PHYSICAL REVIEW
LETTERS

VOLUME 10 15 MAY 1963 NUMBER 10

PHENOMENA ALONG THE hcp-bcc TRANSITION LINE OF He^3 AND He^4†

A. F. Schuch, W. C. Overton, Jr., and R. Brout*
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico
(Received 4 April 1963)

Recently it has become known that in both solid He^3 and He^4 there is a phase transition from the hexagonal-close-packed to the body-centered-cubic structure.[1-4] As illustrated in Fig. 1 the solid-solid phase line for He^3 joins the melting curve at 3.148°K and at 135.9 atm. In He^4 there are two such triple points, one at 1.76°K and 29.67 atm and the other at 1.437°K and 25.94 atm. Quantum mechanical calculations[5-7] have not yet proved able to give a satisfactory explanation of the existence of the bcc phases, although they do indicate that the zero-point energy E_z is largely quantumlike in nature and that there are strong anharmonic effects. Recently available experimental data[8,9] have provided the basis for our present empirical study of the phenomena along the hcp-bcc transition line and the purpose of this Letter is to report the rather remarkable findings of this study. It is believed that the tentative interpretation given below will throw new light on this phase transition.

We shall be concerned mainly with the behavior of the Debye θ's (θ_C along the crystal phase transition line and θ_M along the melting point curve).

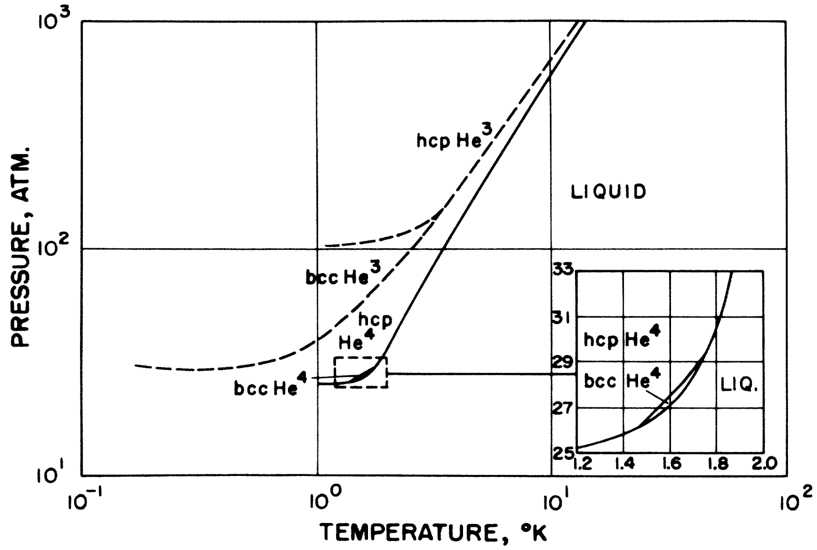

FIG. 1. Phase diagram of helium.

We find that to within about three percent error both He^3 and He^4 obey the relations

$$M\theta_C R^2 = \text{constant}, \tag{1}$$

where M is the mass and R is the nearest-neighbor distance.[10] In the solution of this equation the values of R were obtained from the PVT data of Grilly and Mills[1] and from x-ray diffraction studies.[3,4] The θ_C's were computed from the experimental data of Heltemes and Swenson (HS)[8] in the manner outlined below. In the region of present interest they observed that for both He^3 and He^4 near the melting curve the Grüneisen law $\gamma = d(\ln\theta_M)/d(\ln V)$ is obeyed with $\gamma = -2.24$. Franck[9] has recently measured in hcp He^3 the variation of θ with temperature at a number of molar volumes. Thus the procedure in the case of He^3 for obtaining θ_C(bcc) at the phase line was to take the HS value of θ_M at the selected molar volume and then from Franck's data, assumed valid for bcc as well as hcp, applying a correction to it for the temperature change in going along an isochore from the melting curve to the phase line. With θ_C(hcp) the method was similar but the temperature change was measured from the projection of a metastable hcp-liquid line whose position was located from PVT calculations.[1] In the pressure-temperature range investigated it was observed that the metastable curve lies nearly along the existing bcc-melting line. In He^4 the solid-solid phase line always lies within 0.04°K of the melting line, and so no temperature corrections to θ_M are necessary to within the error of our analysis. Furthermore, no specific-heat data are as yet available for the bcc form of He^4 which prevented any calculations being made on this solid. For this reason our conclusions about He^4 are tentative pending more accurate experimental data. In Table I we give a few values of $M\theta_C R^2$ together with R and θ_C at various temperatures. When comparing the hexagonal phases one also notes how well within experimental error $M\theta_C R^2(\text{He}^3) = M\theta_C R^2(\text{He}^4)$.

It turns out that a simple consistent interpretation is available for these facts. For simplicity we will limit ourselves to low temperatures and neglect thermal effects. From the constancy of $M\theta_C R^2$ we see that along the transition line $\theta_C \sim M^{-1}$ rather than $M^{-1/2}$. This is still consistent with the requirement that $\theta_C \sim (K/M)^{1/2}$, where K is the force constant, since K can be a function of M. These observations indicate the presence of strong quantum effects. In fact, it will be seen that it is the zero-point pressure which is the principal ingredient in our explanation of the data.

We assume that the energy is well approximated by

$$E(R) = \alpha\hbar^2/2MR^2 + V_{\text{att}}(R) + V_{\text{rep}}(R). \tag{2}$$

The first term in (2) is a measure of the kinetic energy. The α is a constant whose value depends upon the kind of potential well considered. The latter two terms are the attractive and repulsive parts of the potential energy. Because we have at hand a Van der Waals solid, $V_{\text{att}}(R) \sim R^{-6}$. However, $V_{\text{rep}}(R)$ is a very difficult quantity to come by. Fortunately, we will have no particular need for the exact form. We will comment on the problems of $V_{\text{rep}}(R)$ at a later point.

At low temperatures the equilibrium value of R is determined by $dE/dV = -p$, and the compressibility is determined by d^2E/dR^2. Accordingly, we have

$$\begin{aligned} K &= d^2E/dR^2 \\ &= 3\alpha\hbar^2/MR^4 + d^2V_{\text{att}}/dR^2 + d^2V_{\text{rep}}/dR^2. \end{aligned} \tag{3}$$

Furthermore, from $\theta_C^{\,2} \sim K/M$ we see that the

Table I. Experimental properties of the bcc phase of He^3 and of the hcp phases of He^3 and He^4 adjacent to the hcp-bcc transition line. Nearest-neighbor distance R is in angstrom units, and the quantity $M\theta R^2$ is in units of 10^{-37} g-deg-cm^2.

t	bcc He^3			hcp He^3			hcp He^4			
T°K	R	θ°K	$M\theta R^2$	R	θ°K	$M\theta R^2$	T°K	R	θ°K	$M\theta R^2$
3.148	3.444	30.8	1.83	3.535	37.8	2.37	1.76	3.649	26.1	2.31
2.80	3.460	30.3	1.81	3.552	37.0	2.34	1.68	3.652	26.0	2.30
2.50	3.471	30.0	1.81	3.564	36.6	2.33	1.60	3.656	25.8	2.29
2.20	3.480	30.0	1.82	3.574	36.4	2.33	1.52	3.659	25.7	2.28
1.90	3.487	30.1	1.83	3.582	36.4	2.34	1.437	3.663	25.5	2.27

crystal phase transition which is given by

$$M^2\theta_C{}^2R^4 = MKR^4 = \text{constant} \tag{4}$$

implies from (3) that

$$d^2V_{\text{att}}/dR^2 + d^2V_{\text{rep}}/dR^2 = 0. \tag{5}$$

In other words, the solid phase transition occurs at the point of inflection of the potential energy versus R curve. In the bcc phase the force constant is governed predominantly by the zero-point repulsion plus some attraction, whereas in the hcp phase it is governed mostly by the zero-point repulsion. It thus appears that in going from the hcp to the bcc phase the crystal undergoes a transition to a more open structure in order to give the zero-point motion more play.

If for $V(R)$ we use the lattice sums of the usual Lennard-Jones 6-12 potential[11] for He, we find that the turnover point is at $R = 3.2$ Å rather than at the observed $R = 3.6$ Å. We would be inclined to attribute this discrepancy more to the repulsive part of the potential than to the above interpretation. Furthermore, the large zero-point motions certainly will affect the expectation value of the potential. To assume that the latter potential energy follows the interparticle potential is certainly subject to some error. What to us is the most convincing point in the interpretation is the observation that along the transition line $\theta_C \sim 1/M$.

The observation[8] that the Grüneisen constant γ is -2.24 implies here that $\theta \sim 1/R^{6.7}$, and hence a force constant going like $1/R^{13.5}$. This is consistent with

$$K_{\text{melting}} = d^2V_{\text{rep}}/dR^2, \tag{6}$$

where apparently here the $(1/R^{12})$ law holds quite well. It was also noted that[8]

$$\theta_M(\text{He}^3)/\theta_M(\text{He}^4) \sim (4/3)^{1/2}, \tag{7}$$

which lends further support to our interpretation.

Thus the melting curve is characterized by

$$3\alpha\hbar^2/MR^4 + d^2V_{\text{att}}/dR^2 = 0. \tag{8}$$

Since $V_{\text{att}} \sim 1/R^6$, this, in turn, implies that on the melting curve in the solid phase, we have

$$\text{zero-point energy/attractive energy} = \text{constant}. \tag{9}$$

This is consistent with London's picture of liquid helium.[12] What is surprising is that the constant in (9) is just such as to insure (8).

[†] Work performed under the auspices of the U. S. Atomic Energy Commission.

[*] Consultant to the Los Alamos Scientific Laboratory; permanent address: Faculte des Sciences, Universite Libre de Bruxelle, Bruxelles, Belgium.

[1] E. R. Grilly and R. L. Mills, Ann. Phys. (N.Y.) 8, 1 (1959); 18, 250 (1962).

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

[3] A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. 110, 775 (1958).

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

[5] N. Bernardes, Phys. Rev. 120, 1927 (1960).

[6] N. Bernardes and D. F. Brewer, Rev. Mod. Phys. 34, 190 (1962).

[7] E. M. Saunders, Phys. Rev. 126, 1724 (1962).

[8] E. C. Heltemes and C. A. Swenson, Phys. Rev. Letters 7, 363 (1961); Phys. Rev. 128, 1512 (1962).

[9] J. P. Franck (private communication). We are indebted to him for information of the θ-T isochores prior to its publication.

[10] We have also observed that along the transition lines, $\langle\mu^2\rangle/R^2$ is a constant. $\langle\mu^2\rangle$ is the mean square vibration amplitude computed on the basis of a Debye model [C. Domb and J. S. Dugdale, Progress in Low-Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 338].

[11] See J. de Boer, Progress in Low-Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 2.

[12] F. London, Superfluids (John Wiley & Sons, Inc., New York, 1954), Vol. II.