THE EQUILIBRIUM DIAGRAM FOR THE He^3-He^4 LIQUID-CRYSTAL SYSTEM

N. G. BEREZNYAK, I. V. BOGOYAVLENSKIĬ, and B. N. ESEL'SON

Physico-technical Institute, Academy of Sciences, Ukrainian S.S.R.

Solidification-onset curves for solutions of He^3 in He^4 have been investigated, and data have been obtained on the width of the liquid-crystal diagram over the temperature range from 1.4 to 4.2°K. It has been found that the width of the diagram in this temperature region amounts to several atmospheres. The solution solidification curves show triple points which correspond to a polymorphic transition in the solid phase, and to the α-γ phase transition in solid He^4. On the basis of known experimental data and thermodynamic analysis, certain opinions are expressed regarding the character of the He^3—He^4 system liquid-crystal diagram over a wide range of temperatures (0—20°K). A description is given of the apparatus employed in the experiments for performing a thermal analysis of the helium isotope mixtures, using a strain gauge for measurement of the pressure within the calorimeter.

THE numerous unique features in the behavior of both He^3 and He^4 in their liquid and solid phases have recently drawn considerable attention to the study of the diagram of state of the helium isotope system.

Besides the fundamental fact of the failure of the pure isotopes to transform into their solid phases when cooled under saturated vapor pressure, the existence of a minimum in the p(T) curve for pure He^3 (the Pomeranchuk effect[1,2]) is of extreme importance. The recently-discovered polymorphic transitions in He^3[3-6] and He^4[7-10], the phase separation in liquid He^3—He^4 solutions[11], and the determination of the behavior of the λ-line for such solutions down to the region in which phase separation occurs[12,13], all testify to the great complexity of the phase equilibrium diagram for this system. With this in view, we have undertaken an investigation of liquid-crystal equilibrium in the He^3—He^4 system; the results of this study are reported in the present paper.

The use of these results, as well as of the data recently obtained in other laboratories, make it possible to draw certain conclusions regarding the character of the phase diagram of the He^3—He^4 system; these are also presented in this article.

1. METHOD OF MEASUREMENT, AND DATA ON THE SOLIDIFICATION-ONSET CURVES AND THE WIDTH OF THE DIAGRAM

Information concerning the onset of solidification in helium isotope solutions was first obtained by Esel'son and Lazarev[14], using the blocked-capillary method; this latter is, of course, incapable of providing complete information on the liquid-solid diagram. To remedy this lack, a thermal analysis method was utilized in the present work to obtain data on liquid-crystal equilibrium.

The construction of the calorimeter used in these experiments (Fig. 1) made it possible at any given instant to measure both the temperature and the pressure of the solution under study. To accomplish this, the lower portion of the calorimeter was made in the form of a thin-walled beaker (beaker diameter 11 mm, wall thickness 0.35 mm) of beryllium bronze, around the outer surface of which was wound a strain gauge (1) of constantan wire (0.03 mm in diameter) having a resistance of $3500\,\Omega$ at 4.2°K. Electrical isolation was achieved by means of a polymerized layer of BF-4 cement. Data on the pressure within the calorimeter was obtained by measuring with a bridge the changes in the resistance of the gauge due to the elastic deformation of the beaker wall. The gauge was calibrated in advance by filling the calorimeter with liquid He^4 and using a standard manometer communicating with the calorimeter via a German silver capillary (2) of 0.3 mm inside diameter. Corrections for the temperature sensitivity of the strain gauge were incorporated by comparing the pure He^4 fusion curve with the data of Swenson[15]. The strain gauge, as described, was found to have a sensitivity of $0.06\,\Omega$/atm.

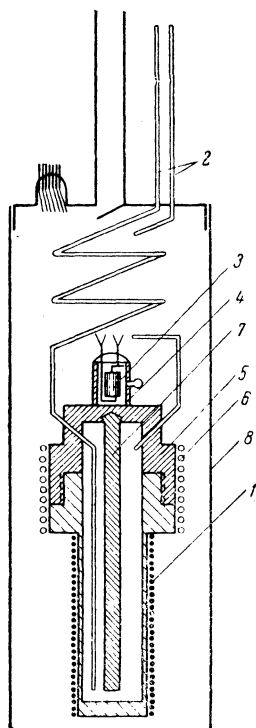For temperature measurement, use was made of a carbon resistance thermometer (3) placed in

FIG. 1. Calorimeter for thermal
analysis of helium isotope mixtures
(see description in text).

FIG. 2. Plan of apparatus for investigation of the
liquid-crystal diagram of the He^3-He^4 system.

a chamber (4) formed in one piece with the upper,
thick-walled, copper portion of the calorimeter
(5), and filled with gaseous He^4 to a pressure of
350 mm Hg at room temperature. A heater of
constantan wire (6) was wound onto the copper
section of the calorimeter. In order to reduce pos-
sible temperature gradients, a copper core (7)
2 mm in diameter was mounted within the calorim-
eter.

Vacuum isolation of the calorimeter was ac-
complished through pumping an exchange gas out
of the jacket (8), by lowering into the latter a
charcoal adsorption pump (P_1 in Fig. 2).

The calorimeter thus described, with a volume
of approximately 5 cm^3, was intended for use in
the temperature range 1.3—4.2°K at pressures up
to 150 atm. The overall plan of the apparatus is
presented in Fig. 2.

At a given temperature of the liquid helium in
the Dewar, and with exchange gas present within
the jacket (i.e., with the charcoal pump P_1 raised)
a mixture of known He^3 concentration was con-
densed from the storage bottle B_1[1] into the calo-
rimeter, the gas being freed of possible contami-

nants by passage through a coiled trap T im-
mersed in liquid hydrogen. A portion of the same
mixture was simultaneously condensed into a sec-
ond container B located in a second Dewar filled
with liquid helium. Upon evaporation of the helium
from this Dewar, pressure was developed in the
container B and applied to the calorimeter A[16].
The pressure thus generated was monitored with
the spiral-tube manometers M_1 and M_2; the pres-
sure at the beginning of the experiment was that of
the solution in the liquid state.

Upon completion of this process the exchange
gas was pumped away from the calorimeter jacket
J (with the charcoal pump P_1 lowered), and the
temperature in the Dewar was reduced, leading to
the formation of solidified plugs in the capillaries
C above the calorimeter. The calorimeter itself,
filled with liquid, was thus isolated from external
contacts, the change in the composition of the liquid
due to the formation of the plugs in the fine capil-
lary tubes being negligibly small.

Under these conditions the calorimeter gradu-
ally cooled down, with measurements of the tem-
perature T and pressure p being made as a func-
tion of time t. Changes in the slope of the T(t)
curves indicated the onset of the formation of the
solid phase for the liquid of the corresponding ini-
tial concentration. Such data were obtained repeat-
edly during the course of a single experiment with
the calorimeter both cooling down and warming up.
Typical curves of T(t) in the vicinity of the onset
of solidification are shown in Fig. 3. Repeated ex-
periments with a mixture of the same composition
at various initial pressures and temperatures per-
mit the construction of the solidification-onset
curve for this mixture.

---

[1]The bottles indicated in Fig. 2 by B_2 and B_3 were used
for testing the apparatus, and the charcoal pump P_2 for col-
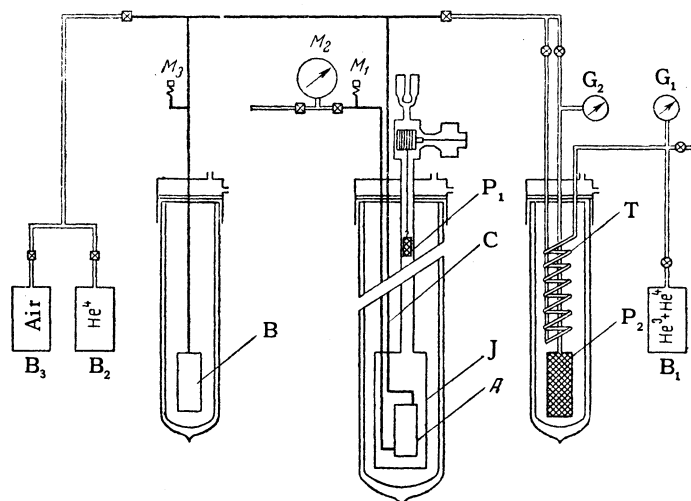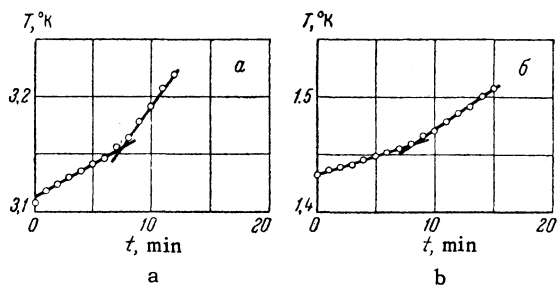lecting the residue of the mixture at the conclusion of the
experiment.

FIG. 3. Warming curves with the calorimeter containing He³-He⁴ solutions near the solidification-onset temperature: a − 24.1% He³, b − 53.0% He³.

As a result of a series of experiments with mixtures containing 10.3, 24.1, 53.0, and 76.4% He³, solidification-onset curves for these mixtures[17] were obtained over the temperature range from 1.5 to 4.2°K, at pressures up to 140 atm (Table I).

Table I. Temperatures* and pressures at the onset of solidification in solutions of varying He³ concentration

x, %	T, °K	p, atm	x, %	T, °K	p, atm
	2.059	45.9		1.460	37.9
	2.360	59.2		1.695	48.0
	2.719	71.7		2.133	65.9
10.3	2.866	78.3		2.394	75.6
	3.104	93.2	53.0±0.1	2.747	95.1
	3.488	109.4		2.912	102.6
	3.949	131.6		3.300	123.6
				3.569	135.8
	1.534	27.7		1.491	49.7
	1.769	37.7		1.580	51.8
	1.974	46.3		1.859	62.9
	2.175	54.0		2.006	73.1
	2.317	59.8		2.081	74.8
24.1±0.1	2.497	67.2	76.4±0.1	2.246	80.6
	2.512	71.1		2.510	93.2
	2.808	83.1		2.644	101.2
	3.154	98.5		3.050	121.8
	3.526	115.3		3.170	125.5
	3.565	119.1			
	3.957	141.9			

*Temperatures were determined from the 1958 temperature scale.[18]

From these data, one can then construct a portion of the liquid-crystal diagram—specifically, the "liquidus" line.

In order to secure information on the width of the diagram, experiments were undertaken with a mixture containing 24.1% He³. In this case, the mixture in the calorimeter was transformed entirely into the solid state by cooling it to a sufficiently low temperature; it was then possible, as the calorimeter was warmed up, to use the method described above to determine the pressure and temperature corresponding to the initial appearance of a liquid phase in equilibrium with the crystal having the original composition.

The degree of establishment of concentration equilibrium in the solid phase over the whole mixed-phase region up to complete solidification may be judged from the absence of hysteresis in experiments conducted with various calorimeter heating and cooling rates. A further indication is provided by the sharpness with which triple points are recorded in this same region (see below). The establishment of concentration equilibrium in the solid phase is also confirmed by recent experiments[19] with solid He³—He⁴ mixtures.

The results obtained in the experiments with the 24.1% He³ mixture over the temperature interval 1.45—3.1°K, at pressures up to 100 atm, are presented in Fig. 4 and listed in Table II. As
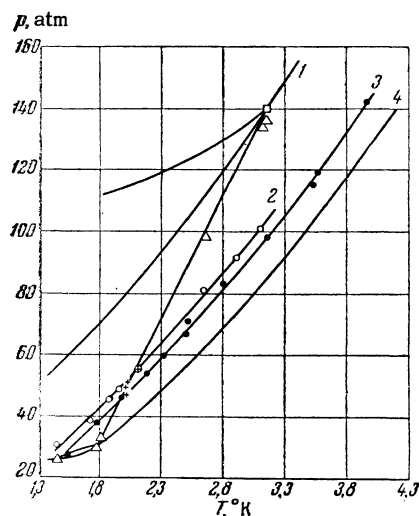

FIG. 4. Curves representing the onset (3) and completion (2) of solidification in a solution containing 24.1% He³; curve 1 — pure He³; 4 — pure He⁴.

Table II. Temperatures and pressures at completion of solidification in a solution of 24.1% He³ concentration

T, °K	p, atm	T, °K	p, atm
1.444	30.6	2.107	55.4
1.720	38.7	2.638	81.2
1.870	45.3	2.904	91.7
1.873	45.6	3.096	101.2
1.960	49.0		

is seen from the diagram, the solidification-onset (3) and -completion (2) curves are displaced from one another by 3.5 atm at 1.5°K, and by 5.5 atm at 3.1°K.

In performing the above-described experiments over the region of coexistence of the liquid and solid phases, the triple points corresponding to

Table III. Triple points observed in the liquid-solid mixed-phase region for a solution of 24.1% initial He³ concentration

$T°$, K	p, atm
1.997	48.4
2.007	49.4
2.024	51.0
2.107	55.4

the polymorphic transition in the solid phase were clearly defined. These triple points are also shown in Fig. 4 (Table III), where for each of them a determination of its temperature and pressure was made for the given initial liquid concentration. It should be noted that these points fall closely upon the line connecting the corresponding triple points for pure He³[3] and He⁴[8]. This is in good agreement with the results obtained by Vignos and Fairbank.[20]

During the course of the experiments with the helium isotope solutions, control experiments were periodically carried out with pure He⁴. During one of these experiments we recorded (Fig. 5)
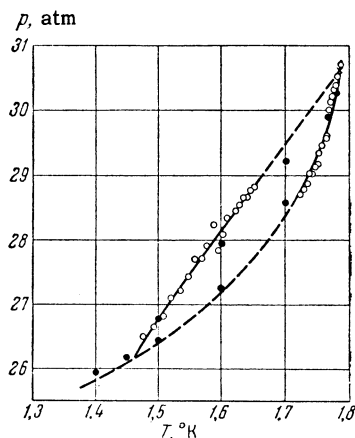
FIG. 5. Solidification curve and polymorphic transition line for He⁴; o — results from the present work; ● — data of Vignos and Fairbank[8]; x — triple point, as determined in the present work.

the polymorphic transition in solid He⁴ ($\alpha - \gamma$), recently detected by Vignos and Fairbank[8], who observed a jump in the speed of sound at the transition from the α to the γ phase. Our data agree closely with the results of their work.

All of the isotope solutions used in these experiments, with the exception of the 10.3% He³

solution, were prepared by mixing pure He³ and He⁴, which guaranteed knowledge of the molar concentrations to an accuracy of not less than 0.001.

The scatter of the data relative to the pressures and temperatures of the transitions did not exceed 0.5 atm or 0.01°, respectively.

2. CHARACTER OF THE He³—He⁴ SYSTEM PHASE DIAGRAM

Making use of the data on liquid-solid phase equilibrium in helium isotope solutions, both from the present article and from the work of other authors, and also using presently-available information concerning liquid-liquid and solid-solid equilibrium, it is possible to make a series of judgments regarding the character of the state diagram for this system.

1. As is well-known, polymorphic transitions have been found both in He³[5,6] and in He⁴[7,9]; the corresponding triple points have the coordinates T = 17.78°K, p = 1608 atm, and T = 14.9°K, p = 1148 atm (Fig. 6a). Investigations of the structure of these solid phases by x-ray diffraction methods have shown that the low-temperature phases possess a hexagonal close-packed structure, while the high-temperature phases have a face-centered cubic lattice. In view of this, it is possible to presume that the solid solutions should undergo polymorphic transformations in the same temperature and pressure region.
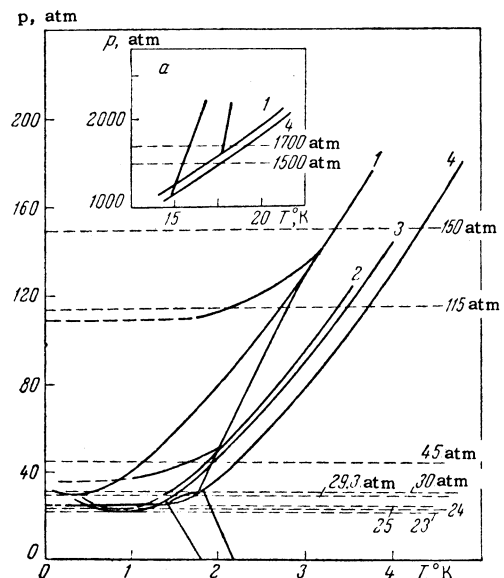
FIG. 6. Schematic phase diagram of the He³-He⁴ system: 1 — solidification and polymorphic transformation curves for pure He³; 2 — mixture solidification-completion curve and polymorphic transition line; 3 — solidification-onset curve for a mixture, and its λ-line; 4 — solidification and polymorphic transition curves and λ-line for pure He⁴.
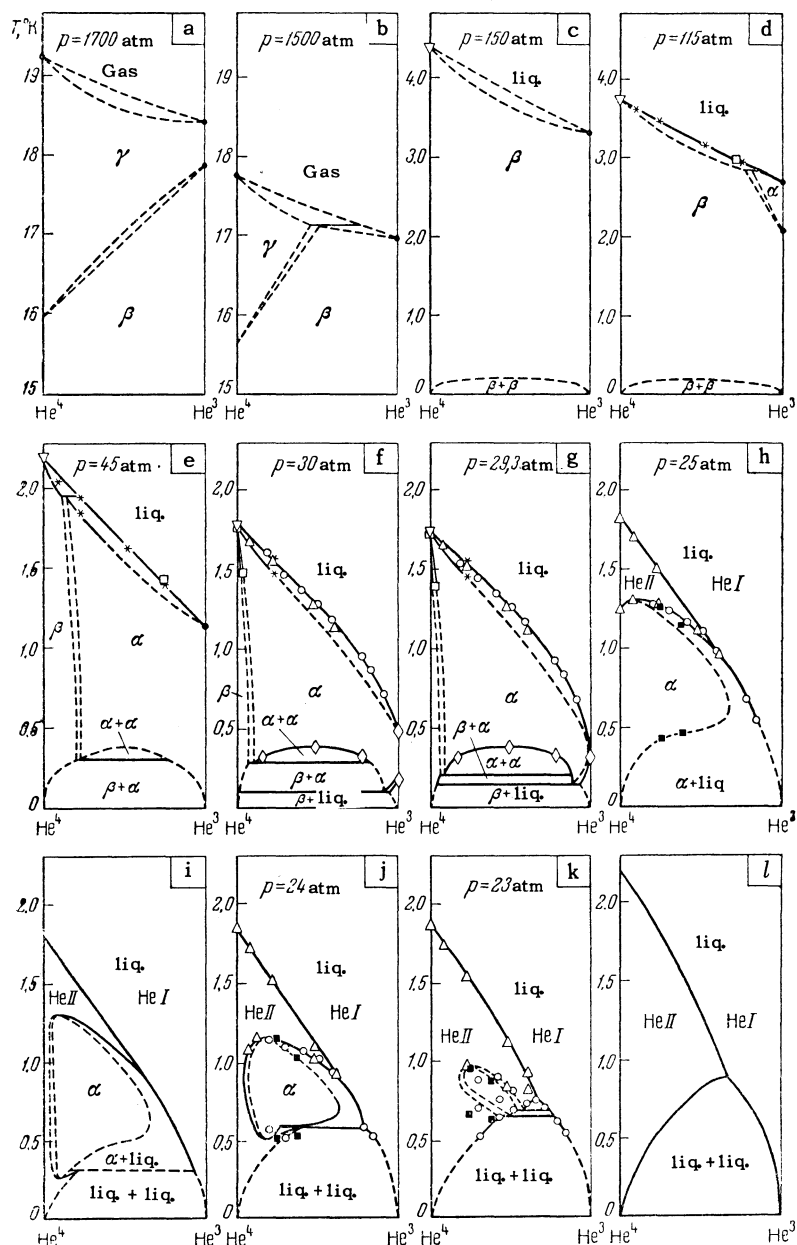
FIG. 7. Phase diagram for the He³-He⁴ system.
Data used: ●_[³]; ▽_[¹⁵]; *_present work and
[¹⁷]; □_[⁸,²⁰], ◇_[²,¹⁹]; ■_[²²]; △_[²³]; ○_[²⁴],
(α — body-centered cubic lattice; β — hexagonal
close-packed lattice; γ — face-centered cubic lat-
tice).

Taking all of this into account, one may con-
clude that the phase diagram for pressures p
> 1608 should have the form indicated in Fig. 7a,
and for 1148 atm < p < 1608 atm and p < 1148
atm, respectively, those indicated in Figs. 7b
and c.

2. At lower temperatures, the polymorphic
transitions in He³[³,⁴], He⁴[⁸,¹⁰] and solid mix-
tures of these isotopes, should also be reflected
in the phase diagrams.

In the pressure range between 140 and 30 atm,
the pure components near their melting curves
possess, respectively, a hexagonal close-packed
structure (He⁴) and a body-centered cubic lattice
(He³).[⁴] Taking into account the fact that poly-
morphic transitions also occur in solutions in

this pressure region[²⁰], as well as the informa-
tion contained in the present paper concerning
the width of the liquid-solid mixed-phase mode,
it follows that the phase diagram should be rep-
resented in the form shown in Fig. 7d and e. Both
here and in what follows, account is taken of the
fact that the polymorphic transition line for He³
has the character indicated in Fig. 6, which is
borne out by the latest specific heat measurements
on solid He³.[²¹] It can probably be assumed that
a similar pattern exists for mixtures, except for
weak solutions of He³ in He⁴, for which, as for
He⁴, there should occur a closed region within
which exists a phase having a body-centered cubic
lattice.

3. According to the data of Edwards, McWilliams,

and Daunt,[19] phase separation occurs in solid solutions at temperatures below 0.4°K and pressures of 36—27 atm; this is indicated in Figs. 7f and g. Here the most probable form of the polymorphic transition region in the vicinity of the phase separation is shown. As noted by Edwards, McWilliams, and Daunt, however, no thermal effect associated with the intersection of the polymorphic transition line with the phase separation curve was observed.

On the basis of generalized thermodynamic considerations, an analogous separation should occur in the solid phase at temperatures near absolute zero at somewhat higher pressures. This situation has been indicated in Figs. 7c, d, and e.

4. At pressures below 32 atm the presence of the minimum in the $p(T)$ curves for He^3[1,2] and for He^3—He^4 mixtures[22,24] exerts a strong influence upon the form of the diagram.[2)]

The characteristic features arising from this effect are incorporated in Figs. 7f and g. In these figures, the presence of the polymorphic transition in He^4[8] was also taken into account. A separation of the mixture into virtually pure liquid He^3 and solid He^4 was observed to occur at T = 0.07°K and p = 30 atm, in [19].

5. Beyond this point, an important part is played by the minima occurring in the $p(T)$ curves for He^3 – He^4 mixtures,[22,24] [3)] at pressures below the solidification pressure for He^4 and at temperatures above that of the minimum for pure He^3.

Taking these circumstances into account, one may construct the phase diagram shown in Fig. 7h. With a slight decrease in pressure, the phase diagram should undergo a fundamental alteration, due to the extremely flat slope of the $p(T)$ curve for He^4 down to absolute zero; a closed solid-phase region is formed (Fig. 7i). As regards the polymorphic transition lines in the solid phase at these pressures, they are rapidly displaced toward the He^4 side of the diagram, the β-phase region contracting and probably vanishing by the time the pressure corresponding to Fig. 7i is reached.

6. At these and lower pressures, account must be taken of the occurrence of phase separation in liquid solutions of He^3 in He^4[11,24], and the diminution in the area occupied by the solid phase (Figs. 7j and k). After the disappearance of the solid phase, the diagram assumes the form shown in Fig. 7l, which refers to saturated vapor pressure.

In Figs. 7h–k the position of the λ-line is taken from the data of Le Pair, et al.[23], and in Fig. 7l, from [13].

It should be noted that the results obtained by Lifshitz and Sanikidze[25] in their theoretical investigation of the phase diagram for weak solutions of He^4 in He^3 are well confirmed, qualitatively speaking, by the available experimental data, as can be seen from Fig. 7.

In conclusion, it should be emphasized that in constructing this diagram it has been assumed that at T = 0°K both the solid and the liquid phases must separate into their pure constituents. It has also been presumed that the Pomeranchuk effect does not occur for weak solutions of He^3 in He^4. In the alternative event, the transition from the diagram of Fig. 7g to that of Fig. 7j would take place in a somewhat different fashion than is indicated in Figs. 7h and i. One of the possible variations of such a transition has been presented by Zinov'eva[24]. In extrapolating the curves in these diagrams to zero temperature, one must allow for the possible existence of the Pomeranchuk effect down to solutions of any given degree of dilution, as well as the occurrence of a region of non-separation of the liquid solution at 0°K. Unfortunately, the insufficient accuracy of experiments performed at these pressures and at temperatures of a few tenths of a degree clearly do not permit us to establish a unique form for the diagram of state under these conditions.

Experiments presently being carried out will in all probability permit a number of details of the diagram to be described with a high degree of confidence.

We take this opportunity to thank I. M. Lifshitz and G. I. Stepanov for extremely helpful discussions concerning the results of the present work.

[2)]The results of measurements by K. N. Zinov'eva have been used in our study of the character of the phase diagram at low pressures. We take this opportunity to thank the author for acquainting us with her work prior to publication.

[3)]As a result of the work of LePair, et al.,[23] a correction amounting to 1 atm has been introduced to give agreement with existing data on the solidification of pure He^4.

[1] I. Ya. Pomeranchuk, JETP 20, 919 (1950).

[2] Baum, Brewer, Daunt, and Edwards, Phys. Rev. Lett. 3, 127 (1959).

[3] E. R. Grilly and R. L. Mills, Ann. of Phys. 8, 1 (1959).

[4] Schuch, Grilly, and Mills, Phys. Rev. 110, 775 (1958).

[5] A. F. Schuch and R. L. Mills, Phys. Rev. Lett. 6, 596 (1961).

[6] J. P. Franck, Phys. Rev. Lett. 7, 435 (1961).

[7] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. 218, 291 (1953).

[8] J. H. Vignos and H. A. Fairbank, Phys. Rev. Lett. 6, 265 (1961).

[9] R. L. Mills and A. F. Schuch, Phys. Rev. Lett. 6, 263 (1961).

[10] A. F. Schuch and R. L. Mills, Phys. Rev. Lett. 8, 469 (1962).

[11] G. K. Walters and W. M. Fairbank, Phys. Rev. 103, 262 (1956).

[12] S. G. Sydoriak and T. R. Roberts, Phys. Rev. 118, 901 (1960).

[13] Esel'son, Ivantsov, and Shvets, JETP 42, 944 (1962), Soviet Phys. JETP 15, 651 (1962).

[14] B. N. Esel'son and B. G. Lazarev, DAN SSSR 97, 61 (1954).

[15] C. A. Swenson, Phys. Rev. 89, 538 (1953).

[16] Brewer, Daunt, and Sreedhar, Phys. Rev. 115, 836 (1959).

[17] Bereznyak, Bogoyavlenskiĭ, and Esel'son, JETP 43, 1981 (1962), Soviet Phys. JETP 16, 1394 (1963).

[18] H. van Dijk and M. Durieux, Physica 24, 420 (1958). Brickwedde, van Dijk, Durieux, Clement, and Logan, J. Res. NBS 64A, 1 (1960).

[19] Edwards, McWilliams, and Daunt, Phys. Rev. Lett. 9, 195 (1962).

[20] J. H. Vignos and H. A. Fairbank, VIII Int. Conf. on Low Temp. Phys. (preprint of papers) London, 1962; p. 87.

[21] E. C. Heltemes and C. A. Swenson, Phys. Rev. 128, 1512 (1962).

[22] Weinstock, Lipschultz, Keller, Tedrow, and Lee, Phys. Rev. Lett. 9, 193 (1962).

[23] Le Pair, Taconis, de Bruyn Ouboter, and Das, Physica 28, 305 (1962); VIII Int. Conf. on Low Temp. Phys. (preprint of papers) London, 1962; p. 79.

[24] K. N. Zinov'eva, JETP 44, 1837 (1963), Soviet Phys. JETP 17, 1235 (1963).

[25] I. M. Lifshitz and D. G. Sanikidze, JETP 35, 1020 (1958), Soviet Phys. JETP 8, 713 (1959).

Translated by S. D. Elliott

90