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Anomalous Liquid-Solid Transformation of Helium-Three

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The present paper is devoted to the study of the anomalous liquid-solid phase transformation of He^3 . By allowing the phase boundary lines of the liquid and solid volumes to have singular pressure derivatives, the melting pressure minimum and the boundary volume line maximas of the liquid and solid occur at two different temperatures. This leads to smooth variations of the anomalous isobars and isochores of the liquid, insuring a single minimum to the isobaric expansion coefficients, in qualitative agreement with data available at the present time. The transformation of a normal family of isotherms into an anomalous one, and vice versa, either on a phase transformation or within a pure phase will be clarified. The geometry of the state surface, on the basis of the stated assumptions, will be shown to justify the existence of thermal anomalies of the cubic solid He^3 over a finite extension of this phase well beyond its boundary line.

1. INTRODUCTION

IN recent work,¹ one of us discussed the phase diagrams of liquid and solid He^3 . These studies were aimed at obtaining from the anomalies of the melting pressure line $P(T)$, the liquid and solid volume boundary lines $V_L(T)$ and $V_S(T)$, determined recently by the one of us in collaboration with Grilly and Sydorik,² some features of the families of characteristic curves of the state surface of He^3 . Throughout the previous work,¹ the guiding assumption consisted of avoiding irregularities of derivatives such as dV_L/dP and dV_S/dP along the phase separation lines. This assumption was sufficient to prove that the extremas of $P(T)$, $V_L(T)$, and $V_S(T)$ had to occur at a unique temperature T_a . A satisfactory proof could be given also, $P(T)$ having a minimum at T_a ,^{3,4,2} for $V_L(T)$ to have a maximum there. The assumption of regularity of the above derivatives was shown to lead to peculiar properties of the families of isobars $V(T,p)$, and isochores $p(T,V)$, particularly in the vicinity of the extremas of the phase separation lines.

Experimental isobaric expansion coefficients of liquid He^3 obtained in the meantime at pressures approaching

the melting pressure and down to quite low temperatures,^{5,6} led us to reinterpret similar data of one of us and his collaborators,² on the isobaric expansion coefficient of liquid He^3 along the melting line. This collection of more extensive data suggested that the assumption of regularity of the derivatives dV_L/dP , dV_S/dP used previously^{1,2} is too restrictive and may not be compatible with the shape of the directly^{2,5} or indirectly⁶ measured isobaric expansion coefficients at higher pressures and lower temperatures. One of the main objects of the present extension of the previous work,¹ is to show that by allowing the derivatives dV_L/dP and dV_S/dP along the phase separation lines to become singular at a point, the anomalous isobaric expansion coefficients of the compressed liquid as well as the temperature coefficients of the pressure tend to agree qualitatively with available experimental determinations.

The results based on the above stated assumption and derived previously,¹ seem to represent in part the situation existing apparently in liquid He^4 II at temperatures around the predicted locus $T_a(P)_{\text{II}}$ of the vanishing expansion coefficients α_p , or vanishing derivatives $(\partial p/\partial T)_V$.⁷ Experimental data on compressed liquid He^4 II at low temperatures are lacking at the present time.

¹ L. Goldstein, Ann. Phys. (New York) **16**, 205 (1962).

² R. L. Mills, E. R. Grilly, and S. G. Sydorik, Ann. Phys. (New York) **12**, 41 (1961); S. G. Sydorik, R. L. Mills, and E. R. Grilly, Phys. Rev. Letters **4**, 495 (1960).

³ D. M. Lee, H. A. Fairbank, and E. J. Walker, Bull. Am. Phys. Soc. **4**, 239 (1959).

⁴ J. L. Baum, D. F. Brewer, J. G. Daunt, and D. O. Edwards, Phys. Rev. Letters **3**, 127 (1959).

⁵ D. M. Lee, H. A. Fairbank, and E. J. Walker, Phys. Rev. **121**, 1258 (1961).

⁶ D. F. Brewer and J. R. G. Keyston, Nature **191**, 1261 (1961).

⁷ L. Goldstein, Phys. Rev. **122**, 726 (1961), Phys. Rev. Letters **5**, 104 (1960).

Another object of the present paper consists of obtaining a new description of the propagation of the thermal anomalies of liquid He^3 into the solid phase in equilibrium with it and into the main domain of this phase, beyond the phase separation line. The thermally anomalous character of solid He^3 , repeatedly discussed previously,^{8,1} will be proved here through the geometry of the thermodynamic state surface. Normal elastic behavior will be assumed throughout the discussion of the solid phase.^{7,2}

2. THE VOLUME-PRESSURE DIAGRAM

The Family of Anomalous Isotherms of Liquid and Solid He^3

Experimental studies of the melting pressure line $P(T)$ indicate,^{5,6,4} that

$$dP/dT=0, \quad d^2P/dT^2>0, \quad T=T_a, \quad P_m=P(T_a), \quad (1)$$

or the melting pressure anomaly consists of its minimum P_m at T_a . Furthermore, the nonmonotonic character of $V_L(T)$ proved previously,¹ requires

$$dV_L/dT=0, \quad d^2V_L/dT^2<0, \quad T=T_a', \quad V_{L,M}=V_L(T_a'), \quad (2)$$

where,

$$T_a'=T_a-\tau, \quad \tau \ll T_a, \quad (3)$$

the location of the maximum of $V_L(T)$ at T_a' being lower but probably quite close to T_a , the temperature of the minimum of $P(T)$. By virtue of (1) and (2),

$$dV_L/dP<0, \quad T<T_a', \quad (4a)$$

$$dV_L/dP>0, \quad T_a'<T<T_a, \quad (4b)$$

$$dV_L/dP<0, \quad T>T_a. \quad (4c)$$

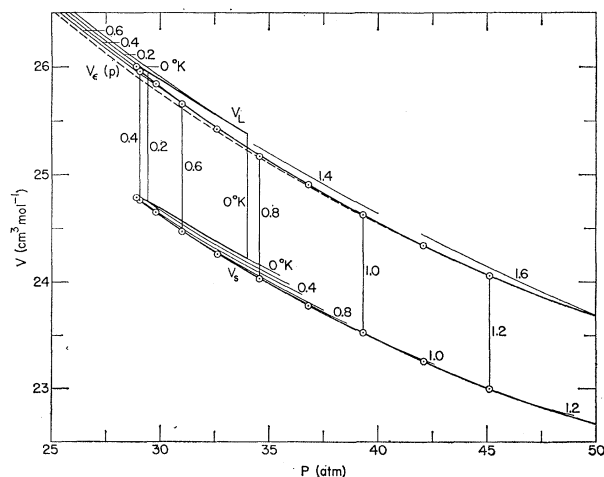


FIG. 1. The volume-pressure diagram of the anomalous liquid and solid He^3 , displaying the invariance of the thermal anomalies in the phase transformation. The circles represent the measurements of Mills, Grilly, and Sydoriak (reference 2). The dashed line is the envelope of a class of isotherms.

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

One also has

$$\lim_{P \rightarrow P(T_a')} dV_L/dP=0, \quad d^2V_L/dP^2<0, \quad T=T_a', \quad (5)$$

and

$$\lim_{P \rightarrow P_{m,-}} dV_L/dP \rightarrow +\infty, \quad \lim_{P \rightarrow P_{m,+}} dV_L/dP \rightarrow -\infty, \quad (6)$$

and

$$\lim_{P \rightarrow P_{m,+}} d^2V_L/dP^2 \rightarrow +\infty, \quad \lim_{P \rightarrow P_{m,-}} d^2V_L/dP^2 \rightarrow -\infty. \quad (7)$$

By (5) and (6), over the small temperature interval τ defined by (3), or the pressure interval

$$P_m - P(T_a') = P(T_a) - P(T_a - \tau),$$

the derivative dV_L/dP must decrease from $+\infty$ to zero. The singular character of $V_L(P)$ at P_m may be described by the discontinuity,

$$\Delta(dV_L/dP)_{P_m} = (dV_L/dP)_{P_{m,+}} - (dV_L/dP)_{P_{m,-}} \rightarrow -\infty, \quad (8)$$

and by

$$\Delta(d^2V_L/dP^2)_{P_m} = (d^2V_L/dP^2)_{P_{m,+}} - (d^2V_L/dP^2)_{P_{m,-}} \rightarrow +\infty. \quad (9)$$

It is useful to consider now the (V,P) diagram, Fig. 1. In this diagram, the edge $V_L(P)$ of the state surface of the pure liquid has been determined in this Laboratory,² for pressures $P > P_m(T_a)$, $V_L < V_L(P_m)$, $T > T_a$, together with the edge $V_S(P)$ of the solid domain of the state surface, over the similar intervals of the variables of state P and T , and $V_S < V_S(P_m)$. The region of the state surface connecting these edges, which is associated with the mixed phase is thus also determined.

The extensions of the edge lines $V_L(P)$ and $V_S(P)$, beyond P_m and T_a , that is toward lower temperatures, are only approximate. They are based on a reasonable extrapolation of data available at the present time.^{2,5} The edge vertices are $(V_L(P_m), P_m)$, $(V_S(P_m), P_m)$. The very sharp rounding of these edge lines is connected with the still somewhat hypothetical situation described by the relations given above, with these lines displaying the volume maximas $V_{L,M}(P > P_m)$, $V_{S,M}(P > P_m)$. The extrapolated arcs beyond P_m have been drawn to end at 34 atm, which is strictly a conjectured value of $P(0)$, the melting pressure in the limit of the absolute zero, together with the corresponding volumes $V_L(P(0))$ and $V_S(P(0))$. The value of $P(0)$ is not inconsistent with experimental determinations of $P(T)$ to quite low temperatures.⁹ The limiting arcs of $V_L(P)$ and $V_S(P)$ at the approaches of $P(0)$ are strictly schematic, but their

⁹ 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 He^3* (Ohio State University Press, Columbus, Ohio, 1960), p. 126; A. L. Anderson, G. L. Salinger, H. A. Steyert, and J. C. Wheatley, *Phys. Rev. Letters* **7**, 295 (1961).

monotonic character could result from the nuclear paramagnetism of liquid and solid He³ on the two edges $V_L(P)$ and $V_S(P)$.⁸

It may not be entirely superfluous to recall here the strictly affine character of the space spanned by the primary variables of state, where in absence of the definition of angles, the choice of an apparently Cartesian coordinate system is a mere convention. The same remark applies to the projections on to the coordinate planes of the state surface and the families of curves defined on it.

The (V, P) diagram of Fig. 1 displays a series of qualitative isotherms, up to the temperature of 1.6°K on the region of the state surface of the liquid phase. As would be expected, the edge of this region is formed by the isotherm at the absolute zero. As one follows counterclockwise the $V_L(P)$ line starting at $V_L(P(0))$, where the isotherm at the absolute zero reaches the latter from the region of low pressures and large volumes, the successive points on this edge line are the end points of isotherms of increasing temperature of the liquid, whereby

$$V(p, T) > V(p, T + \Delta T) > V(p, T + 2\Delta T) > \dots,$$

or, at a given pressure the isotherms of lower temperature lie at higher volumes than those of higher temperature. This is, of course, one aspect of the fundamental thermal anomaly of liquid He³ displayed through the succession of the members of the family of isotherms. In a pure phase this grouping of neighboring isotherms can only change if they intersect each other. The locus of the intersections of any two neighboring isotherms of temperature T and $(T + \Delta T)$ is a characteristic line of the state surface; it is indicated by the dashed line in Fig. 1. As known from the measurements, all isotherms $T \lesssim 0.45\text{--}0.50^\circ\text{K}$ are free of intersections. Clearly these intersections are strictly apparent, since the isotherms on the state surface are intersections of the latter with planes of different temperature index, which, by definition, do not cross.

Actually, the locus of intersections of the projected isotherms in the (V, P) diagram is a locus of points on the state surface where the latter has a sharp fold, the upturning sheet extending toward larger volumes. The isotherms on this latter portion of the state surface appear in projection on the large volume side of the edge $V_L(P)$ and in the normal order, as illustrated by the two isotherm arcs at 1.4 and 1.6°K, which belong to a normal family with

$$V(p, T) < V(p, T + \Delta T) < V(p, T + 2\Delta T) < \dots.$$

The anomalous succession of the isotherms corresponds to the following thermal properties:

$$(\partial p / \partial T)_V \leq 0; \quad (\partial V / \partial T)_P \leq 0, \quad (13)$$

or

$$(\partial S / \partial V)_T \leq 0; \quad (\partial S / \partial p)_T \geq 0, \quad (14)$$

where $S(V, T)$ or $S(p, T)$ stand for the entropy.

Before entering into the discussion in depth of the isotherms, it seems worthwhile to consider at this juncture the isobars and isochores. These characteristic lines are of constant pressure and volume index, and in the (V, P) diagram they appear as parallel to the coordinate axes, within the limitations of the meaning of this metric term used in the affine plane at hand. Both the isobars and isochores can be divided into three groups, a classification used earlier.¹

The three groups of isobars of the liquid, in increasing order of the pressures, are

$$p_I < P_m(T_a); \quad P_m(T_a) \leq p_{II} \leq P(0); \quad p_{III} > P(0). \quad (15a)$$

The lowest pressure isobars, p_I , extend throughout the state surface of the liquid. The class of isobars p_{II} are double valued functions of the liquid and solid volumes, $V_L(P)$ and $V_S(P)$, since they intersect both edge lines at two different values of the liquid volume and two different values of the solid volume. The limiting isobar $p_{II} = P_m(T_a)$ has its two intersections with the volume line $V_L(P)$ degenerating into a single point, this isobar is tangent to the edge line $V_L(P)$ at the point of anomaly $V_L(P_m(T_a))$. As stated already, this same isobar of anomaly is also tangent to the edge of the solid phase $V_S(P)$ at its vertex $V_S(P_m(T_a))$, actually it reduces there to a point.

The third group of isobars have a single common point with the volume lines $V_L(P)$ and $V_S(P)$, and extend indefinitely toward volumes $V_L > V_L(P)$ on the surface of the liquid. On the surface of the solid, these isobars extend toward volumes $V_S > V_S(P)$, starting at $V_S(P)$.

The isochores also form three groups. In decreasing order of volumes, these are

$$V_I > V_{L,M}(P(T_a')); \quad V_L(0) \leq V_{II} \leq V_{L,M}(P(T_a')); \\ V_{III} < V_L(0). \quad (15b)$$

Here $V_{L,M}$ is the maximum volume of the edge line $V_L(P)$ at $T_a' < T_a$. While neither the isobars nor isochores have been drawn in the (V, P) diagram, the preceding volume groups can be clearly distinguished on the diagram.

A characteristic reciprocity between the relative positions of the isobar and isochore of anomaly, associated with the boundary vertex $P_m(T_a)$ and the volume maximum $V_{L,M}$ at $P(T_a')$ may be noted here. While the isochore $V_L(T_a')$ crosses the volume line $V_L(P)$, the isobar $p(T_a)$ is tangent to it at this vertex. At the point $(V_L(T_a'), P(T_a'))$, the situation is reversed: The isochore $V_L(T_a')$ is tangent to $V_L(P)$, while the isobar $p(T_a')$ crosses it at this second point of anomaly.

On the surface of the solid, the isochore $V_S(T_a')$ reduces to a point, or in this phase both the isobar and isochore of anomaly reduce to a point. All the other isobars and isochores are finite arcs.

We now return to a detailed study of the isotherms in the (V, P) diagram.

The isotherms of the liquid form three groups. Let, indeed, $T_{\alpha,L}(p)$ be the locus of the vanishing isobaric expansion coefficient of the liquid. The three groups of isotherms are

$$T_I < T_{\alpha,L}(p_{\text{sat}}); \quad T_{\alpha,L}(p_{\text{sat}}) \leq T_{II} \leq T_{\alpha,L}(P); \\ T_{III} > T_{\alpha,L}(P). \quad (16)$$

The lowest temperature group T_I originates at the saturated liquid volume line $V_L(p_{\text{sat}})$ at $T \lesssim 0.5^\circ\text{K}$ to end on the volume line $V_L(P)$ in equilibrium with the solid. We give in Fig. 1 the schematic high-pressure segments of several of these T_I isotherms at 0.0, 0.2, and 0.4°K , respectively.

The intermediate class of neighboring isotherms T_{II} between 0.5 and about 1.2°K intersect along their envelope so as to lead to the anomalous grouping of the successive members of the family, through $V(p, T) > V(p, T + \Delta T)$ at $V < V_\epsilon(p, T)$, where $V_\epsilon(p)$ is the common volume of intersection at the envelope (ϵ) of the two infinitesimally close isotherms of temperature T and $(T + \Delta T)$.

The isotherms T_I reach the $V_L(P)$ line with slopes

$$\lim_{p \rightarrow P} [\partial V(p, T_I) / \partial p]_T = (dV_L/dP) \\ - [\partial V(p, T) / \partial T]_p / (dP/dT).$$

Now, since over the liquid phase,

$$(\partial V / \partial T)_p < 0, \quad \text{at } T \leq T_{\alpha,L}(p_{\text{sat}}),$$

it is seen that

$$\lim_{p \rightarrow P} [\partial V(p, T_I) / \partial p]_T \\ = (dV_L/dP) + |(\partial V / \partial T)_p| / (dP/dT) \quad (17a)$$

and

$$\lim_{p \rightarrow P} [\partial V(p, T_I) / \partial p]_T < dV_L/dP, \quad 0 \leq T \leq T_a, \quad (18a)$$

and

$$\lim_{p \rightarrow P} [\partial V(p, T_I) / \partial p]_T > (dV_L/dP), \\ T_a < T \leq T_{\alpha,L}(p_{\text{sat}}). \quad (18b)$$

In comparing the pressure slopes of the isotherms at their foot on the edge line $V_L(P)$ and the pressure slopes of the latter, some caution is necessary at the approaches of the temperature of anomaly T_a where the melting pressure is minimum. We have with (17),

$$\lim_{p \rightarrow P, T \rightarrow T_a} (\partial V / \partial p)_T = \lim_{T \rightarrow T_a} [1 / (dP/dT)] \\ \times [(dV_L/dT) - (\partial V / \partial T)_p] \quad (17b)$$

and (dP/dT) is increasing toward zero from negative values at $T < T_a$. Since the left-hand side is certainly negative, it is seen that the quantity inside the square brackets is necessarily positive, and in order to have a

normal isothermal compressibility, the right-hand side must have the indeterminate form $(0/0)$ at T_a , or

$$dV_L/dT = (\partial V / \partial T)_{P_a}, \quad T = T_a, \quad (19)$$

showing the isobaric expansion coefficient to be finite at the point of anomaly. The limit of $(\partial V / \partial p)_T$ at T_a is then obtained at once using L'Hospital's theorem, or

$$\lim_{p \rightarrow P_a, T \rightarrow T_a} (\partial V / \partial p)_T = \lim_{p \rightarrow P_a, T \rightarrow T_a} [(d^2P/dT^2)]^{-1} \\ \times [(d^2V_L/dT^2) - (\partial^2V / \partial T^2)_p], \quad (20)$$

and since $P(T)$ is minimum at T_a ,

$$(d^2P/dT^2)_{T \rightarrow T_a} > 0.$$

Also, since $V_L(T)$ is beyond its maximum at T_a' , and $V(p, T)$ is approaching its minimum on the locus $T_{\alpha}(p)$,

$$d^2V_L/dT^2 < 0, \quad (\partial^2V / \partial T^2)_p > 0,$$

then the quantity between square brackets in (20) is negative, yielding the required normal value of the derivative $(\partial V / \partial p)_T$ at (P_a, T_a) or a normal compressibility.

The connection between the pressure slopes of the isotherms and the edge line (18b) remains valid for the isotherms of the class T_{II} also. The latter isotherms have their envelope $V_\epsilon(p)$ defined by the two equations

$$V = V(p, T_{II}); \quad (\partial V / \partial T)_p = V_T(p, T_{II}), \quad (21)$$

which yield, on eliminating T_{II} , the equation of the envelope

$$V = V_\epsilon(p). \quad (22)$$

Consider, indeed, two isotherms T and $T + \Delta T$, belonging to the class T_{II} . We have for these

$$V_1 = V(p, T); \quad V_2 = V(p, T + \Delta T),$$

and, expanding the latter, one has

$$V(p, T + \Delta T) - V(p, T) = (\partial V / \partial T)_p \Delta T + \dots \quad (23)$$

If V_ϵ , p_ϵ are the state coordinates of their intersection,

$$\lim_{\Delta T \rightarrow 0} [V_\epsilon(p_\epsilon, T + \Delta T) - V_\epsilon(p_\epsilon, T)] = 0, \quad (24)$$

because

$$\lim_{V \rightarrow V_\epsilon, p \rightarrow p_\epsilon} (\partial V / \partial T)_p = 0. \quad (25)$$

At $p < p_\epsilon$, $(\partial V / \partial T)_p > 0$, and

$$V(p, T + \Delta T) - V(p, T) > 0, \quad (26)$$

the situation is normal and the higher temperature isotherm has, at constant pressure, the larger volume. At $p > p_\epsilon$, $(\partial V / \partial T)_p < 0$, and

$$V(p, T + \Delta T) - V(p, T) < 0, \quad (27)$$

the higher temperature isotherm lies at smaller volume than its lower temperature neighbor. The isotherms T_{II}

are all on the larger volume-larger pressure side of the envelope $V_\epsilon(p)$.

The isotherm at $T_{\alpha,L}(P)$ is the last member of the class T_{II} and its contact with the envelope $V_\epsilon(p)$ occurs at the edge $V_L(P)$. By (17) and (25),

$$\lim_{T \rightarrow T_{\alpha,L}(P)} dV_L/dP = (\partial V/\partial p)_{T_{\alpha,L}(P)} = dV_\epsilon/dp, \quad (28)$$

or the edge line $V_L(P)$, the isotherm $V(p, T_{\alpha,L}(P))$ and the envelope $V_\epsilon(p)$ have a common contact at the end point of the isotherm arc and the envelope. Hence, at this point of contact

$$\lim_{T \rightarrow T_{\alpha,L}(P)} V_L^{-1}(dV_L/dP) = V_L^{-1}(\partial V/\partial T)_P, \quad (29)$$

or the isothermal compressibility of the liquid in the state $(P, T_{\alpha,L})$ is identical with the corresponding quantity defined along the phase edge line $V_L(P)$. This result was derived previously in a different way.¹ The same result is obtained in the limit of the absolute zero, where the isotherm at the absolute zero is tangent to the $V_L(P)$ line at the limiting point of the latter in the state $(V_L, P, T=0)$.

The third group of isotherms T_{III} is located on that portion of the state surface of the liquid which appears to have turned around the envelope $V_\epsilon(p)$. These isotherms, on the (V, P) diagram, seem to reach the edge line $V_L(P)$ from its concave side. Indeed, their pressure slopes at the $V_L(P)$ line are more negative than the slope of the edge line at their point of intersection, and, hence, they can only reach the edge from the region of larger volumes. These isotherms are, of course, normal with

$$V(p, T+\Delta T) - V(p, T) > 0, \quad T > T_{\alpha,L}(P). \quad (30)$$

We give in Fig. 1 limited arcs of the 1.4 and 1.6°K isotherms drawn to scale.

We are now prepared to study the isotherms on the state surface of the solid. As the diagram of Fig. 1 shows, the anomalous families of isotherms of the liquid, T_I and T_{II} , conserve their anomaly over the state surface reserved to the mixed phase. In order for these anomalous classes of isotherms to become normal in the solid phase whose edge line is similar to $V_L(P)$ they must intersect and reform an envelope of the type $V_\epsilon(p)$ existing on the state surface of the liquid. In order for the solid to become completely normal, it is necessary that the solid edge line $V_s(P)$, almost parallel to $V_L(P)$, be the locus of intersections of neighboring isotherms. Stated in other terms, this locus should correspond by (25) to the locus of vanishing isobaric expansion coefficients, or to the locus of the vanishing derivatives

$$(\partial p/\partial T)_V = 0,$$

of the isochores. In order that the envelope of the solid isotherms coincide with the $V_s(P)$ line it is necessary

that the isobars have maximas on the $V_s(T)$ line in the (V, T) diagram, and the isochores to have maximas on the melting pressure line $P(T)$.

If $V_s(P)$ were in part the envelope of the solid isotherms, then, over the arc where $V_s(P)$ is actually the envelope, the slope of $V_s(P)$ has to be identical with the partial derivatives $(\partial V_s/\partial p)_T$ at the locus. The latter being proportional to the negative of the isothermal compressibility, must be negative. But, clearly this is not possible for the isotherms of the interval $T_a' < T < T_a$, where

$$dV_s/dP > 0.$$

This proves that on the assumption of the two distinct points of anomaly at T_a and T_a' , associated with the melting line $P(T)$ and the solid volume line $V_s(T)$, the edge $V_s(P)$ cannot be the envelope of solid isotherms. Solid He³ must, therefore, be anomalous over at least a finite temperature interval $(T_a - T_a')$. Actually, one of the main results of the experimental investigations of the liquid-solid equilibrium in He³,² was to show that solid He³ was thermally anomalous along the melting line over the temperature range 0.4–1.2°K, and became normal at $T \gtrsim 1.20$ – 1.25°K , that is, at about the same temperature as the liquid, in agreement with an earlier prediction.⁸ Direct experimental investigations of solid He³ have not as yet been made, so that at the present time the diagrams of the solid phase can only be given with qualifications. At or very near the edge line $V_s(P)$, the pressure slopes of the isotherms can be compared with that of the edge $V_s(P)$. The relation (17) again yields in the region of the diagram of the solid,

$$\lim_{p \rightarrow P} [\partial V_s(p, T_I)/\partial p]_T < dV_s/dP, \quad 0 \lesssim T_I \leq T_a, \quad (31a)$$

and

$$\lim_{p \rightarrow P} [\partial V(p, T_I)/\partial p]_T > dV_s/dP, \quad T_a \leq T_I \leq T_{\alpha,L}(P), \quad (31b)$$

or that at low temperatures the anomalous isotherms have a steeper negative pressure slope than the edge line $V_s(P)$, while at $T > T_a$ the isotherms become flatter than the volume line $V_s(P)$.

As mentioned already there have been no direct experimental investigations of the static thermal properties of the low pressure solid He³, that is the body centered cubic α -solid,¹⁰ besides the studies of the liquid-solid equilibrium.² The latter do indicate that the solid in equilibrium with the liquid is thermally anomalous in the sense of the relations (13) and (14) up to the temperature $T_{\alpha,L}(P)$. This then appears to justify qualitatively, at least, the situation pictured schematically on the region of the α -solid of the state surface, Fig. 1, according to which the anomalous family of low temperature isotherms of the liquid are continued over

¹⁰ A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. **110**, 775 (1958).

a finite domain of the state surface of the solid. That is, the solid is thermally anomalous not only at the phase separation line but over a finite region of existence of this phase. As noted briefly in Sec. 1, the solid is assumed to be elastically normal.^{7,2}

The family of anomalous isotherms of the solid appear all inside the region limited by the 0°K isotherm and the edge line $V_s(P)$. At higher temperatures, where the nuclear spin system approaches asymptotically its state of complete thermal disorder measured by the limiting value $R \ln 2$ of the molar spin entropy, the thermal excitations of the solid might be described by superimposing upon the spin excitations those of the phonons. The solid would then be expected to become normal, and its isobaric expansion coefficient to become positive, $(\partial V_s / \partial T)_p > 0$. The pressure slopes of these higher temperature isotherms are thus such that

$$\lim_{p \rightarrow P, T \text{ large}} (\partial V_s / \partial p)_T < dV_s / dP, \quad (32)$$

showing that these isotherms with their steeper negative slopes extend now below the edge line $V_s(P)$, starting of course on the latter line.

In the earlier work of one of us,⁸ the discussion of the nuclear spin system of the liquid responsible for its thermal anomalies was extended to the solid phase, and the likely continuation of the locus $T_{\alpha,L}(p)$ into the solid phase was pointed out. This means, that in order for the anomalous family of isotherms of the solid to transform itself into a normal family, a partial family of the latter over a finite temperature interval must form an envelope $V_{\epsilon,s}(p)$ as was the case in the liquid phase. This envelope $V_{\epsilon,s}(p)$ must, of course, extend between two limiting lines of the state surface of the solid, or, possibly, it might be an arc connecting two points of the $V_s(P)$ line. In the earlier work,⁸ it appeared as if the envelope $V_{\epsilon,s}(p)$ should extend from the $V_s(P)$ line to the edge $V_{\alpha}(P)$ of the α solid. This suggests that the thermal anomalies of the α solid might be continued into

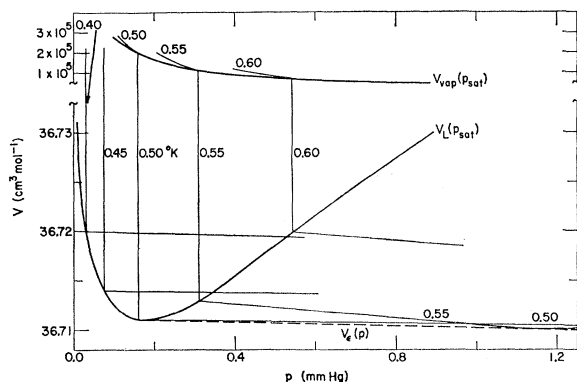


FIG. 2. The volume-pressure diagram of the normal vapor and the anomalous liquid He³, showing the family of normal isotherms of the vapor and the mixed phases, and the anomalous isotherms of the pure liquid phase. The dashed line is the envelope of a class of isotherms.

the hexagonal close-packed β solid,^{10,11} on the completion of the α - β phase transformation, as discussed briefly in the earlier work.⁸

In order to complete the geometrical discussion, it seemed instructive to show how the normal family of isotherms of He³ vapor becomes anomalous on liquefaction, Fig. 2. It is seen that as long as the pressure derivatives of the phase boundary lines $V_{\text{vap}}(p_{\text{sat}})$, $V_L(p_{\text{sat}})$ of the vapor and liquid are such that

$$dV_{\text{vap}}/dp_{\text{sat}} < 0; \quad dV_L/dp_{\text{sat}} < 0, \quad T < T_{\alpha,L}(p_{\text{sat}}), \quad (33)$$

the normal family of vapor isotherms becomes anomalous on $V_L(p_{\text{sat}})$ up to the minimum of the latter, at $T_{\alpha,L}(p_{\text{sat}})$. Or, the fundamental anomaly of the pure dense phase is responsible for the formation of the anomalous family of isotherms of the latter, after the phase transformation has been completed. At $T > T_{\alpha,L}(p_{\text{sat}})$, the normal vapor isotherms stay normal in the liquid also, the boundary line of the latter being now an increasing function of p_{sat} ,

$$dV_L/dp_{\text{sat}} > 0, \quad T > T_{\alpha,L}(p_{\text{sat}}). \quad (33a)$$

The isotherms $T_{\alpha,L}(p_{\text{sat}}) < T_{II} < T_{\alpha,L}(P)$ of this second group are normal on the boundary line and beyond, and become anomalous only after formation of the locus envelope $V_{\epsilon}(p)$, which starts on the $V_L(p_{\text{sat}})$ line at $T_{\alpha,L}(p_{\text{sat}})$, and extends over the region of the pure liquid phase.

Geometrically, it is clear in Fig. 2, that the normal isotherms of the vapor intersect the boundary line $V_{\text{vap}}(p_{\text{sat}})$, which is a decreasing function of p_{sat} , with steep negative pressure slopes, while the liquid edge line $V_L(p_{\text{sat}})$ has a steeper negative pressure slope than the anomalous isotherms $V_L(p, T)$ of the liquid which leave the $V_L(p_{\text{sat}})$ edge at $T < T_{\alpha,L}(p_{\text{sat}})$. The normal vapor isotherms reach the boundary line $V_{\text{vap}}(p_{\text{sat}})$ on its concave side and become anomalous on the liquid boundary line $V_L(p_{\text{sat}})$ by leaving the latter on its concave side. Beyond $T_{\alpha,L}(p_{\text{sat}})$, the normal character of the vapor isotherms is preserved on liquefaction, whereby the isotherms of the liquid leave the edge line $V_L(p_{\text{sat}})$ on its convex side.

It is seen on Fig. 1 that the continuation of the anomalous family of isotherms T_I of the liquid phase into the solid phase is insured by the very similar pressure variations of $V_L(P)$ and $V_s(P)$, with the isotherms approaching the former on its convex side and leaving the latter on its concave side.

3. THE PRESSURE- AND VOLUME-TEMPERATURE DIAGRAMS

The combined schematic diagrams in the (p, T) and (V, T) representations are given in Fig. 3. The extremas of the various characteristic curves have been very much exaggerated. In particular, the apparent curva-

¹¹ E. R. Grilly and R. L. Mills, Ann. Phys. (New York) **8**, 1 (1959).

tures of the isochores $p(T, V)$ in the (p, T) representation, and those of the isobars $V(T, p)$ in the (V, T) representation have been overemphasized. Also, the shapes and locations of the loci $T_a(p)$ and $T_a(V)$ are strictly schematic.

The assumption of the existence of two distinct temperatures T_a and T_a' associated, respectively, with the minimum of the melting pressure $P(T)$, and the maximum of the liquid volume $V_L(T)$ may be justified in a straightforward way. Since,

$$dV_L/dT = (\partial V_L/\partial T)_P + (\partial V_L/\partial P)_T (dP/dT), \quad (17b)$$

with

$$(\partial V_L/\partial T)_P \leq 0, \quad 0 < T \leq T_{a,L}(P), \quad (34)$$

and since the compressibility is normal, or $(\partial V_L/\partial P)_T < 0$ at all temperatures, it is seen that at temperatures $T_a < T \leq T_{a,L}(P)$ both terms on the right-hand side are negative, and the liquid volume V_L decreases with increasing temperatures. Beyond $T_{a,L}(P)$, the partial $(\partial V_L/\partial T)_P$ becomes positive, but the negative product of the second term is larger numerically than the positive first term, and the decreasing character of $V_L(T)$ with T has been verified up to quite high temperatures by the one of us in collaboration with Grilly.¹¹ On approaching T_a from its high-temperature side, (dP/dT) decreases from large positive values,^{4,2} toward zero at T_a , where

$$dV_L/dT = (\partial V_L/\partial T)_P < 0, \quad T = T_a. \quad (35)$$

As T decreases below T_a , (dP/dT) decreases from zero toward increasingly large negative values, while the partial derivative $(\partial V_L/\partial p)_T$ or $[-K_T(T, p)V_L(T, p)]$ with $p \rightarrow P$, K_T standing for the isothermal compressibility of the liquid along the phase separation line, is reasonably expected to vary only slowly, so that the positive product on the right-hand side of (17b) increases with decreasing T . This positive term should overtake rapidly the first negative term on the right-hand side of (17b), assuring thus first the zero of (dV_L/dT) close to T_a but at $T_a' < T_a$, and then its positive sign, increasing with decreasing temperatures. By the Nernst theorem, (dV_L/dT) must have at least one maximum below T_a' , since it vanishes again at the absolute zero. It should be noted that the shapes of the $P(T)$ and $V_L(T)$ lines of Fig. 3, in the limit of $T \rightarrow 0$, are strictly schematic, their actual form is of no consequence in the present studies. With reasonable values of α_p and K_T , one estimates from (17b) that $T_a' - T_a \sim 0.02^\circ\text{K}$.

In view of the discussion given earlier,¹ on the isobars $V(T, p < P(T_a))$, and isochores $p(T, V > V_L(T_a'))$, we will limit ourselves here to the high-pressure and low-volume isobars and isochores. The higher temperature region of the (V, T) diagram has been given by Sherman and Edeskuty.¹² These isobars and isochores are in the

¹² R. H. Sherman and F. J. Edeskuty, Ann. Phys. (New York) 9, 522 (1960).

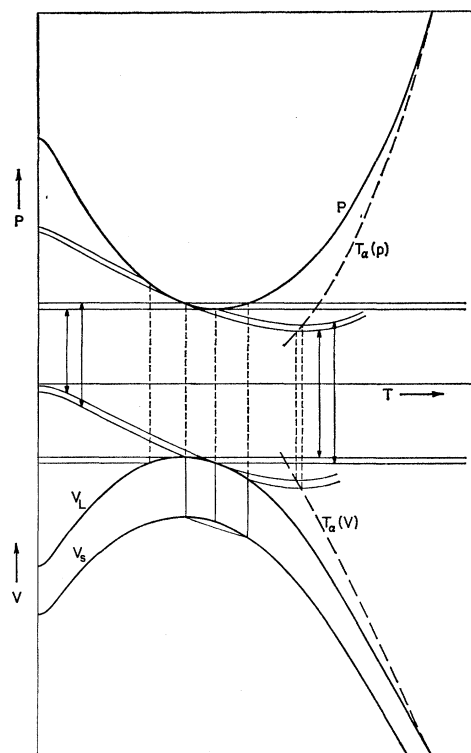


Fig. 3. The schematic combined pressure-temperature and volume-temperature diagrams of liquid and solid He³. The arrows connect the two isobars of pressure $p(T_a)$, and the two isochores of volume $V_L(T_a')$, in the two diagrams. T_a and T_a' are the temperatures of the melting pressure minimum and the liquid volume maximum at the phase boundary.

group (I) by the classifications (15a) and (15b). The corresponding isobars and isochores in the two representations,

$$V = V(T, P_m); \quad p = P_m,$$

in the (V, T) and (p, T) diagrams, or

$$p = p(T, V_{L,M}); \quad V = V_M,$$

in the (p, T) and (V, T) diagrams are given schematically. As shown in the course of the discussion of the (V, P) diagram, these characteristic lines are continuous throughout the state surface, having a simple contact with the phase separation lines $P(T)$ and $V_L(T)$ at the points of anomaly of the minimum melting pressure $P(T_a)$ and maximum liquid volume $V_{L,M}(T_a')$.

All isochores $p(T, V < V_M)$ and isobars $V(T, p > P(T_a))$ intersect the $V_L(T)$ and $P(T)$ lines and have thus a finite gap. We give schematically two of these, the isochore

$$p = p(T, V_L(T_a) < V_{L,M}),$$

and the isobar

$$V = V(T, p > P(T_a)).$$

The latter reaches the $V_L(T)$ line at $V_{L,M}(T_a')$. This isobar is then followed through the mixed phase region,

as the isotherm T_a' , and reaches the solid volume line $V_s(T)$ at $V_s(T_a')$. The shape of this isobaric arc is sketched schematically, with the isotherm-isobar returning into the liquid phase at the volume $V_L(T > T_a)$, to continue in the pure liquid phase with increasing temperatures toward its minimum on the locus $T_\alpha(p)$.

Similarly, this isobar being a straight line in the (p, T) diagram intersects the melting line at $P(T_a')$ where it penetrates the solid region to emerge at $T > T_a$ and continue in the liquid phase.

In the (p, T) representation, the isochore $p(T, V < V_{L,M})$ reaches the melting pressure at a pressure $p > P(T_a)$, then it develops a gap, and resumes at $P(T_a)$ by re-entering the liquid phase and decreasing with increasing temperatures toward the locus $T_\alpha(p)$. In the (V, T) diagram this isochore is just a straight line which ends on the $V_L(T)$ line at $T < T_a'$ and leaves it at T_a .

The anomalous isobars and isochores of the liquid are seen to impose similar characteristic lines on to the solid, or in the latter phase and at low enough temperatures one has

$$[\partial V_s(T, p)/\partial T]_p < 0, \quad [\partial p(T, V_s)/\partial T]_{V_s} < 0. \quad (36)$$

In the solid phase, it will be observed that the isobar $p = P(T_a)$ and the isochore of maximum volume $V = V_{s,M}(T_a')$ reduce to a point. That the solid has its maximum volume also at T_a' as the liquid has been assumed here for the sake of simplicity since its location is not exactly determined by experiment. A limiting process indicated previously,¹ can be applied here to show that

$$\lim_{T \rightarrow T_a} [\partial V_s(T, P(T_a))/\partial T]_{P(T_a)} < 0,$$

$$\lim_{T \rightarrow T_a'} [\partial p(T, V_{s,M})/\partial T]_{V_{s,M}} < 0,$$

or these derivatives in the limit of the degenerate point isobar and point isochore of the solid remain finite.

Concerning the isobars and isochores of the liquid, these have vanishing temperature derivatives at the absolute zero and at the loci $T_\alpha(p)$ and $T_\alpha(V)$. They must have, in the range $0 \leq T \leq T_\alpha(p)$ at least one inflection point. The assumption used in the present work and justified above on the existence of two different states of the liquid and solid, associated with the melting pressure minimum $P(T_a)$ and the volume maximas $V_L(T_a')$, is now equivalent to insuring the existence of a unique inflection point on the isobars and isochores. These have been shown to be determined by the nuclear

spin system.¹³ They all occur at temperatures $T_V < T_a$, which explains the shape of the schematic isobars and isochores of Fig. 3. The shape of the isochore and isobar of anomaly which have simple contacts with the melting line at T_a' and the $V_L(T)$ line at T_a defines the shape of all the other isochores and isobars of group (I), defined by (15a) and (15b). These lines extend indefinitely, at $p > p_c$ and $V < V_c$, (p_c, V_c) referring to the critical pressure and volume. Since the expansion coefficient $\alpha_p(T, p)$ or the derivative $(\partial p/\partial T)_V$ vanish both at the absolute zero and the loci $T_\alpha(p)$, $T_\alpha(V)$, being negative over this temperature interval, they have a minimum at the locus $T_\beta(p)$ or $T_\beta(V)$, where

$$[\partial \alpha_p(T, p)/\partial T]_p = -[\alpha_p(T, p)]^2 + [V(T, p)]^{-1}(\partial^2 V/\partial T^2)_p = 0. \quad (37)$$

At pressure $p < P(T_a)$, $\alpha_p(T, p)$ reaches values of about $(5 \times 10^{-3}/^\circ\text{K})$ on the average. It is thus seen that the locus of the minimas $T_\beta(p)$ or $T_\beta(V)$ of α_p or $(\partial p/\partial T)_V$ correspond to temperatures somewhat larger than the temperatures $T_V(p)$ of the inflection points of the isobars or isochores.

The single inflection points of the isobars and isochores as well as the single minimas of the isobaric expansion coefficients of pressures $p_c < p < P(T_a)$ and volumes $V_c < V < V_{L,M}(T_a')$, appear to describe qualitatively the observations available at the present time.

The groups (II) and (III) of the isobars and isochores have been discussed previously,¹ and their behavior remains unchanged with the existence of the two extremas at T_a and T_a' assumed in the present work on the shapes of the melting pressure line $P(T)$ and the liquid and solid volume lines $V_L(T)$ and $V_s(T)$.

In concluding, it seems justified to state that the discussion of the thermodynamic state surface of He^3 in the affine space of the primary variables of state has led to a precise geometrical description of the change-over of families of isotherms, from a normal to an anomalous group, whether over a region of the state surface of a pure phase or at a phase transformation. Also, a rather clear picture could be obtained of the way the anomalous thermal properties of liquid He^3 are propagated into the solid phase, beyond the phase boundary line of the latter. By allowing the melting pressure, and the liquid and solid volume lines to have their anomalous extremas to occur at two distinct points of the state surface, the thermal anomalies of the liquid phase become of smooth variation, in qualitative agreement with the still meager data at low temperatures and higher pressures.

¹³ L. Goldstein, Phys. Rev. **112**, 1285 (1958).