blasted. The instability was again observed only for one polarity of the magnetic field but, in contrast to our case, it was associated with a falling region in the current-voltage characteristic.

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Translated by A. Tybulewicz

A phenomenological theory of the liquid-to-crystal phase transition in He^3

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(Submitted July 3, 1975)
Zh. Eksp. Teor. Fiz. 70, 578–585 (February 1976)

A theory of the liquid-to-crystal transition in He^3 is proposed on the basis of the assumption that this transition is nearly of second order. In the theory are derived the well-known unusual properties of solid He^3: the formation of a non-closepacked structure and the increase in the compressibility as compared to the compressibility of the liquid. The theory yields a number of dependences that can be experimentally verified.

PACS numbers: 64.70.−p, 61.30.+w

1. FORMULATION OF THE PROBLEM

The theory of the liquid-to-crystal phase transition in helium is based on a variational approach: trial wave functions of the liquid and the crystal are given and the variational parameters are determined by a computer calculation.[1] The accuracy of such a method does not turn out to be high enough for preference to be given to any of the structures: face-centered cubic (fcc), hexagonal close-packed, or body-centered cubic (bcc). Therefore, one of the unusual properties of He^3 that distinguishes this substance from the other inert elements–the formation of a non-close-packed (bcc) structure–is not explained.

In the present paper we propound for the liquid-to-crystal phase transition in He^3 a phenomenological theory based on the assumption that this is a nearly second-order phase transition. Then we can, in the spirit of the well-known Landau idea, use the expansion of the thermodynamic potential in powers of a small parameter, which, in the present case, is the deviation of the density from a constant.

Let us give the reason for such a description. Liquid He^3 is extremely sensitive to pressure changes. Let us consider the function $f(\mathbf{k}, \sigma; \mathbf{k}', \sigma')$, which was introduced by Landau in the theory of the Fermi liquid,[2] or, more precisely, the dimensionless quantity $2\nu f = F + (\sigma\cdot\sigma')Z$, where $\nu = m^* k_F / 2\pi^2$ is the density of states per spin at the Fermi surface. It turns out (see the review article[3]) that the mean—with respect to the angles—quantity $\langle F\rangle$ undergoes the most rapid variation: There is almost a threefold change in its value (from 31.7 to 94.1) in the interval of pressures from 9 to 34.36 bar (the melting curve), whereas the density increases by only 20% in the same pressure range. This can be ascribed to that part of the interaction between the He^3 atoms that approximates the interaction between hard spheres.[4] On the other hand, the presence of the hard cores of the atoms is the principal cause of the solidification of He^3 (in the opposite case the Fermi liquid would approach the ideal Fermi gas as the pressure increased, and solidification would not occur). Thus, the large values and the rapid variation of the quantity $\langle F\rangle$ apparently indicate that liquid He^3 has, as it were, a "premonition" of crystallization. In other words, the curve of absolute instability of the liquid with respect to crystallization (the spinodal) is located near the melting curve (the binodal).

Since the above-given reason is connected with the properties of the Fermi liquid, the proposed description can be valid at sufficiently low temperatures.

Let us note at once that we obtain, as a result, an explanation for the following unusual properties of solid He^3: the formation of a non-close-packed (bcc) structure and the increase in the compressibility as compared to the compressibility of the liquid, which is an additional argument in favor of the theory.

In the present paper it is convenient to take as the independent thermodynamic variables the pressure and temperature, i.e., to carry out an expansion of the chemical potential μ. The small parameter is the deviation of the density from a constant. The expansion of μ has the form:

$$\mu-\mu_0=\sum_{\mathbf{k}}\left[A+\frac{(k-k_0)^2}{m}\right]|x_{\mathbf{k}}|^2+\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0}B_{\mathbf{k}_i}x_{\mathbf{k}_1}x_{\mathbf{k}_2}x_{\mathbf{k}_3}+\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}C_{\mathbf{k}_i}x_{\mathbf{k}_1}x_{\mathbf{k}_2}x_{\mathbf{k}_3}x_{\mathbf{k}_4}, \tag{1}$$

where μ_0 is the chemical potential of the liquid, $x_{\mathbf{k}}$ is the Fourier component of the density fluctuations:

$$\frac{\rho(\mathbf{r})-\bar{\rho}}{\bar{\rho}}=\sum_{\mathbf{k}}x_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}$$

($\bar{\rho}$ is the mean crystal density), $x_{\mathbf{k}}=x_{-\mathbf{k}}^*$. Let us explicitly separate out the pressure dependence of the expansion parameters. (As to the temperature, we shall assume that $T=0$, since the generalization to the case of finite temperatures requires a special treatment.) The quantity $A=A'(P-P_0)$ vanishes on the spinodal (at the point P_0), and is positive for $P<P_0$, i.e., $A'<0$. It is also necessary to take into account the dependence of the momentum k_0 on P, which determines the lattice constant. We shall assume the coefficients B and C to be pressure independent.

Such type of expansion was first considered by Landau.[5]

2. TYPE OF LATTICE

The model (1) without the x^3 term gives a second-order phase transition at the point $A=0$. In order for this term to "operate," it is necessary that there be among the nonzero Fourier components $x_{\mathbf{k}}$ some for which $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$. In this case there occurs a first-order transition (when $A>0$). It can be seen at once that only the $x_{\mathbf{k}}$ with $|\mathbf{k}|\approx k_0$ are different from zero. Let us make the following assumptions: the $x_{\mathbf{k}}$ with the same $|\mathbf{k}|$ are nonzero and these $x_{\mathbf{k}}$ are equal and real (phases of the type $\mathbf{k}\times$ an arbitrary vector, which correspond to the displacement of the lattice as a whole, are of no interest to us; the reality of $x_{\mathbf{k}}$ implies that the lattice possesses a center of inversion). The necessary equilateral momentum triangles in the two-dimensional case can be obtained by taking a triangular lattice. Let $\varkappa_1$ and $\varkappa_2$ be reciprocal-lattice vectors. Then the nonzero x_k are those with momenta $\mathbf{k}=\pm\varkappa_1$, $\pm\varkappa_2$, $\pm(\varkappa_1-\varkappa_2)$. In the three-dimensional case there is yet a third lattice vector $\varkappa_3$, which has the same length and does not lie in this plane.

It is necessary to compare the following structures: 1) two-dimensional (triangular); 2) three-dimensional with momentum $\varkappa_3$, such that $|\varkappa_1|=|\varkappa_2|=|\varkappa_3|=|\varkappa_1-\varkappa_2|=|\varkappa_3-\varkappa_2|\neq|\varkappa_1-\varkappa_3|$; 3) three-dimensional with such $\varkappa_3$ that all the six momenta are equal in magnitude. Formally, we can obtain a minimum of the expression (1) apparently for any of these structures. Physically, however, it is necessary to give preference to that structure that leads to the most symmetric arrangement of the lattice sites in coordinate space. This will be in the case (3) when the vectors $\varkappa_1$, $\varkappa_2$, and $\varkappa_3$ form a regular tetrahedron (fcc), which corresponds to a bcc lattice in coordinate space. Precisely such a structure obtains for He^3. In the case (2) the lattice vectors in coordinate space differ in magnitude, i.e., the distances between the "nearest" neighbors are not the same, which would be strange for such a symmetric atom as helium. The case (1) bears no relation at all to the transition under consideration.

For a tetrahedral arrangement of the vectors $\varkappa_1$, $\varkappa_2$, and $\varkappa_3$, the nonzero $x_{\mathbf{k}}$ are those with the momenta, besides those given above, $\mathbf{k}=\pm\varkappa_3$, $\pm(\varkappa_1-\varkappa_3)$, $\pm(\varkappa_2-\varkappa_3)$ (in the second case there are no components with the momenta $\pm(\varkappa_2-\varkappa_3)$). Thus, there are in all 12 nonzero Fourier components.

Let us emphasize that among the various C there are indeed some that lead to a minimum of (1) for a bcc lattice. This can easily be verified in the simplest cases, when, for example, the function C does not depend on the angles between the vectors, i.e., when $C=\text{const}$.

A few words about the quantity $\varkappa=|\varkappa_i|$, which determines the lattice constant. The quantity $\varkappa\neq k_0$ for the following reason. It is necessary to take the dependence of the coefficients B and C on $\varkappa$ into account. Then the condition for a minimum of (1) with respect to $\varkappa$ gives

$$\varkappa-k_0=B'x+C'x^2, \tag{2}$$

where B' and C' are clearly related with the derivatives with respect to the momentum modulus of the quantities B and C at the point k_0 ($x_{\mathbf{k}}\equiv x$). After this, we can, in general, eliminate the explicit momentum dependence from (1), redefining the coefficient attached to the fourth power, and replace (1) by the expansion:

$$\mu-\mu_0={}^1/_2\alpha x^2+{}^1/_3\beta x^3+{}^1/_4\gamma x^4, \tag{3}$$

where we have taken into account the fact that all the $x_{\mathbf{k}}$ are real and equal, $x_{\mathbf{k}}=x$; $\alpha=\alpha'(P-P_0)$, $\alpha'<0$. We shall henceforth use precisely this expansion, (3), and the relation between the coefficients α, β, and γ with A, B, and C will not be needed. As to the assumptions made at the beginning of the section, for the symmetric structure (the fcc lattice in reciprocal space) of interest to us they are natural, and we need not concern ourselves with their justification (concerning the phases of $x_{\mathbf{k}}$, see the following section).

3. THE PROPERTIES OF SOLID He^2

The extrema of the expression (3) are attained at the following values:

$$x=0, \tag{4a}$$

$$x=-\frac{\beta}{2\gamma}-\sqrt{\left(\frac{\beta}{2\gamma}\right)^2-\frac{\alpha}{\gamma}} \tag{4b}$$

$$x=-\frac{\beta}{2\gamma}+\sqrt{\left(\frac{\beta}{2\gamma}\right)^2-\frac{\alpha}{\gamma}}\,. \tag{4c}$$

We shall assume that $\beta>0$. The state (4a) is the liquid state ($\alpha>0$) and the state (4b) is the solid state ($\alpha<\beta^2/4\gamma$). The branch (4c) is unstable when $\alpha>0$. For $\alpha<0$, it is also unstable for complex $x_{\mathbf{k}}$. This instability for $\alpha<0$ is connected with the cubic term (the quadratic term does not depend on the phases, while the fourth-

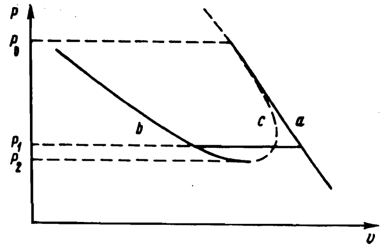

FIG. 1.

order term can be neglected for $\alpha \to 0$), which has the form

$$B \sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0} x_{\mathbf{k}_1} x_{\mathbf{k}_2} x_{\mathbf{k}_3} = B|x|^3 \sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0} \cos(\varphi_{\mathbf{k}_1}+\varphi_{\mathbf{k}_2}+\varphi_{\mathbf{k}_3}),$$

where $\varphi_{\mathbf{k}_i}$ is the phase of the quantity $x_{\mathbf{k}_i}$; all the moduli $|x_{\mathbf{k}_i}|$ are assumed, as before, to be equal (although in the present case this is not important); $B > 0$. It can be seen at once from this that arbitrarily small phases lead to a decrease in μ, which indicates the instability of the branch (4c). This pertains only to the structure under consideration; apparently, for $\alpha < 0$, instead of (4c) a stable structure of another symmetry can appear. This question was not investigated.

As to the branch (4b), it is stable in, for example, the case when the fourth-order terms do not depend on the phases, i.e., have the form

$$\sum_{\mathbf{k},\mathbf{k}'} C|x_{\mathbf{k}}|^2 |x_{\mathbf{k}'}|^2.$$

Then again everything is determined by the cubic term, and it is a minimum for phases $\varphi_{\mathbf{k}_i} = \pm\pi$, i.e., for negative x, which occurs precisely on the branch (4b). In the general case it is necessary to take the fourth-order terms into account too. It turns out that the branch (4b) is stable in some pressure interval (the lower limit of this interval is the point of absolute instability of the crystal), which includes the transition point if the condition for the realization of the bcc lattice under consideration is fulfilled.

The liquid-to-crystal phase transition ($\mu - \mu_0 = 0$) occurs under the condition that

$$\alpha = \frac{2}{9}\frac{\beta^2}{\gamma}, \quad x = -\frac{2}{3}\frac{\beta}{\gamma}. \tag{5}$$

To metastable states correspond the values

$$0 < \alpha < \frac{2}{9}\frac{\beta^2}{\gamma} \tag{6}$$

("supercooled" liquid) and

$$\frac{2}{9}\frac{\beta^2}{\gamma} < \alpha < \frac{\beta^2}{4\gamma} \tag{7}$$

("superheated" crystal). From the formulas (5) and (7) we can obtain the relation:

$$(P_0 - P_1)/(P_0 - P_2) = {}^8/_9, \tag{8}$$

where P_1 is the phase-transition point and P_2 is the point of absolute instability of the crystal (see Fig. 1).

The change in the specific volume at the transition point is equal to

$$v - v_0 = {}^2/_9 \alpha' (\beta/\gamma)^2 \tag{9}$$

(quantities with the index zero pertain to the liquid), $\alpha' \equiv d\alpha/dP < 0$.

Let us consider the expression for the compressibility. At the transition point we have

$$-\frac{1}{v}\frac{dv}{dP} = -\frac{1}{v_0}\frac{dv_0}{dP} - \left(\frac{1}{v} - \frac{1}{v_0}\right)\frac{dv_0}{dP} + \frac{2}{v}\frac{(\alpha')^2}{\gamma}. \tag{10}$$

It can be seen from this that the compressibility of the solid is greater than the compressibility of the liquid. This unusual property is characteristic of He^3 at sufficiently low temperatures.[6]

The volume of the crystal as a function of pressure is

$$v = v_0 + {}^1/_2 \alpha' x^2, \tag{11}$$

where the P dependence of x is given by the formula (4b). The isotherm is shown in Fig. 1. The continuous curves correspond to stable states (a and b; see (4)), while the dashed curve (c) corresponds to the unstable state. A horizontal straight line corresponds to a region of coexistence of the phases. Let us draw attention to the fact that in the metastable states the liquid and the crystal may have equal volumes (it is precisely this case that is shown in the figure), which is realized under the condition

$$\frac{(\alpha')^2}{2\gamma} < \left|\frac{dv_0}{dP}\right|. \tag{12}$$

The condition is most probably fulfilled for He^3, since otherwise the compressibility of the crystal would be more than five times greater than the compressibility of the liquid (see (10)), which can hardly happen (there are no data on the compressibility for $T \to 0$).

As to the lattice constant, this quantity somehow varies with the pressure (see (2)). The volume, generally speaking, varies according to another law, (11). For the number of particles to be equal to the number of lattice sites, it is necessary that

$$v\kappa^3 = \text{const}, \tag{13}$$

where the constant is determined by the type of lattice, in the present case a bcc lattice. This condition can be depicted by expanding v_0 and k_0 about P_0 and separating out different types of terms: not depending on pressure, proportional to $(P - P_0)$, and proportional to $[(\beta/2\gamma)^2 - \alpha/\gamma]^{1/2}$. As a result, we obtain, in particular, that

$$(v_0 k_0^3)_{P=P_0} = \text{const} \tag{14}$$

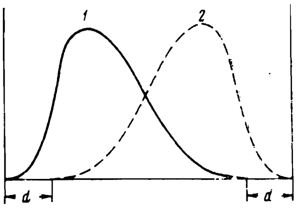

FIG. 2.

(the same constant). Such a limitation arises for the liquid on the spinodal from the requirement that the number of lattice sites be equal to the number of particles. Apparently, this condition is not fulfilled, since the liquid is not connected in a continuous fashion with the bcc structure (the branch 4c is not stable). Therefore, the number of particles is most likely not equal to the number of lattice sites.

4. DISCUSSION

The condition of applicability of the theory, based on an expansion of the type (3), is $x \ll 1$, i.e., $\beta/\gamma \ll 1$. We do not see how this small parameter can be related to some parameter of the Fermi liquid.

The Fermi system under consideration is a two-component system (because of spin). Into the expansion (1) enters only the total density, which implies the neglect at $T=0$ of the exchange energy in the solid state. Such is the accuracy of this expansion.

Let us explain why the proposed description is more suitable for He^3 than for He^4. First, the decrease in mass leads to a decrease in the localization of the particles in the crystal. Second, the type of statistics plays an important role. As has been shown by Nosanow *et al.*,[7] a system of Bose particles with the mass of He^3 and with the same interaction will undergo the transition at a pressure higher by a factor of two than the pressure at which a Fermi system undergoes the transition; this is understandable if we take into account the fact that the crystals in the two cases will be identical (because of the weakness of the exchange), i, e., the curve *b* in Fig. 1 is the same for Fermi and Bose systems, while the horizontal straight line, corresponding to the equilibrium of the phases, for Bose particles will lie higher with respect to pressure than for a Fermi system. Thus, the transition in a Fermi system occurs nearer to the point of absolute instability ot the crystal, i.e., such a description is more probable.

It is well known that the exchange energy in He^3 is very small. In this connection, there arises the question: Is a weak exchange compatible with a large overlap of the distributions of the neighboring atoms ($x \ll 1$)? Usually, weak exchange effects are associated with small overlaps; thus, the variational approach[1] yields quite a good localization of the particles at the lattice sites, by which the weakness of the exchange effects in He^3 is explained. However, there is not always a connection between overlap and exchange. Let us cite an example in which the exchange interaction is exactly equal to zero, but there is overlap.

Let us consider two one-dimensional hard "spheres" located in a potential well. In Fig. 2 we schematically show the distributions of the particles 1 and 2; *d* is the "diameter" of the hard sphere. These distributions overlap, but the exchange interaction is equal to zero. Indeed, let the wave function of some state be $\psi(1, 2)$, which corresponds to the case when the particle 1 is located to the left of the particle 2 (we can say this, since, by assumption, the particles cannot infiltrate through each other—they are "hard"). To the same energy corresponds the wave function with interchanged particles $\psi(2,1)$. These functions are linearly independent, since they are orthogonal; therefore, we can construct from them a symmetric and an antisymmetric combination $\psi(1, 2) \pm \psi(2, 1)$, which thus correspond to one and the same energy. This means that the exchange interaction is equal to zero.

If the spheres are not absolutely hard, i.e., if there is a small penetration probability, then an exchange interaction appears; clearly, the splitting of the level $\sim \hbar/\tau$, where τ is the time during which the particles will change places.

It is evident from this example that a strong overlap of particle distributions can be compatible with a small exchange energy. Therefore, the assumption of a strong overlap in solid He^3 is not devoid of sense.

5. THE EXPERIMENT

The most suitable experiment for the direct verification of the theory is a scattering experiment. For example, let us consider the elastic scattering of neutrons by the crystal. The matrix element of such a process $\sim M_{\mathbf{k}} x_{\mathbf{k}}$, where **k** is the transferred momentum and $M_{\mathbf{k}}$ is the matrix element for scattering by an individual atom. We assume that $T=0$, so that the averaging is performed over the ground state of the crystal (elastic scattering). Thus, only 12 reflections can appear in the diffraction pattern (conforming to the number of nonzero $x_{\mathbf{k}}$). In the model the rest formally do not appear at all; in reality, of course, they may appear, but their intensity will be low.

Let us now compare this result with the result that can be expected from the picture obtained by the variational method.[1] In the latter case the particle distribution is far from being a constant, since the particles are quite well localized at the lattice sites and the overlap of the distributions of the neighboring atoms is small. Therefore, the structure factor, which is proportional to the Fourier transform of the density ($x_{\mathbf{k}}$), will here decrease considerably more slowly with increasing *k*, i.e., besides the 12 principal reflections there should be others of roughly the same intensity. Thus, a neutron-scattering experiment can answer e the question precisely which picture is obtained in He^3.

Usually, x rays are used in the study of He^3 (because of the capture of neutrons by nuclei). For x rays, the electron density, which has a smoothed-out form in comparison with the density of the nuclei, is important. Therefore, here the necessary information will not be obtained, although in certain cases it may turn out to be sufficient.

The theory gives the same pressure dependence for some quantities, and this can also be the object of an experimental verification. To wit, the intensity of the neutron reflections and the difference between the crystal and liquid volumes $(v - v_0)$, (11), are proportional to the quantity x^2, the pressure dependence of which is given by the formula (4b).

It would be interesting to verify whether the relation (8) is fulfilled, for which purpose it is necessary to know the pressures up to which the liquid (P_0) and the crystal (P_2) exist in the metastable states (P_1 is known). Furthermore, knowledge of one of these pressures will allow the determination of the parameters of the theory α, β, and γ (for example, with the aid of (5), (9), and (10)), and elucidate the question whether the ratio β/γ is indeed small.

Let us emphasize that the experimentally verifiable theoretical results discussed in this section are consequences of a model in which there is a small parameter $x \ll 1$. On the other hand, the results that are of a qualitative nature (the formation of a bcc lattice, the increase of the compressibility in the transition to the crystal state, as well as the absence of a correspondence between the numbers of sites and particles) are, generally speaking, valid right up to $x \sim 1$.

Notice that the proximity of the spinodal and the binodal can also affect the superfluid properties of liquid He^3; to wit, besides the Anderson-Brinkman mechanism[8] there may be another mechanism connected with the short-wave fluctuations in the density. Then in the supercooled liquid the transition to the superfluid state at pressures higher than some value will be a first-order transition, since the magnitude of a correction of the Anderson-Brinkman type for short-wave density fluctuations increases without restriction as the spinodal is approached.

In conclusion, I thank V. L. Pokrovskiĭ for a discussion of the main ideas and the preliminary results and for a number of valuable comments, the S. K. Savins for interest in the work and encouragement, as well as L. P. Mezhov-Deglin, A. V. Chaplik, and M. V. Éntin for a discussion.

Note added in proof (*January* 9, 1976). In an experiment by D. S. Greywall (Phys. Rev. **B11**, 1070 (1975)) x rays were used for the orientation of He^3 crystals. Two types of reflections were observed: in the (110) direction and in the (200) direction, and the intensity of the reflections of the first type was considerably higher than that of the reflections of the second type. This latter circumstance supports the supposition that the parameter x is small.

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Translated by A.K. Agyei