Spin-ordering transformation in low-pressure solid ³He

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Currently available equilibrium thermodynamic data will be used to obtain approximate phase-boundary pressure values $p_0(T)$ in the pressure-temperature plane of solid ³He in its low-pressure and low-temperature phases. In contrast with the earlier determined spin-ordering molar-entropy change of about $R/3$, at the triple point at melting, the changes in pressure, temperature, and molar volume are quite small. In a constant-volume transformation, near the triple point, the pressure change or width across the mixed-phase region is about 10 millibars. The temperature width is in the microkelvin range. In constant-temperature and constant-pressure phase changes the estimated volume width is about 10^{-3} cm³/mol. Temperature derivatives of pressure and molar volume in the mixed-phase regions are quite large. As a consequence, the excess constant-volume heat capacities in the mixed phase may reach very large values. The required experimental resolving powers for accurate measurements of very small transformation temperatures and molar volumes as well as of very large mixed-phase heat capacities appear to be barely accessible at the present time.

I. INTRODUCTION

The main object of this paper is the discussion of some schematic equilibrium thermodynamic phase diagrams of solid ³He in and around its spin-ordering low-pressure transformation region. Temperature and pressure ranges explored here refer to about 0.35–1.05 mK and 35–55 bars. At the present time, data required for construction of a satisfactory phase diagram in the pressure-temperature (p, T) plane are incomplete in the relevant range of interest, i.e., in the region of the spin-ordering transformation. However, recent data at medium-low and very low temperatures used with plausible assumptions seem to lead to schematic phase diagrams of solid ³He over limited state-coordinate ranges.

In this paper, we will be giving schematic pressure-temperature and molar-volume temperature diagrams near the transition region. The volume data extend down to about 0.30 mK from the transition temperature $T_{N,M}$, at melting, or about 1.0 mK. The data omit the first-order character of the spin-ordering transformation as a consequence of the very small transformation molar volumes. The single-volume approximate phase-boundary data could nevertheless be used to derive boundary pressure values via isochoric pressures obtained at temperatures much higher than the transformation temperatures. The lengths of various state-coordinate intervals such as pressure, molar volume, and temperature are very small across the mixed or two-phase transformation regions. At the present time, only pressure-shift or pressure-width measurements are accessible experimentally in constant-volume transformations. These data enable one to estimate the temperature width of the phase change with the prior determination of the temperature derivatives of the pressure-boundary line.

Heat-capacity measurements in the solid phases at melting and at a molar volume somewhat lower than the melting volume confirm the expected anomaly over the mixed-phase region. However, the measured heat-capacity anomalies are relatively modest. Thermodynamic calculations of the constant-volume heat capacity over the two-phase region field very high heat-capacity peaks. The large discrepancy between measured and calculated heat capacities arises in part from the poor experimental temperature resolution available at the present time.

II. LOW-PRESSURE PHASES AND BOUNDARY LINES OF SOLID ³He

In the construction of phase diagrams of solid ³He, we will attempt to use some incomplete sets of data available currently on the transformation of solid ³He from its spin-ordered region, the antiferromagnetic or A solid, into its disordered or paramagnetic phase, the P solid. Scarcity of data for an initial description of the spin-ordering transformation suggests the use of data obtained at higher temperatures,[1] i.e., at temperatures large in comparison with those relevant to the spin-ordering transformation.[2] In the pressure-temperature (P, T) plane, the phase-boundary pressure line $p_0(T)$, or $p_b(T)$, originates at the melting-pressure line $P_M(T)$, at the triple-point temperature $T_{N,M}$-where liquid ³He-B, the A solid and P solid coexist at equilibrium.[3] The pressure at the triple point was estimated to be about 34.4 bars, while $T_{N,M}$ is somewhat above 1.0 mK provided the A-point temperature at melting is taken to be 2.75 mK.[3,4]

Systematic investigations of the A-solid–P-solid transformation along a set of solid isochores have been performed by Shigi et al.,[2] through low-field-strength magnetization measurements. Similar magnetization data have been obtained earlier.[5] These measurements confirmed the still earlier observations at melting,[6] which implied the first-order character of the transformation. Pressure measurements along isochores across the transformation region have been made by Mamiya and co-

workers.[7] These were interpreted also in terms of a first-order transformation.

It is instructive to follow an isochore $p(T, V = \text{const})$ from a state in the A phase at $T < T_N(V)$, $T_N(V)$ being the mean transformation temperature. The isochore first reaches the phase-boundary pressure $p_0(T_N)$ at the pressure $p_0(T_{N,i} V)$, where the mixed $(A + P)$ phase starts to develop. As the system proceeds from $T_{N,i}$ toward $T_{N,f}$, the two-phase isochore follows the phase-boundary pressure line $p_0(T)$. The initial all A-phase solid at $T_{N,i}$ changes progressively into the final all P phase at $T_{N,f}$. Beyond $p_0(T_{N,f}, V)$ the isochore penetrates the P phase. In the transition region $T_{N,f} > T_{N,i}$ and $p_0(T_{N,i}, V) > p_0(T_{N,f}, V)$. This is a characteristic feature of the solid-A-solid-P first-order phase change described through an isochore. Figure 1, to be discussed below, depicts an isochoric transformation.

Using the asymptotic high-temperature isochoric pressure data[1] and the fractional mK low-field strength isochoric magnetization results,[2] it became possible to derive to some degree of approximation boundary-pressure values $p_0(T)$ over the temperature range of the measured mean- or single-volume phase-boundary line $V_0(T)$. The approximate $p_0(T)$-line data resulted from the zero-point or temperature-independent components of the isochoric pressures at higher temperatures,[1] $T \gg T_{NM}$. It should be recalled that the temperature-dependent isochoric pressures at $T \geq 20$ mK had already been measured by the University of Florida investigators.[8]

Early formal discussions[9] of the P solid clearly indicated the dominant $(1/T^2)$ asymptotic entropy term as well as those of its pressure and volume derivatives. On temperature integration the dominant $(1/T)$ term results in the isochoric pressure or isochoric molar-volume expansions of the nuclear-spin system. The dominance of the spin system was restricted to that temperature range where the phonon excitations of the model solid could be safely neglected in comparison with those of the spin system.

At $T >> T_N(V)$, the isochoric temperature-dependent component of the pressure resulted in the form

$$p(T, V) - p_0(V) \approx [a(V)/T] + .. ,$$
$$T_N \ll T \leq 100 \text{ mK} , \tag{1}$$

where $p_0(V)$ is the temperature-independent part of the pressure along the isochore V. The coefficient $a(V)$ in (1), in the single-parameter asymptotic Heisenberg exchange-coupling formalism[10] refers to

$$a(V) = \tfrac{3}{2} R d [J(V)/k]^2 / dV , \tag{2}$$

$J(V)$ being the magnitude of the nearest-neighbor-pair-exchange energy of the model.

In contrast with earlier isochoric pressure measurements,[7,8] Van Degrift and co-workers[1] determined the zero-point-pressure term $p(V)$ along a number of isochores. These investigators also gave a three parameter formal fit of $p(V)$ to which we will return below.

At the present time, data on isochoric pressures in the A solid at $T < T_N(V)$ are very scarce.[7] However, melting pressures have been measured[4] down to about 0.4 mK. These measurements suggest that at $T < T_{N,M}$ the melting pressure $p_M(T)$ is such that

$$p_M(T) = p_{M,0} - \delta p_M(T) , \tag{3}$$

where $p_{M,0}$ is the melting pressure in the limit $T \rightarrow 0$ and $\delta p_M(T)$ is a small temperature-dependent term, with

$$\delta p_M(T) \ll p_{M,0} \quad T < T_{N,M} . \tag{4}$$

The melting pressure may approach its limit at the absolute zero from below if one disregards the contribution of the phonon pressure at the very low temperatures.

It appears reasonable to assume that the pressure $p(T, V)$ along the isochore $V = \text{const}$, takes on a form similar to (3), in the A solid or

$$p(T, V) = p_0(V) - \delta p(T, V), \quad T < T_{N,M} , \tag{5}$$

$$\lim_{T \rightarrow 0} \delta p(T, V) \rightarrow 0, \quad \delta p(T, V) \ll p_0(V) . \tag{6}$$

While (5) is well founded in the P solid, in the A phase the sign of $\delta p(T, V)$ has not been fully established yet. The inequalities (4) and (6) suggest that, in a starting approximation, one may neglect the component $\delta p(T < T_N, V)$ in comparison with $p_0(V)$. The latter was observed in the P solid to be some three or four orders of magnitude larger than $\delta p(T, V)$. It should, however, be kept in mind that neglecting $\delta p(T, V)$ may be justified in the present discussion directed toward the determination of a schematic phase diagram of solid ^{3}He restricted to a limited range of the state coordinates around the triple
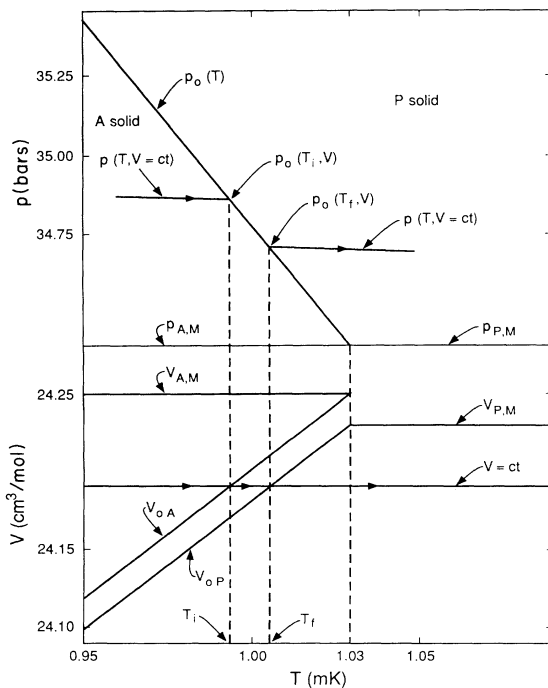

FIG. 1. Schematic linear (p, T) and (V, T) phase diagrams of solid ^{3}He near its triple point at melting.

point at melting. Clearly, knowledge of the properties included in $\delta p(T,V)$ is necessary for some level of understanding of the A-solid properties. Boundary volumes are increasing functions of the temperature,[2] or boundary pressures are decreasing functions of the temperature. Even though the empirical connection $p_0(V)$ was derived with the P-solid isochores,[1] $p(V=\text{const}, T)$, $p_0(V)$ being the temperature-independent component of the measured total pressure, we will assume its approximate validity in the A solid also at $T < T_N(V)$.

The three-parameter fit[1] is

$$p_0(V) = \varphi(v/V)^n ,$$

$$\varphi = 36.357 \text{ bars} ,$$

$$v = 24 \text{ cm}^3/\text{mol} ,$$

$$n = 5.597 .$$

$$(7)$$

We given in Table I, the calculated phase-boundary pressures $p_0(V)$ associated with the measured isochores by Van Degrift and co-workers,[1] and the molar volumes of the isochores investigated by Shigi and co-workers[2] through their magnetization measurements. Table I is seen to omit the two-valued character of the function $T_N(V)$ implied by the first-order character of the P-A transformation. This omission might be justified in a starting approximation, since the volume change in the solid-solid transition at some mean transformation temperature $T_N \leq T_{N,M}$ is expected to be quite small or

$$\Delta V_{AP}(T_N) = |V_P(T_N) - V_A(T_N)|$$

$$\ll V_p(T_N)$$

$$\approx V_A(T_N) .$$

$$(8)$$

The small order of magnitude value of ΔV_{AP} at $T_{N,M}$ can be estimated by combining the early experimental temperature $T_{N,M}$ and the approximate transformation or transition entropy ΔS_{AP} due to Halperin et al.,[6] with the earlier solid bcc-hcp extrapolated transformation pressure in the limit of very low temperatures due to Grilly and Mills.[11] This leads to a rough estimate of $|\Delta V_{AP}(T_{N,M})|$ of the order of 10^{-4}–10^{-3} cm^3/mol, a very small molar-volume change.

Table I with its direct and indirect data may lead to a better estimate of $\Delta V_{AP}(T_{N,M})$. At the present time, derivation of ΔV_{AP} values is still restricted to the triple point at melting, where a determination of the individual solid entropies[4] $S_A(T_{N,M})$ and $S_p(T_{N,M})$ became accessible to a satisfactory degree of approximation. The $p_0(T_N)$ values of Table I lead through a graphical approach to the approximate temperature slope

$$dp_0(T_{N,M})/dT = \lim_{T_N \to T_{N,M}} dp_0(T_N)/dT ,$$

$$(9)$$

by extrapolating the graph of the derivatives (dp_0/dT) values resulting approximately from the smoothed $p_0(T_N)$ pressures in Table II and included in Table III.

It should be remembered that the empirical zero-point pressures defined by the fit (7) are assumed to refer also to the boundary-pressure line $p_0(T_N)$ or $p_b(T_N)$. As discussed briefly above in connection with the formal equation of state of the A solid, Eqs. (5) and (6), the boundary pressure $p_0(T_N)$ is assumed to be close to the pressure axis in the (p,T) plane. This is justified roughly because of the temperature-dependent component $\delta p(T,V)$ of the total pressure along isochores is very much smaller than the zero-point pressure as stated in (6).

In order to exploit the data collected in Table I, it is

TABLE I. Molar volume V of the experimentally investigated solid ^{3}He isochores: their approximate phase-boundary pressures $p_0(V)$ and phase-boundary temperatures $T_N(V)$.

V (cm^3/mol)	$p_0(V)$ (bars)	$T_N(V)$ (mK)
22.43[a]	53.05	0.29
22.52[b]	51.87	0.32[c]
22.67[a]	50.02	0.37
23.01[a]	46.02	0.44
23.13[b]	44.67	0.48[c]
23.38[a]	42.09	0.58
23.63[a]	39.66	0.67
23.81[a]	38.01	0.78
23.83[b]	37.80	0.80[c]
23.85[a]	37.65	0.81
24.14[a]	35.19	1.00
24.16[b]	35.00	
24.22[b]	34.53	
24.24[d]	34.40	1.03

[a]Reference 2.
[b]Reference 1.
[c]Read off a large $T_N(V)$ graph, Ref. 2.
[d]Melting condition.

TABLE II. Smoothed state coordinates of the phase-boundary lines.

T_N (mK)	$p_0(T_N)$[a] (bars)	$V_0(T_N)$[b] (cm^3/mol)
0.30	52.8	22.4
0.35	50.1	22.7
0.40	47.8	22.9
0.45	45.9	23.0
0.50	44.3	23.2
0.55	43.0	23.3
0.60	41.7	23.4
0.65	40.6	23.5
0.70	39.7	23.6
0.75	38.8	23.7
0.80	37.9	23.8
0.85	37.1	23.9
0.90	36.3	24.0
0.95	35.5	24.1
1.00	34.8	24.19
1.03	34.4	24.24

[a]Pressure read off a large graph of the transition pressures of Table I.
[b]Calculated with the second column with the fit (7) of the text.

TABLE III. Estimated total derivative properties of the A-P phase-boundary lines.

T (mK)	$(-)dp_0/dT$[a] (bar/mK) $\left[\dfrac{S_P-S_A}{V_A-V_P}\right]$	dV_0/dT[a] (cm^3/molmK)	$(-)dV_0/dp_0$[b] (V_0/np_0) (cm^3/molbars)	$\chi_0=1/np_0$[c] $(-)(1/V_0)dV_0/dp_0$ (10^{-3} bars)
0.35	50.0	4.04	0.081	3.34
0.40	41.5	3.54	0.085	3.71
0.45	35.0	3.13	0.089	3.87
0.50	29.5	2.76	0.093	4.09
0.55	25.5	2.47	0.097	4.16
0.60	23.5	2.35	0.100	4.28
0.65	20.5	2.12	0.138	4.38
0.70	18.5	1.97	0.106	4.49
0.75	17.5	1.91	0.109	4.60
0.80	17.0	1.906	0.112	4.71
0.85	16.5	1.90	0.115	4.81
0.90	16.0	1.89	0.118	4.92
0.95	15.0	1.82	0.121	5.02
1.00	14.5[d]	1.80	0.124	5.13
1.03	14.4[d]	1.81	0.126	5.19

[a]Calculated with Table II.
[b]Calculated using the fit (7) of the text; $n = 5.597$.
[c]Calculated with the fourth column and Table II.
[d]Graphical extrapolation.

useful to obtain smoothed values of the boundary pressure and boundary volume. As indicated above, so far, we have neglected the two-valued character of the boundary-volume function $T_N(V_A)$ and $T_N(V_P)$. Large graphs of the measured $V_0(T_N)$ values[2] and their associated $p_0(T_N)$ values, resulting from the fit (7), yielded smoothed mean volumes V_0 and pressures p_0 at even temperature intervals ΔT_N. These are given in Table II. These smooth, if approximate, boundary coordinates then gave estimates of the temperature slopes (dp_0/dT_N) and (dV_0/dT_N). The derivatives (dp_0/dV_0) resulted from the fit (7), together with the compressibilities χ_0 along the boundary. The various derivatives are included in Table III. Their estimative character should be kept in mind.

III. VARIOUS ASPECTS OF THE SPIN-ORDERING TRANSFORMATION

Tables I and II represent, over a limited range of several state variables, the approximate partial phase diagrams of solid ^{3}He in its A phase. Several derivative properties of these variables are included in Table III. Limitations of validity in the numerical values of properties indicated in the preceding section should be remembered in the discussions to follow. These will refer to the transformation region of the two solid phases.

The temperature range of the A solid explored so far is about 0.35–1.00 mK, on the currently accepted temperature scale. The A-P phase-boundary pressure line resulting from the measured single molar-volume boundary-line data extends from about 34 to 53 bars, over the volume range of 22.4–24.2 cm^3/mol. The respective approximate temperature derivatives are

$$(-)50 \lesssim dp_0/dT \lesssim (-)14\text{bars}/mK ,$$

$$1.8 \lesssim dV_0(T)/dT \lesssim 4.0 \text{ cm}^3/\text{mol mK} , \qquad (10)$$

$$0.35 \lesssim T \lesssim 1.0 \text{ mK} .$$

These temperature slopes are very large. The empirical value of

$$dp_0/dT \text{ at } T \to T_{N,M}, \text{ or } (-)14.4 \text{ bars/mk}$$

approximately, leads through the Clausius-Clapeyron relation to the volume difference at $T_{N,M}$, or

$$\Delta V_{AP}(T_{N,M}) = \Delta S_{AP}(T_{N,M})/[dp_0(T \to T_{N,M}/dT] . \qquad (11)$$

The transformation entropy[4,6] $\Delta S_{AP}(T_{N,M})$ is a fair fraction of the asymptotic spin entropy $R \ln2$.

At the present time, there is only one unique state on the boundary pressure line $p_0(T)$ where data became accessible enabling the derivation of the individual solid-A and solid-P entropies This state is the triple point with coordinates $p_0(T_{N,M})$, $V_{AM}(T_{N,M})$, $V_{PM}(T_{N,M})$, and $V_{LM}(T_{N,M})$ where the superfluid B, the solid A, and solid P coexist at equilibrium. Accurate melting-pressure measurements $p_M(T)$, from below up to somewhat above $T_{N,M}$ yielded temperature derivatives of the melting line $[d_{PM}(T)/dT]$ across $T_{N,M}$. Assuming that the melting-volume differences $\Delta V_M(T)$ between the normal liquid ^{3}He and the solid P remained nearly constant below about 20 mK, and accepting an earlier extrapolated value from quite high temperatures[12] and a later experimental value,[13] the approximate individual solid entropies

$S_A(T_{N,M})$ and $S(T_{N,M})$ result via the Clausius-Clapeyron relation.

Melting-pressure data lead directly to the temperature slopes of the melting line (dP_{M-}/dT) and (dP_{M+}/dT) at $T_{N,M-}$ and $T_{N,M+}$. By the Clausius-Clapeyron relation

$$dp_{M-}/dT = \Delta S_{AM}(T_{N,M}/\Delta V_{AM}(T_{N,M}) \ ,$$
$$dp_{M+}/dT = \Delta S_{PM}(T_{N,M})/\Delta V_{PM}(T_{N,M}) \ , \qquad (12)$$

with the melting-entropy and melting-volume differences at the triple point

$$\Delta S_{\binom{AM}{PM}}(T_{N,M}) = S_L(T_{N,M}) - S_{\binom{A}{P}}(T_{N,M}) \ ,$$
$$\Delta V_{\binom{AM}{PM}}(T_{N,M}) = V_L(T_{N,M}) - V_{\binom{A}{P}}(T_{N,M}) \ . \qquad (13)$$

In a starting approximation the melting volume differences $\Delta V_{AM}(T_{N,M})$ and $\Delta V_{PM}(T_{N,M})$ are taken to be equal,

$$\Delta V_{AM}(T_{N,M}) \approx \Delta V_{PM}(T_{N,M}) \ , \qquad (14)$$

and their common value is the much higher-temperature melting-volume difference[12,13]

$$\Delta V_{PM}(T \sim 20 \text{ mK}) = 1.31 \text{ cm}^3/\text{mol} \ . \qquad (15)$$

The empirically derived melting-pressure temperature slopes (12) thus define the individual solid-A and solid-P entropies at the triple point $T_{N,M}$ to within the small corrective entropy $S_L(T_{N,M})$, or

$$S_A(T_{N,M}) - S_L(T_{N,M}) = (-)1.31(dp_{M-}/dT) \ ,$$
$$S_P(T_{N,M}) - S_L(T_{N,M}) = (-)1.31(dp_{M+}/dT) \ , \qquad (16)$$
$$S_A(T_{N,M}) \gg S_L(T_{N,M}); \quad S_P(T_{N,M}) > S_A(T_{N,M}) \ .$$

Numerically,[4] the molar entropies are

$$S_A(T_{N,M}) - S_L(T_{N,M}) = 0.175R \ln 2 \ ,$$
$$S_p(T_{N,M}) - S_L(T_{N,M}) = 0.618R \ln 2 \ . \qquad (17)$$

The molar-entropy change in the A-P transformation is thus

$$\Delta S_{AP}(T_{N,M}) = S_P(T_{N,M}) - S_A(T_{N,M})$$
$$= 0.31R$$
$$\approx (1/3)R \ , \qquad (18)$$

of the expected order of magnitude in this spin-disordering process. The associated molar latent heat is thus

$$L_{AP}(T_{N,M}) = T_{NM}\Delta S_{AP}(T_{N,M})$$
$$\approx (1/3)RT_{N,M} \ . \qquad (19)$$

The entropy difference $\Delta S_{AP}(T_{N,M})$ is seen to be free of the small corrective superfluid entropy $S_L(T_{N,M})$.

Tables I, II, and III display various features of the A and P solids along their phase-boundary lines. They clearly indicate that over the temperature range of the data

$$dp_0(T)/dT < 0; dV_0(T)/dT > 0; T \leq T_{N,M} \ . \qquad (20)$$

In addition, Table III implies

$$d^2p_0(T)/dT^2 > 0, \quad d^2V_0(T)/dT^2 < 0 \ . \qquad (21)$$

The pressure-boundary line $p_0(T)$ is thus a decreasing function of the temperature and is concave upward, toward increasing pressures. The approximate single- or mean-volume boundary line is concave downward, toward decreasing volumes.

Isothermal crossing of the pressure-boundary line from the A solid into the P solid is thus accompanied by pressure increase, or, except along the phase-boundary pressure line $p_0(T_N)$,

$$p_A(T) < p_P(T) \ , \qquad (22)$$

along the isotherm T_N. Isothermal crossing of the volume-boundary line from the A solid into the P solid is accompanied by a volume decrease, or

$$V_{0A}(T_N) > V_{0P}(T_N) \ . \qquad (23)$$

Smoothed $p_0(T)$ values of Table II yielded rough temperature slopes $[dp_0(T)/dT]$. On graphical extrapolation of the derivative function to $T \rightarrow T_{N,M}$, one obtains the estimate mentioned already,

$$\lim_{T \rightarrow T_{N,M}} dp_0(T)/dT \approx 14.4 \text{ bars/mK} \ , \qquad (24)$$

a rather larger temperature slope. As mentioned above, in connection with (10), this large limiting value at $T_{N,M}$ is implied by the large transformation entropy of about $\frac{1}{3}R$ and a small transformation volume $\Delta V_{AP}(T_{N,M})$. One has indeed, with the Clausius-Clapeyron relation,

$$\Delta V_{AP}(T_{N,M}) = V_P(T_{N,M}) - V_A(T_{N,M})$$
$$= \Delta S_{AP}(T_{N,M})/(dp_0(T \rightarrow T_{N,M})/dT)$$
$$\approx (-)1.8 \times 10^{-3} \text{ cm}^3/\text{mol} \ , \qquad (25)$$

a rather small molar-volume change. The strictly estimative character of this transformation volume should be kept in mind.

It is instructive to construct a schematic phase diagram of solid ^{3}He in the neighborhood of the triple point at melting. Such a diagram is given in Fig. 1. This is a combined (P, T) and (V, T) diagram used previously at high temperature.[14] The temperature range of the graph refers to 0.95–1.09 mK, the pressure range is 34.40–35.45 bars, and the molar-volume interval is 24.05–24.40 cm^3/mol. For graphical and visual convenience the scales of the ordinates are such as to overestimate the actual changes occurring in the state variables p, V, T, in the transformation process.

In the A-P phase transformation along an isochore of molar volume V, the anomalous negative temperature coefficient of the pressure $(\partial P/\partial T)_V$ in the P phase has been recognized in early work on the model formalism of this phase.[9] In Fig. 1 the A phase is assumed to be thermally anomalous at the outset. Satisfactory justification of this assumption is lacking at the present

time. It does not affect the discussion to follow referring mostly to the two-phase or mixed-phase region of the first-order spin-ordering transformation.

The combined (p,T) and (V,T) diagrams have a common abscissa scale. The melting-pressure segments p_{AM} and p_{PM} are drawn with vanishing temperature slopes, since over the temperature interval of the graph these slopes are much too small to be visible with the scale of the pressure ordinate. The molar volumes at melting V_{AM} and V_{PM} are also drawn with vanishing temperature slopes. The molar-volume scale is quite large and, in the absence of data, the boundary-volume lines V_{0A} and V_{0P} are drawn linearly with a constant separation ΔV_{PA} much larger than the difference $\Delta V_{PA}(T_{N,M})$ estimated through (25). The schematic volume diagram displays the double-valued character of the boundary single volume or mean volume used above.

The upper part of Fig. 1 is seen to refer to the local (p,T) diagram, with the phase-boundary pressure $p_0(T)$ drawn schematically as a straight line over the temperature interval of about 80 μK. The graph depicts qualitatively an isochore $p(T,V)$ starting in the A solid and crossing into the P solid. The isochore V on warming reaches the phase-boundary $p_0(T)$ at temperature T_i. Here the initial all-A solid enters the two-phase $(A+P)$ system along the phase-boundary pressure to recall the all-P solid phase at $p_0(T_f) < p_0(T_i)$, and $T_f > T_i$. In the mixed phase, with the mixture index x, at $T_i < T < T_f$, in the isochoric transformation

$$V = \text{const}$$
$$= x V_{0A}(T) + (1-x)V_{0P}(T) , \qquad (26)$$

provided one neglects all surface effects. Hence,

$$x = [V - V_{0P}(T)]/[V_{0A}(T) - V_{0P}(T)] , \qquad (27)$$

and

$$x = 1, \text{ at } V = V_{0A}(T) ,$$
$$x = 0, \text{ at } V = V_{0P}(T) .$$

Figure 1 is seen to define the pressure shift or pressure width of the mixed-phase region in the A-P transformation, through

$$\Delta p_0(T_f, T_i) = p_0(T_i) - p_0(T_f) , \qquad (28)$$

as well as the temperature width

$$\Delta T(p_{0,i}, p_{0,f}) = T_f(p_0) - T_i(p_0) . \qquad (29)$$

The present discussion postulates the regular character of the state-coordinate functions. Hence, by the mean-value theorem over the explored ranges of the state coordinates

$$\frac{\Delta p_0(T_f, T_i)}{\Delta T(p_{0,i}, p_{0,f})} = \frac{dp_0(T)}{dT} , \qquad (30)$$
$$T_i < T < T_f .$$

If the derivative $[dp_0(T)/dT]$ is known at T, measurement of Δp_0 over the interval $(T_f - T_i)$ yields the temperature width ΔT of the $i \rightarrow f$ transformation.

At the present time there are some data[7] on the pressure variation in the A-P isochoric transformation. In the case of the isochore $V = 24.19$ cm^3/mol, the mean transformation temperature is about 1.01 mK. The pressure shift in this phase change, read off a small graph,[7] is estimated to be

$$\Delta p_0(T_N \approx 1.01 \text{ mK}, \quad V = 24.19 \text{ cm}^3/\text{mol})$$
$$\approx (-)(7-8) \text{ mbars } . \qquad (31)$$

With the boundary-pressure temperature slope of about $(-)14.4$ bars/mK, by Table III, (30) yields the rough estimate

$$\Delta T(p_{0,i}, p_{0,f}) \approx 0.5 \ \mu\text{K} , \qquad (32)$$

or a width in the μK range. At the present time such a small temperature width may escape direct experimental control, in contrast with the measurement of the transformation-pressure shift $\Delta p_0(T_f, T_i)$. Both the graphically derived value of (dp_0/dT) and the experimental isochoric pressure shift $\Delta p_0(T_f, T_i)$ may be expected to be of moderate precision. Hence, the width ΔT is expected to be of largely estimative character.

We turn now to an experimentally more accessible property of the A-P mixed phase, subject, however, to limitations, at the present time. This is the heat capacity at constant volume of the A-P two-phase system. Accurate measurements in the transition region raise difficulties, partly from lack of the necessary temperature resolution, at the present time. The expected large excess mixed-phase heat capacity arises from the temperature rate of the energy supplied to the system, subject to the partial conversion of the A phase into the P phase, i.e., the temperature rate of the latent heat supplied to the A phase for its partial conversion to the P phase. This heat capacity of conversion is additive to the normal pure-phase heat capacities arising from the differential temperature increase of the mixture from T to $T+dT$, in proportion of their mixture indices x and $(1-x)$ of the A and P solids, respectively. In the case of the A-P transformation, however inaccurate, observation of the large excess heat capacity may be helpful to locate the approximate mean transformation temperature as well as a point on the mean boundary-volume line $V_0(T)$.

In the mixed phase with the fraction x of the A solid, and the fraction $(1-x)$ of the P solid, the entropy is, neglecting surface or capillary effects,

$$S(x,T,V) = x S_{0A}(T,V_A) + (1-x)S_{0P}(T,V_P)$$
$$\approx x S_{0a}(T,V) + (1-x)S_{0P}(T,V) , \qquad (33)$$

since by (25), $V_A \approx V_P = V$, the molar volumes of the components are very close in the present case. Hence, the constant-volume heat capacity of the mixed phase is, approximately, with the pure-phase heat capacities C_{0A} and C_{0P},

$$C_v(x,TV) \approx x C_{0A} + (1-x)C_{0P} + \Delta C_v(T,V) , \qquad (34)$$

with

$$\Delta C_v(T,V) = (-)L(T,V)(dx/dT) , \qquad (35)$$

the excess conversion heat capacity, and

$$L(T,V) = T(S_{0P} - S_{0A}) ,$$

the latent heat in the isothermal A-P transformation. As noted above, the heat-capacity anomaly is determined by (ΔC_v).

Before considering the explicit form of (dx/dT), at constant volume, it is instructive to obtain an estimate of some mean value of ΔC_v replacing $(-)(dx/dT)$ in (35) by the ratio $(\overline{\Delta x/\Delta T})$ over the width of the transformation region. With $\overline{\Delta X}$ taken to be about 0.5 at $T_{N,M}$, one has with (19) and (32),

$$\Delta C_v \approx L(T_{N,M})/2\Delta T$$

$$\approx \frac{1}{3}RT_{N,M}/2\Delta T$$

$$\approx 300R , \tag{36}$$

a large but finite heat capacity. A more complete form of ΔC_v results at once by calculating (dx/dT) at constant volume. Using (26) one obtains

$$dV/dT = 0$$

$$= [V_{0A}(T) - V_{0P}(T)](dx/dT)$$

$$+ (dV_{0P}/dT) + x(d/dT)(V_{0A} - V_{0P}) ,$$

or (37)

$$(-)dx/dT$$

$$= [1/(V_{0A} - V_{0P})] \left[x\frac{dV_{0A}}{dT} + (1-x)\frac{dV_{0P}}{dT} \right] ,$$

and by (35), using again the Clausius-Clapeyron relations, the excess constant-volume heat capacity in the mixed-phase region is

$$\Delta C_v(x,T,V) = (-)T(dp_0/dT)[(dV_{0P}/dT) + x(d/dT)(V_{0A} - V_{0P})] . \tag{38}$$

We saw above in, Eq. (23), that, while $V_{0a}(T_{N,M})$ is larger than $V_{0p}(T_{N,M})$, the volume difference is very small and may not be accessible to measurements. Empirically, according to the indirect data of Table III, taking approximately

$$dV_{0P}/dT \approx dV_0/dT , \tag{39}$$

the first term inside the brackets on the right-hand side of (38) is expected to be considerably larger than the second term proportional to the temperature slope of the boundary-volume difference $(d/dT)(V_{0A} - V_{0P})$. Hence, with (39), it is reasonable to expect that the reduced heat-capacity form,

$$\Delta C_v(x,T,V) \approx (-)T(dp_0/dT)(dV_0/dT) , \tag{40}$$

should represent an acceptable approximation to the form (38).

At or near $T_{N,M}$, using the derivatives given in Table III, one verifies that ΔC_v given by (40) is very close to the estimate (36). The heat-capacity estimates over the temperature about $300R$ to interval of Table III are found to range from about $300R$ to $850R$ at 0.35 mK, using the single-volume temperature slopes of this table.

At the present time, we are aware of two independent sets of heat-capacity measurements across the transformation region of the A-P spin-ordering process. The expected anomalous major heat-capacity peaks observed in these experiments near or at melting referred to about $4R$ and $10R$ in the earlier and more recent work,[15,16] respectively. The pure-phase constant-volume heat capacities at or near the boundaries of the two-phase region reached about $(R/5)$ in both sets of measurements. The order of magnitude differences between the extreme ΔC_v values at or near $T_{N,M}$ estimated here and the experimental values arise, in large part, from the temperature resolution

achieved in the experiments. Improved experimental temperature resolution is expected to yield increasingly large excess constant-volume heat-capacity values on crossing the very narrow temperature width of the two-phase region. To the approximation of the treatment of the two-phase heat-capacity problem any other property involving the temperature rate of variation of the mixing index should exhibit an anomaly similar to that of the heat capacity. These anomalies arise from the temperature rate of exhaustion of the initial pure starting phase of the system at the beginning of its transformation into the final phase.

The temperature derivative of the paramagnetic susceptibility is expected to exhibit a large anomaly on crossing the two-phase region. To the approximation of the above treatment of the two-phase system, the paramagnetic susceptibility may be written in the two-phase system at the total volume V of the mixed phase, Eq. (26),

$$\chi(x,T,V) = x\chi_A(T,V) + (1-x)\chi_P(T,V), \tag{41}$$

χ_A and χ_P denoting the pure-phase susceptibilities on the mixed-phase boundaries. The temperature derivative of $\chi(x,T,V)$ is seen at once to lead to an excess susceptibility derivative through the term in (dx/dT), as was the case with the entropy of the two-phase system in (32) above. The temperature derivative is seen to be in the A-P transition region

$$d\chi/dT = x(d/dT)(\chi_A - \chi_P) + (d\chi_P/dT)$$

$$+ (dx/dT)(\chi_A - \chi_P) . \tag{42}$$

The last term on the right-hand side is the excess susceptibility temperature slope in this isochoric transformation. This excess is thus with (dx/dT) given by (37)

$$\Delta(d\chi/dT) = [(\chi_P - \chi_A)/(V_{0A} - V_{0P})](dV_P/dT) + x(d/dT)(V_A - V_p)]$$

$$\approx [(\chi_P - \chi_A)/(V_{0A} - V_{0P})](dV_0/dT) , \tag{43}$$

neglecting the term in x on the right-hand side of the first Eq. (43). At $T_{N,M}$, the volume difference ($V_{0A} - V_{0P}$) Eq. (24), was seen to be about 10^{-3} cm^3/mol, and (dV_0/dT) from Table III is of the order of 2 cm^2/mol mK. The susceptibility difference was measured to be quite large, or

$$\chi_P - \chi_A \approx \chi_P \approx \chi_A . \tag{44}$$

A verification of (43), however, may not be easily accessible. Indeed, the susceptibility derivatives must be obtained indirectly, since the measured property is the susceptibility itself and not its temperature slope.

In concluding, the entropy change in the transformation at $T_{N,M}$ is a fair fraction of the asymptotic high-temperature spin entropy or $R \ln 2$, as was to be expected. In contrast, the state coordinates p, V, and T undergo only very small changes across the two-phase region. Of these, only the pressure change, in a constant-volume transformation, is accessible to measurements. Acquisition of data across the transformation region at pressure above the melting pressure and below the triple-point temperature may encounter technical difficulties as a consequence of insufficient volume and temperature resolution. In particular, constant-volume heat-capacity measurements across the two-phase or transformation region seem to have only qualitative significance, at the present time.

ACKNOWLEDGMENTS

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