substances, the liquid phase does not exist down to the absolute zero, the equal sign in (35) could be safely omitted, since the equality could only refer to vanishing normal expansion coefficients, realized by the Nernst theorem, at the absolute zero only. The empirical rule of thermodynamic character (35) arises from the generally reduced thermal stability of the volume of liquids as compared with the thermal stability of the volume of solids. The isobaric volume expansion coefficient or the relative differential volume change caused by a differential temperature increase under constant pressure is a measure of the thermal volume stability.

The rule (35) may perhaps be justified on the basis of a proposition put forward by Debye,²³ according to

²³ P. Debye, *Göttinger Vorträge* (B. G. Teubner, Leipzig, 1914), p. 17.

which the thermal expansion of a solid must originate with the anharmonic terms appearing in the expression of the energy of a solid considered to be an elastic medium. These terms are representative of the deviations from what would result from Hooke's law alone in the expression of the elastic energy. In liquids, considered qualitatively from the point of view of elastic media, the importance of anharmonicity may be expected to be far greater, in general, reducing the thermal stability of their volumes below that of the volumes of solids.

It should be noted that rule (35) is actually a strong relation, and the inequality,

$$[\partial V_l(\phi_m) / \partial T]_p > [\partial V_s(\phi_m) / \partial T]_p, \quad (36)$$

may be a better representation of the relative thermal stability of liquid and solid volumes along the phase separation line.

More generally, let $\alpha_{p,0}(\phi_{\text{sat}})$ be the isobaric expansion coefficient of the vapor in equilibrium with the liquid along the saturation line $\phi_{\text{sat}}(T)$; one has here in general, omitting the vicinity of the critical point,

$$\alpha_{p,0}(\phi_{\text{sat}}) \geq \alpha_{p,l}(\phi_{\text{sat}}). \quad (37)$$

In addition, one has, *a fortiori*,

$$\alpha_{p,0}(\phi_s') \geq \alpha_{p,s}(\phi_s'), \quad (38)$$

where $\phi_s'(T)$ refers to the sublimation line.

Consider now the case that in the inequalities (35), (37), or (38), the more dilute phase has normal thermal properties, and the denser phase is anomalous in the sense of the relations (1). It is easy to see that in this case, the preceding empirical rules remain valid and unchanged. Indeed, the anomalies refer, among others, to the existence of negative isobaric expansion coefficients in the denser phases, so that the expansion coefficients of the latter are necessarily smaller than those of the normal low-density phase in equilibrium with them along $\phi_{\text{sat}}(T)$ or $\phi_s'(T)$.

It is of interest to note here that the above rules connecting the isobaric expansion coefficients of two phases in equilibrium along the phase separation line remain valid in the singular case of the water-ice I equilibrium. This because here the liquid phase is the denser phase, so that the inequalities (34) and (35) have to be modified simultaneously, yielding the larger expansion coefficient of the low-density solid as compared with that of the thermally anomalous high-density liquid.

The rules (36) and (37) lose their validity in the case where the low-density phase is anomalous in the sense of the relations (1a) and (1b). It is assumed now that the low-density phase is the liquid phase so that the inequality (34) between the liquid and solid volumes remains unchanged throughout the length of the phase separation line $\phi_m(T)$. According to the observations, the volume change $\Delta V_m(T)$ is positive as stated above,

(30a). Since along the phase separation line

$$[V_{l,m}(T)]^{-1}(dV_{l,m}/dT) = \alpha_{p,l}(p_m) - \kappa_{T,l}(p_m)(dp_m/dT), \quad (39)$$

the volume change in the phase transformation at some temperature T_f or melting pressure $p_{m,f}$ is, obtained from the volume change at $T_i < T_f$, $\Delta V_m(T_i)$, as

$$\begin{aligned} V_{l,m}(T_f) - V_{s,m}(T_f) &= \Delta V_m(T_f) = \Delta V_m(T_i) \\ &+ \int_{T_i}^{T_f} [V_{l,m}(T)\alpha_{p,l}(T) - V_{s,m}(T)\alpha_{p,s}(T)]dT \\ &- \int_{p_i}^{p_f} [\kappa_{T,l}(p_m)V_{l,m}(p_m) \\ &\quad - \kappa_{T,s}(p_m)V_{s,m}(p_m)]dp_m. \end{aligned} \quad (40)$$

By (30a), $\Delta V_m(T_f)$ must be positive throughout the whole length of the phase separation line. This requires that

$$\begin{aligned} \Delta V_m(T_i) &+ \int_{T_i}^{T_f} [V_{l,m}(T)\alpha_{p,l}(T) - V_{s,m}(T)\alpha_{p,s}(T)]dT \\ &> \int_{p_i}^{p_f} [\kappa_{T,l}(p_m)V_{l,m}(p_m) - \kappa_{T,s}(p_m)V_{s,m}(p_m)]dp_m. \end{aligned} \quad (41)$$

Now, whether the two phases in equilibrium along the phase separation line are thermally normal or anomalous, there does not seem to be any exception to the rule

$$\kappa_{T,l}(p_m) > \kappa_{T,s}(p_m), \quad (42)$$

which requires that the isothermal compressibility of the liquid in equilibrium with the solid along the phase separation line be larger than that of the solid. As long as $\alpha_{p,l}$ and $\alpha_{p,s}$ are both positive and obey rule (35), it seems justified to expect that, whatever the range of integration in (40), the inequality (41) will be satisfied. However, if $\alpha_{p,l}$ is negative, over even a finite length of the phase separation line, (41) cannot be expected to be satisfied over arbitrary intervals $(T_f - T_i)$, although it could still remain satisfied over shorter temperature intervals or finite arcs of the phase separation line. If $\alpha_{p,s}$ were also negative, that is, if the solid were thermally anomalous along the phase separation line, then, in general, the integral on the left-hand side of (41) could allow it to be satisfied over a longer interval $(T_f - T_i)$ than if $\alpha_{p,s}$ were positive. Excluding the case of the extreme anomaly whereby $\alpha_{p,s}$ would be more negative over the phase separation line than $\alpha_{p,l}$, one is led to expect, in general, the anomalous regions of the liquid and the solid to be limited to finite segments of the phase separation line.

The problem which arises now concerns the generalization of the normal rule (35) to include the anomalous situations, subject always to the normal volume condition (34). Clearly, (35) cannot be valid in these cases of thermal anomaly, since it would require the liquid to be

less anomalous than the solid, both $\alpha_{p,l}$ and $\alpha_{p,s}$ being negative. Numerically, (35) would require the expansion coefficient of the solid to be larger than that of the liquid in equilibrium with it. Such a situation appears to be one of extreme anomaly as briefly alluded to above in connection with (41), although (35), subject to (34), is compatible with it. However, the less anomalous situations considered above are not compatible with the rule (35). If we exclude the rather unlikely occurrence of the case of extreme anomaly, it will be seen that (35), subject to (34), may be generalized so as to correlate the isobaric expansion coefficient of the anomalous liquid with that of the almost normal or anomalous solid. One is thus led to rewrite (35) as

$$|\alpha_{p,l}(p_m)| \geq |\alpha_{p,s}(p_m)|, \quad (43)$$

which, of course, reduces to (35) when the liquid and the solid are normal. This rule is fully compatible with the case of the anomalous liquid He⁴, whose anomaly extends over the temperature range defined by (7). The correlation of the anomalous thermal properties of liquid He⁴ with the thermal properties of solid He⁴ in equilibrium with it along the melting line has to be discussed in terms of (43) under the restriction of omitting the case of extreme anomaly.

In the present case of He⁴, the extreme anomaly could occur over a limited temperature range. This is because the lambda transition leads to large negative values of $\alpha_{p,l}$, and unless there is some similar transition in the solid phase, rule (35) could not be valid throughout the whole range of the anomaly. Since $\alpha_{p,s}$ would be lower than $\alpha_{p,l}$ over some range, the two negative expansion coefficients would cross at some $T_x < T_\lambda(p_m)$ with rule (35) being contradicted at $T > T_x$. Such a situation would be difficult to contemplate.

The relation (43) allows only two possible behaviors of solid He⁴ over the interval $[T_\alpha(p_m)_I - T_\alpha(p_m)_II]$. In both cases, (43) imposes anomalous thermal properties on solid He⁴ over this temperature interval. These two possibilities correspond, respectively, to what may be called the case of least anomaly, case (A), and to that of the completely anomalous solid, case (B). The study of these two possible anomalous solids follows.

Case (A)

In this case of least anomaly, $\alpha_{p,s}(p_m)$ may be such that

$$\alpha_{p,s}(p_m) \geq 0, \quad (44)$$

or the solid is normal with the exception of isolated points at the melting line, such as $T_\alpha(p_m)_II$ and $T_\alpha(p_m)_I$, where $\alpha_{p,s}$ must vanish by (43), in addition to its vanishing at the absolute zero, by the Nernst theorem. Since $\alpha_{p,s}(p_m)$ is a continuous and differentiable function of the macroscopic variables of state, together with its derivative, $\alpha_{p,s}$ must have at least one maximum between the absolute zero and $T_\alpha(p_m)_II$, and it must have

at least one other maximum between $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$.

The rule (43) requires that the coefficients $\alpha_{p,i}$ and $\alpha_{p,s}$ intersect at their common zeros but at no other points. Hence, in case (A), the solid is necessarily anomalous at $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$. Since

$$\begin{aligned}\alpha_{p,s}(p_m) &= -[V_s(p_m)]^{-1}(\partial S_s/\partial p)_T \\ &= 0, \quad T = T_\alpha(p_m)_{II}, \quad T = T_\alpha(p_m)_I, \quad (45)\end{aligned}$$

$S_s(p, T)$, being a decreasing function of the pressure, has maximas at the melting line at two temperatures, while it has no such maximas at any other points along the melting line, reached along isothermal curves in the solid phase. That is, $S_s(p, T)$ increases with decreasing pressure, at constant T values, but reaches its upper limit at $p_m(T)$ with a finite slope, $(\partial S_s/\partial p)_T$ being finite though negative, in general.

In this case of least anomaly, the vanishing of $\alpha_{p,s}$ at the isolated finite temperatures, $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$, where $\alpha_{p,i}$ vanishes also, may be reasonably attributed to the competition between at least two groups of thermal excitations, as is the case with the liquid. As briefly discussed in the preceding sections, the thermal anomalies of the liquid may be ascribed approximately to the competition between the normal phonon excitations and the anomalous higher energy excitations of the normal fluid fraction. Or, if we denote by the subscripts a and n the quantities associated with the anomalous and normal excitations of the solid, one is led to represent the total entropy of the system as

$$S_s(p, T) = S_{s,a}(p, T) + S_{s,n}(p, T), \quad (46)$$

which yields at once

$$\alpha_{p,s}(p, T) = \alpha_{p,a}(p, T) + \alpha_{p,n}(p, T), \quad (47)$$

where

$$\alpha_{p,n}(p, T) \geq 0, \quad \alpha_{p,a}(p, T) \leq 0. \quad (48)$$

In the case of least anomaly, one has

$$\alpha_{p,n}(p, T) \geq -\alpha_{p,a}(p, T), \quad (49a)$$

and

$$\begin{aligned}\alpha_{p,n}(p_m, T_{\alpha, II}) &= -\alpha_{p,a}(p_m, T_{\alpha, II}), \\ \alpha_{p,n}(p_m, T_{\alpha, I}) &= -\alpha_{p,a}(p_m, T_{\alpha, I}).\end{aligned} \quad (49b)$$

The vanishing of the isobaric expansion coefficient of the solid at $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$ may be ascribed to the mutual cancellation of the partial expansion coefficients arising from the groups of normal and anomalous thermal excitations. The group of normal excitations would dominate the anomalous group over the whole temperature range with the exception of the isolated temperatures $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$. Actually, the possibility still exists here that $\alpha_{p,s}(p_m)$ vanishes at isolated points between these temperatures along the melting line. Such an oscillatory behavior of $\alpha_{p,s}$ is still compatible with the rule or conditions used above.

Case (B)

In this case, solid He^4 , in equilibrium with liquid He^4 along the phase separation line, is completely anomalous over at least a limited temperature range between $T_\alpha(p_m)_{II}$ and $T_\alpha(p_m)_I$. Clearly, rule (43) still allows $\alpha_{p,s}(p_m)$ to be positive over certain regions of the interval $[T_\alpha(p_m)_I - T_\alpha(p_m)_{II}]$ and negative over other regions of this interval. The oscillatory behavior of the thermal properties of the solid, oscillating between normal and anomalous behaviors would, however, be strange, since it would suggest that the partial thermal properties of the groups of normal and anomalous thermal excitations would be themselves oscillatory. In this case (B) of the completely anomalous solid He^4 , the simplest situation seems to be the one in which the anomalies exist over the whole temperature range $[T_\alpha(p_m)_I - T_\alpha(p_m)_{II}]$, as is the case with the liquid in equilibrium with it.

II.4. Negative Isobaric Volume Expansion Coefficient of Solid He^4

The prediction, in the previous sections, of the anomalous character of solid He^4 in equilibrium along the phase separation line with the anomalous liquid He^4 will now be verified in terms of somewhat incomplete data on these two phases along the melting line. We will thus evaluate approximately the expansion coefficients $\alpha_{p,i}$ and $\alpha_{p,s}$ along the melting line $p_m(T)$. The data to be used^{12,14,17} extend from about 1.1–1.2°K upward. There are no data available on solid He^4 above the melting line at pressures $p_m(T) \leq p \leq 50$ atm, so that an evaluation of the thermally anomalous properties (1a) or (1b) of the solid in this pressure range is excluded at the present time.

In the numerical evaluation of the expansion coefficients, the rigorous thermodynamic formula, used already above, Eq. (39),

$$\begin{aligned}\alpha_p(p_m) &= [V(p_m)]^{-1}[\partial V(p_m)/\partial T]_{p_m} \\ &= [V(p_m)]^{-1}[dV(p_m)/dT] \\ &\quad + \kappa_T(p_m)(dp_m/dT), \quad (39a)\end{aligned}$$

will be applied. Here $V(p_m)$ refers to $V_l(p_m)$ or $V_s(p_m)$, the volume of the liquid and solid along the melting line $p_m(T)$, $\kappa_T(p_m)$ stands for the isothermal compressibility $\kappa_{T,l}(p_m)$ or $\kappa_{T,s}(p_m)$, and the straight temperature derivative is to be taken along the phase separation line. It should be clearly kept in mind that the direct evaluation of $\alpha_{p,i}(p_m)$ or of $\alpha_{p,s}(p_m)$ with the exact formula (39a) and the available data is, to within the approximations of the latter, strictly rigorous in that it represents a truly empirical check on the existence or nonexistence of the thermally anomalous solid over the temperature range to be explored. This verification of the predicted anomalies is thus strictly independent of the various arguments of either thermodynamic or of the two-fluid theoretical background which have been

TABLE I. Approximate isobaric expansion coefficients of liquid and solid He⁴ along the phase separation line.

| T (°K) | $\alpha_{p,l}^I$ | $\alpha_{p,l}^{II}$ $10^{-3}/(^{\circ}\text{K})$ | $\alpha_{p,s}^I$ | $\alpha_{p,s}^{II}$ |
|-------------|------------------|---|------------------|---------------------|
| 1.15 | -15.9 | | -6.03 | |
| 1.20 | -19.1 | -19.3 | -6.31 | -6.47 |
| 1.25 | -22.5 | | -6.34 | |
| 1.30 | -25.8 | -26.1 | -6.00 | -6.25 |
| 1.35 | -29.1 | | -5.21 | |
| 1.40 | -32.4 | -33.5 | -4.05 | -5.12 |
| 1.45 | -35.6 | | -2.35 | |
| 1.50 | -38.6 | -41.1 | +0.044 | -2.50 |
| 1.55 | -41.1 | -44.3 | 3.40 | +0.23 |
| 1.60 | -43.5 | -46.1 | 7.40 | 4.80 |

advanced above in connection with the probable behavior of $\alpha_{p,s}(\rho_m)$ or the associated thermal properties of the solid.

In (39a), with the exception of $\kappa_{T,s}(\rho_m)$, the quantities $V_l(\rho_m)$, $V_s(\rho_m)$, and $\rho_m(T)$ are available over a finite temperature range through direct measurements^{12,14,16} while the various derivatives and $\kappa_{T,l}(\rho_m)$ could be obtained from the measured quantities and the derived diagrams¹² of liquid He⁴. The derived isothermal compressibilities¹² of liquid He⁴ at $p \gtrsim 20$ atm appear to be somewhat out of line at temperatures $T \gtrsim 1.55$ – 1.60°K . These derived liquid compressibilities, through the partial derivatives $(\partial \rho_l / \partial p)_T$ of the liquid densities ρ_l , seem to imply the increase of the isothermal compressibilities at constant temperature with increasing pressure. As a consequence, the compressibilities $\kappa_{T,l}(\rho_m)$, obtained by extrapolation to the melting line, may already be larger than their correct values at $T \gtrsim 1.4$ – 1.5°K . Hence, by (39a), the calculated isobaric expansion coefficients $\alpha_{p,l}(\rho_m)$ are upper limits of these quantities.

In order to evaluate the expansion coefficients $\alpha_{p,s}(\rho_m)$ of the solid, we had to use the approximate compressibilities of the liquid along the melting line, there being no data whatsoever available on $\kappa_{T,s}(\rho_m)$. Now rule (42) requires that the isothermal compressibility of the solid be smaller than that of the liquid in equilibrium with it at the phase separation line. Since an exception to this rule is rather unlikely, it seems reasonable to state that the calculated $\alpha_{p,s}(\rho_m)$ values are necessarily upper limits of this property. Actually, at $T \gtrsim 1.4$ – 1.5°K , the calculated $\alpha_{p,s}(\rho_m)$ values would be upper limits already, independently of the requirement of rule (42) because of the upper limit character of the $\kappa_{T,l}(\rho_m)$ values themselves, as mentioned above.

We give in Table I the calculated approximate coefficients $\alpha_{p,l}(\rho_m)$ and $\alpha_{p,s}(\rho_m)$, the latter being upper limits as just noted. There are two series of values for both liquid and solid expansion coefficients. They originate with two series of values of the derivatives $(d\rho_m/dT)$. These were obtained through analytical fits²⁴

²⁴ Thanks are due to Dr. R. K. Zeigler for the various analytical fits, to Mrs. J. E. Powers for the numerical calculations, and to Mrs. B. M. Hindman for the preparation of the graphs.

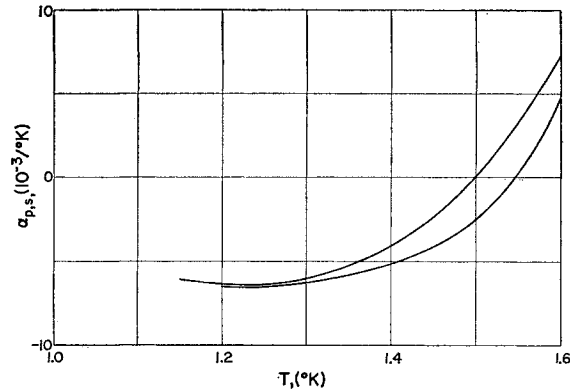


FIG. 2. Approximate isobaric volume expansion coefficients $\alpha_{p,s}^I$ and $\alpha_{p,s}^{II}$ of solid He⁴ ($10^{-3}/^{\circ}\text{K}$) along the phase separation line, as a function of the temperature ($^{\circ}\text{K}$).

by the method of least squares of the liquid and solid volumes, $V_{l,m}(T)$ and $V_{s,m}(T)$ and of the melting pressure $p_m(T)$. These analytical fits gave rise to $\alpha_{p,l}^I$ and $\alpha_{p,s}^I$. Using values of $(d\rho_m/dT)$ given by Swenson¹⁷ and obtained through a different analytical fit of his measured $p_m(T)$ values, one obtains the second set of expansion coefficients $\alpha_{p,l}^{II}$ and $\alpha_{p,s}^{II}$.

It is seen that both $\alpha_{p,l}^I$ and $\alpha_{p,l}^{II}$ are negative and decrease rapidly with increasing temperatures as expected. The major results exhibited by Table I concern the values of the isobaric expansion coefficients $\alpha_{p,s}^I$ and $\alpha_{p,s}^{II}$ of the solid. These are both negative at low temperatures. One of them, $\alpha_{p,s}^I$ exhibits a minimum, while $\alpha_{p,s}^{II}$ seems to have such a minimum. They increase with increasing temperatures toward zero and positive values. The zero of these calculated $\alpha_{p,s}^I$ functions is close to 1.5°K , that of $\alpha_{p,s}^{II}$ is close to 1.55°K . The two sets of coefficients $\alpha_{p,s}^I$ and $\alpha_{p,s}^{II}$ are close to each other, and their differences are of no particular significance.

According to Table I, solid He⁴ has anomalous thermal properties over a finite temperature range along the melting line. Hence, case (B) of the completely anomalous solid, discussed in the preceding section, is at hand here. Inasmuch as the existence of the negative $\alpha_{p,s}$ values also means that, (1a),

$$[\partial S_s(\rho_m)/\partial p]_T > 0, \quad (1c)$$

it is seen that the anomalous solid must extend over a finite pressure range at pressures $p > p_m(T)$ over the relevant temperature range of the anomaly. This conclusion results directly from the continuity and differentiability of $S_s(p, T)$ and of its first derivatives. Indeed, the finite positive partial pressure derivative at the melting line has to decrease first continuously toward zero at constant temperature at increasing pressures to become normal or negative at higher pressures in the solid phase.

We give in Fig. 2 the graphs of the two solid expansion coefficients $\alpha_{p,s}^I$ and $\alpha_{p,s}^{II}$. A further discussion of these

coefficients would not be fully justified at the present time, because the $\alpha_{p,s}(T)$ curves refer strictly to upper limits, so that the final correct form of the $\alpha_{p,s}(T)$ function is not available. The correct curves must be depressed below those given in the graph. It should also be remembered that the temperature values of the zeros of the $\alpha_{p,s}$ curves are essentially lower limits, the true zero of $\alpha_{p,s}$ must be higher than about 1.50–1.55°K.

As emphasized above, the numerical values of the α_p coefficients are strictly rigorous and their limitations result essentially from the approximate character of the experimental data used to derive them. It thus appears justified to conclude that they conform to the predictions based on the thermodynamic correlation of the thermal anomalies of a liquid and solid in equilibrium along the phase separation line, developed in the present work. The results obtained, with the data available at the present time, yield thus an affirmative answer to the question, stated in the Introduction, of whether the thermal anomalies of liquid He⁴ persist or not in solid He⁴ of higher density than the liquid at or near the phase separation line and over a finite temperature range.

At temperatures $T \gtrsim 2.0^\circ\text{K}$, the liquid is normal,¹⁴ and the solid should also be normal. This higher temperature region is of a somewhat reduced interest from the standpoint adopted in this work, namely, the investigation of the nature of the solid in equilibrium with the anomalous liquid. Still, the trend of variation of the entropy of the solid beyond $T_\lambda(p_m)$ would be of great interest in connection with a determination of the ways the anomalous solid becomes normal at these higher temperatures.

III. SOLIDIFICATION OF LIQUID He⁴ AT LOW TEMPERATURES

We should like to study in this section the liquid-solid transformation at low enough temperatures where the dominant thermal excitations of liquid He⁴ II are phonons. As mentioned earlier, the empirical basis for the existence of such a phonon region at low temperatures consists of the heat capacity measurements¹⁰ which yielded a T^3 -type heat capacity in accord with the hypothesis originally put forward by Tisza¹¹ on the probable Debye-liquid character of liquid He⁴ at sufficiently low temperatures. Inasmuch as only longitudinal phonons are expected to be propagated essentially, the longitudinal characteristic temperature evaluated⁹ with the observed liquid density and small amplitude, fairly low frequency compressional wave velocity,¹² is very close to the observed one.¹⁰ These heat capacity measurements refer only to the saturated liquid. No heat capacity measurements are available in compressed liquid He⁴ at low temperatures. However, in this low-temperature region, the liquid may reasonably be expected to be normal. This limited region of the phase diagram of the liquid is outside its anomalous region,

discussed above in detail, or

$$\begin{aligned} [\partial S_l(p, T)/\partial p]_T &< 0, \\ T &< T_\alpha(p_m)_{II}. \end{aligned} \quad (1d)$$

This normal behavior is imposed by the dominance of phonons in the thermal excitations of the compressed liquid whose characteristic longitudinal temperature increases in compression. Since

$$\lim_{T \ll \Theta_l} S_l(p, T)/R = (4\pi^4/15)(T/\Theta_l)^3, \quad (50)$$

the entropy of the liquid must decrease on compression, omitting in $S_l(p, T)$ small contributions arising with thermal excitations other than phonons.

We saw above that both liquid and solid He⁴, in equilibrium along the phase separation line, at $T \gtrsim 1.1$ – 1.2°K , have entropies whose temperature variations are very rapid. This suggests that at these higher temperatures where the thermal properties of both phases are anomalous, the thermal excitations are also anomalous. However, it seems reasonable to assume that solid He⁴ may itself become a Debye-type solid at the low temperatures where its static thermal properties become normal as is the case with the saturated liquid and probably also with the compressed liquid.

It is an experimentally established fact that solid He⁴ is a hexagonal close-packed crystal^{12,25} so that for a description of its elastic properties, it would require five elastic constants.²⁶ Strictly speaking, there are no data available on the elastic constants of solid He⁴, above all near the phase separation line and at the low temperatures of interest to us here. However, the axial ratio of the hexagonal crystal (c/a) is practically the ideal one or $2(2/3)^{1/2}$. As a consequence, it would appear justified, at the present time, to assume that this close-packed structure is of high elastic isotropy to some fair degree of approximation.²⁷ The five independent elastic constants reduce then to approximately two, namely, λ and μ , the two Lamé coefficients, as in the limit of complete elastic isotropy.²⁶ In terms of the Poisson ratio σ of the solid, that is, the ratio of lateral contraction to longitudinal extension under terminal pull,

$$\sigma = \lambda/2(\lambda + \mu), \quad (51)$$

the characteristic temperature of the solid Θ_s is given by²⁸

$$\begin{aligned} 3\Theta_s^{-3} &= \Theta_L^{-3} + 2\Theta_l^{-3} \\ &= (k/h)^3(4\pi V_s/3N)(\rho_s \kappa_s)^{1/3} \varphi(\sigma), \\ \varphi(\sigma) &= [(1+\sigma)/3(1-\sigma)]^{1/2} \\ &\quad + 2[2(1+\sigma)/3(1-2\sigma)]^{1/2}, \end{aligned} \quad (52)$$

²⁵ A. F. Schuch, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 45.

²⁶ A. E. H. Love, *Elasticity* (Dover Publications, New York, 1944), p. 160.

²⁷ For recent work in connection with this problem, see L. J. Slutsky and C. W. Garland, *Phys. Rev.* **107**, 972 (1957).

²⁸ L. Brillouin, *Les Tenseurs en Mécanique et en Élasticité* (Dover Publications, New York, 1946), pp. 324–6.

Θ_L and Θ_t being the longitudinal and transverse characteristic temperatures, V_s the molar volume of the solid, N is Avogadro's number, ρ_s the density, and κ_s the adiabatic compressibility of the solid, along the phase separation line. Since in the liquid,

$$\Theta_t^{-3} = (k/h)^3 (4\pi V_l/3N) (\rho_l \kappa_l)^{\frac{1}{2}}, \quad (53)$$

and

$$\lim_{T \ll \Theta_t} S_s(p, T)/R = (4\pi^4/15) T^3 [\Theta_L^{-3} + 2\Theta_t^{-3}], \quad (54)$$

one obtains at once for the entropy change in the liquid-solid transformation, on the assumption of the thermal excitations of both phases being essentially phonons,

$$\begin{aligned} \Delta S_m(p_m, T)/R &= [S_l(p_m, T) - S_s(p_m, T)]/R \\ &= [S_l(p_m, T)/R] \\ &\quad \times [1 - (V_l/V_s)^{\frac{1}{2}} (\kappa_s/\kappa_l)^{\frac{1}{2}} \varphi(\sigma)]. \end{aligned} \quad (55)$$

At the low temperatures under consideration, the normal behavior of the liquid requires that

$$S_l(p_m, T) < S_l(p_{\text{sat}}, T)$$

or the liquid entropy at the melting line must be lower than the entropy under saturation pressure p_{sat} at the same temperature. Using the experimental volumes or densities at saturation¹² and along the melting line, as well as the liquid compressibilities¹² $\kappa_l(p_{\text{sat}}, T)$ and $\kappa_l(p_m, T)$, all available only at $T \gtrsim 1.0^\circ\text{K}$, making the reasonable assumption that neither the volumes nor the compressibilities will change significantly toward lower temperatures, one finds that the liquid entropy along the melting line may be only some 25% of the entropy at saturation.

The quantity inside the brackets on the right-hand side of (55) depends essentially on $\varphi(\sigma)$. Here $V_l \sim 1.1V_s$, and κ_s could be as small as $0.75\kappa_l$. In isotropic solids,²⁶ σ varies between 0.25 and 0.43, approximately. The function $\varphi(\sigma)$ varies, for this range of σ , between 4.72 and 36.3. In general then, ΔS_m is negative, or the solidification over the low-temperature region is accompanied by an increase in entropy, the entropy of the solid being larger than that of the liquid.

The temperature slope of the melting pressure line $p_m(T)$ is, by (32), with ΔS_m given by (55), at low temperatures

$$\begin{aligned} \lim_{T \text{ small}} (dp_m/dT) &= (4\pi^4/15) (T/\Theta_t)^3 \\ &\quad \times [1 - (V_l/V_s)^{\frac{1}{2}} (\kappa_s/\kappa_l)^{\frac{1}{2}} \varphi(\sigma)] / \Delta V_m. \end{aligned} \quad (56)$$

It is seen that if (dp_m/dT) turned out to be negative at low temperatures, this slope would increase rather rapidly toward zero at very low temperatures. Since at $T \gtrsim 1.2^\circ\text{K}$, (dp_m/dT) is observed to be positive, it is likely that if (56) gave effectively a negative melting pressure slope, the zero of this slope will occur at a temperature higher than the temperatures associated

with the complete dominance of the phonon type of thermal excitations. Accordingly, an experimental search for the anomaly of the melting pressure $p_m(T)$ should start at $T \gtrsim 1.0^\circ\text{K}$ and should be extended downward. Also, because of the rapid numerical decrease of (dp_m/dT) with decreasing temperatures, the observation of the probable anomaly of $p_m(T)$ might be more advantageous at medium temperatures.

A remark is of interest here concerning the precise meaning of the coefficients λ and μ in (51) or (52), appearing in the latter through the ratio σ . Inasmuch as the solid phase is obtained through compression, the lowest pressure solid at a precise temperature at the phase separation line corresponds, in a limiting sense, to a normal solid under essentially vanishing external pressure. All internal pressure effects due to thermal excitations are included in the above elastic coefficients.²⁸ The pressure effects on these coefficients in the compressed solid may then depend, to a certain approximation, on the excess pressures $(p - p_m)$ above the melting pressure.

The physical basis of the preceding formal discussion of the predicted entropy increase on solidification in the temperature range where the thermal excitations are overwhelmingly phonons is associated with the development of the finite rigidity coefficient μ of the solid. This elastic coefficient vanishes essentially in the liquid phase. As a consequence, the degrees of freedom of the solid other than the compressional ones become available for thermal excitations, yielding necessarily an increased thermal disorder or increased entropy, compared with that of the liquid at the same temperature. If the anomaly of the He⁴ melting line became observable, this anomaly would be similar in its origin to the observed anomaly^{14,29} of the melting line of He³. In the latter case, the solidification is accompanied by the release of spin degrees of freedom. This results through the decrease in the solid of the strength of the apparent internal field existing already in the liquid, tending to align the spins antiparallel, yielding thus an increased spin disorder in the solid as compared with that of the liquid, the two phases being in equilibrium along the phase separation line. The increase of spin entropy on solidification is large enough to compensate, at the low temperatures, $T \lesssim 0.3^\circ\text{K}$, for the entropy decrease of the normal degrees of freedom, assuring thus the development of the minimum of the melting line. Experimental indications at the present time³⁰ seem to be compatible with a monotonic increase of dp_m/dT toward zero in the limit of the absolute zero with the melting line developing an inflection point between the temperature of its minimum and the absolute zero. This would be in

²⁸ J. L. Baum, D. F. Brewer, J. G. Daunt, and D. O. Edwards, *Phys. Rev. Letters* **3**, 127 (1959).

³⁰ D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, *Proceedings of the Second Symposium on Liquid and Solid He³*, edited by J. G. Daunt (Ohio State University Press, Columbus, 1960), p. 126.

agreement with our previous work¹ on the melting pressure line $p_m(T)$ of He^3 .

IV. CONCLUDING REMARKS

According to the studies described in the present work, solid He^4 , in equilibrium with liquid He^4 , has anomalous thermal properties over a finite temperature interval, over which the liquid is also anomalous. Various arguments of macroscopic thermodynamic character lead one to predict thermal anomalies in the solid in equilibrium with the liquid along the phase separation line or near this line. Experimental information, however scarce, available in these two phases allow one to actually prove, with the help of a rigorous thermodynamic formula, that the solid is anomalous over a finite temperature range. This proof is entirely independent of the rules of thermodynamic background which helped to predict the existence of the anomalous solid. The sharpness of the proof is only reduced by the unavailability of certain data needed for it, as well as by the ever-present limitation in the precision of the available data entering into its numerical evaluation. As a consequence, the temperature range of the anomalies could only be deduced approximately through its lower limit.

These results suggest that extensive experimental investigations of the anomalous solid He^4 near the melting line and over a pressure range above the melting line would be of interest. Independently of the intrinsic properties of this solid, some of which appear to become anomalous at the approach of the temperature associated with the characteristic liquid He^4 II \rightarrow He^I transformation at the melting line, the investigation of the anomalies of the solid could also shed additional light on the above transformation as well as on the anomalous properties of the liquid itself.

The existence of the anomalous solid raises, of course, the problem of the origin of this behavior. In the liquid phase, the thermal anomalies have not been explained satisfactorily either. Actually, the suggested explanation of these anomalies was shown to be associable with the one used in accounting for the anomalies of similar macroscopic character of liquid He^3 in a different though finite temperature range. Namely, in liquid He^4 , these anomalies may be assigned to the dominance of high-energy excitations as compared with the excitations of low-energy states associated with the longitudinal or compressional modes of elastic vibrations, that is, longitudinal phonons. At low enough temperatures, the thermal excitations of the latter modes dominate and insure the normal behavior of the liquid.⁹ The thermal anomalies of the liquid appearing at higher temperatures have to originate with a group of thermal excitations of anomalous character. The thermal anomalies of the solid could also originate with the competition between at least two groups of thermal excitations, one

normal, the other anomalous. In view of the low-temperature normal liquid being a Debye-type system whose shear modes of elastic motions are inhibited through the essentially vanishing rigidity modulus, it seems reasonable to expect the low-temperature solid to become also a conventional solid in full possession of all its elastic modes of motion. The probable occurrence of the low- or medium-temperature anomaly of the melting line has been discussed in some detail in Sec. III.

The fundamental problem raised by the thermodynamic proof obtained here of the anomalous solid He^4 concerns the similarities and differences between the anomalous groups of higher energy excitations in the liquid and the solid. Suppose that the anomalous thermal properties of the solid actually extended over about the same temperature interval as those of the liquid along the melting line. This would suggest that the liquid-solid phase change, leading at the temperatures under consideration to close packing of the atoms, has not completely modified the anomalous character of the high-energy thermal excitations of the liquid, and these persist in possibly milder form in the solid phase also, at least at pressures just necessary to produce solidification and at somewhat higher pressures. At the present time, we saw above, the available data tend to reduce the temperature range of the solid anomaly below the one exhibited by the liquid. Nevertheless, with the deduced temperature region of the solid anomaly being a lower limit, it seems necessary to recognize the possibility that, ultimately, the anomalies of the solid and the liquid at equilibrium have the same or similar roots. Assume, indeed, that a successful proof could be advanced for the role played by quantum statistical symmetry in the determination of the anomalous thermal properties of liquid He^4 . It would then appear justified to attempt at a generalization of the statistical symmetry through its explicit intervention, with the necessary modifications, in the description of the collection of close-packed atoms occupying some ten percent smaller volume than that of the liquid phase compressed to the phase separation line and forming the solid of enormous compressibility. It should be remembered, in this connection, that a similar situation appears to be realized in solid He^3 in equilibrium with liquid He^3 along the phase separation line. Here, antisymmetric statistics seem essentially to be involved in the explanation of the anomalous thermal properties of the liquid phase,⁴⁻⁶ extending over a fairly wide temperature interval, through its nuclear spin system. The idea that this same cause should be responsible for the thermal anomalies of the solid, along the phase separation line and at least over a finite pressure range above it, led one to effectively predict¹ the existence of these anomalies in solid He^3 over a finite temperature interval in agreement with the observations.¹³