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POMERANCHUK EFFECT AND DIAGRAM OF STATE FOR He^3-He^4 SOLUTIONS

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The influence of the Pomeranchuk effect upon equilibrium between the liquid and solid phases in He^3-He^4 solutions is investigated thermodynamically.

THE equilibrium diagram for the liquid and solid phases in He^3-He^4 solutions should show interesting features associated with the Pomeranchuk effect in He^3. It was shown by Pomeranchuk that the melting curve for He^3 should have a minimum in the P-T diagram, and that below the minimum point the heat of fusion should be negative.[1,2] This effect has been observed experimentally by Walters and Fairbank.[3] It follows from the experimental data on the entropy of He^3 that the minimum is located at $P_0 \approx 30$ atmos and $T_0 \approx 0.5°K$.

In the present paper we investigate the influence of the Pomeranchuk effect upon liquid-solid phase equilibrium in He^3-He^4 solutions is investigated.

1. WEAK SOLUTIONS OF He^4 IN He^3

Let us consider phase equilibrium in weak solutions of He^4 in He^3. The conditions for equilibrium between the liquid and solid phases can, as is well-known,[4] be written in the form:

$$\mu_0'(P, T) - x'kT = \mu_0''(P, T) - x''kT, \qquad (1)$$

$$kT\ln x' + \psi'(P, T) = kT\ln x'' + \psi''(P, T), \qquad (1')$$

where x′ and x″ are the He^4 concentrations in the liquid and solid phases, respectively, $\mu_0'(P, T)$ and $\mu_0''(P, T)$ are the chemical potentials for the two phases in pure He^3, and $\psi'(P, T)$ and $\psi''(P, T)$ are functions characterizing the He^4 atoms in the solutions.

In Eq. (1) let us expand $\mu_0'(P, T)$ and $\mu_0''(P, T)$ in the neighborhood of the minimum, in powers of $P - P_0 = \Delta P$ and $T - T_0 = \Delta T$. Since at the minimum point both the chemical potentials and their first derivatives with respect to temperature are equal, the zero-order terms in (1) and the terms linear in ΔT will fall out. We obtain, therefore, for the difference between the concentrations in the two phases:

$$x' - x'' = \Delta x = \frac{v' - v''}{kT_0}\Delta P - \frac{c' - c''}{2kT_0^2}(\Delta T)^2, \qquad (2)$$

where c′ and c″ are the specific heats, respectively, of liquid and solid He^3, and v′ and v″ are the volumes (per particle) for pure He^3.

From (1′) we see that the ratio of the concentrations in the two phases depends only upon P and T, and therefore that in the region near x = 0 this ratio may be regarded as a constant quantity

$$\varkappa = \frac{x'}{x''} = \exp\left\{\frac{\psi'(P_0, T_0) - \psi''(P_0, T_0)}{kT_0}\right\}. \qquad (3)$$

From (2) and (3) we obtain for the concentrations in the liquid and solid phases

$$x' = \frac{\varkappa}{\varkappa - 1}\Delta x, \qquad x'' = \frac{1}{\varkappa - 1}\Delta x. \qquad (4)$$

The pressure P_0 corresponding to the minimum in the P − T melting curve for He^3 is greater than the minimum pressure at which He^4 solidifies (P ~ 25 atmos). It is of interest therefore to consider three possible cases.

1. ΔP = 0; then

$$x' = \frac{\varkappa}{\varkappa - 1}\frac{c'' - c'}{2kT_0^2}(\Delta T)^2, \qquad x'' = \frac{1}{\varkappa - 1}\frac{c'' - c'}{2kT_0^2}(\Delta T)^2. \qquad (5)$$

Thus, for $P = P_0$ the equilibrium curves in the limit of small concentrations are parabolas tangent to one another at the point $T = T_0$ (Fig. 1).

2. ΔP < 0; it is then clear from (2) that Δx < 0 everywhere. The equilibrium curves in the small concentration region are parabolas, one lying within the other (Fig. 2). In this case the two curves do not intersect at any point and do not touch. The vertices of the parabolas are situated for $T = T_0$ at

$$x' = \frac{\varkappa}{\varkappa - 1}\frac{v' - v''}{kT_0}\Delta P, \qquad x'' = \frac{1}{\varkappa - 1}\frac{v' - v''}{kT_0}\Delta P,$$

The concentration difference is

$$\Delta x = \frac{v' - v''}{kT_0}\Delta P$$

(for ΔP ~ 1 atmos, $\Delta x \sim 10^{-2}$).

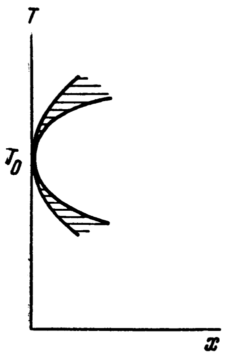

FIG. 1

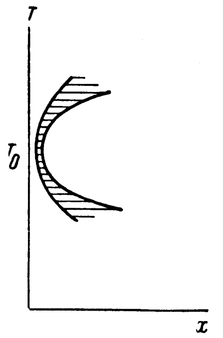

FIG. 2

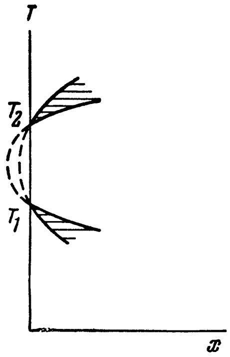

FIG. 3

3. If $\Delta P > 0$, the curves are parabolas intersecting at the points T_1 and T_2, which in the P-T diagram for pure He^3 correspond to the two melting temperatures for the pressure P (Fig. 3). From (2) we can readily obtain

$$T_{1,2} = T_0 \mp \left[\frac{2T_0(v' - v'')}{c' - c''}\Delta P\right]^{1/2}. \tag{6}$$

The concentration difference for a given T may be calculated from Eq. (2). It is more convenient, however, to employ the formula which is obtained if we expand in (1) the chemical potentials about the points (P, T_1) and (P, T_2). At T_1 and T_2 the first derivatives of the chemical potentials in the two phases are unequal, and the expansion begins with the term linear in ΔT. For small ΔP, where $T_2 - T_1 \ll T_0$, it is necessary to retain in the expansion the second-order term in ΔT as well, since the coefficient of the linear term is very small. We thus obtain for the concentration difference for $T < T_1$:

$$\Delta x = -\frac{Q_1}{kT_1^2}(T - T_1) + \frac{c''(T_1) - c'(T_1)}{2kT_1^2}(T - T_1)^2, \tag{7}$$

where Q_1 is the heat of fusion of pure He^3 at $T = T_1$. An analogous expression is obtained for $T > T_2$.

In the general case, for ΔP not small and $T_2 - T_1 \sim T_0$, we may confine ourselves to the term linear in ΔT. In this case the equilibrium curves, in the limit of small concentrations, are straight lines intersecting at T_1 and T_2. For the concentrations in the liquid and solid phases we obtain

$$x_1' = -\frac{\varkappa_1}{\varkappa_1 - 1}\frac{Q_1}{kT_1^2}(T - T_1), \quad x_1'' = -\frac{1}{\varkappa_1 - 1}\frac{Q}{kT_1^2}(T - T_1), \tag{8}$$

where κ_1 is determined from Eq. (3) at the point (P, T_1). Analogous equations are obtained for the curves intersecting at T_2.

As the pressure is further increased $T_1 \rightarrow 0$, and for $P \sim 40$ to 45 atmos the lower portion of the diagram vanishes completely.

2. "IMPURITY GAS" EXCITATION MODEL

Let us consider the energy spectrum for liquid He^3 containing a small number of He^4 atoms. The interaction of the He^4 atoms with the He^3 atoms leads to the appearance within the mixture of additional energy levels. Thus in addition to the fundamental He^3 energy spectrum there arises in the mixture a second branch due to the dissolved impurity atoms. Two forms of energy spectrum for the impurity particles are logically possible — in one case the energy minimum corresponds to a momentum equal to zero, in the other case, to nonzero momentum:

$$\varepsilon = \varepsilon_0 + p^2/2\mu, \tag{9}$$

$$\varepsilon = \varepsilon_0 + (p - p_0)^2/2\mu. \tag{9'}$$

The energy distribution for the impurity atoms is determined by Boltzmann statistics down to temperatures for which either the phenomenon of quantum degeneracy in the "impurity gas" or the interaction of the impurity particles with one another becomes significant. The conditions under which the deviation from classical statistics sets in have been established by Pomeranchuk.[5] For the case of a spectrum of the type (9), the degeneracy begins before it becomes necessary to consider the interaction, and the condition for applicability of classical statistics is $x \ll (T/T_d)^{3/2}$. The degeneracy temperature for a Bose gas:

$$T_B = 3.31\,(\hbar^2/\mu k)\,(\rho_3 x/m_3)^{2/3},$$

where ρ_3 is the density of He^3, m_3 is the mass of the He^3 atom, μ is the effective mass of the impurity particles, and x is the concentration of He^4 in the mixture.

For the case of a spectrum of the type (9′), however, the limit of applicability for classical statistics is determined by the condition $x \ll (kT/U)$, where U is an energy characterizing the interaction of the He^4 atoms, on the order of several degrees.

Applying the general formulas for the free energies of dilute solutions and of an ideal gas, we obtain,[5,2] respectively:

$$F' = F'_3 - xkT \ln\left[\frac{em_3}{\rho_3 x}\left(\frac{\mu kT}{2\pi\hbar^2}\right)^{3/2}\right] + x\varepsilon_0, \qquad (10)$$

$$F' = F'_3 - xkT \ln\left[\frac{em_3}{\rho_3 x}\frac{p_0^2}{\hbar^3}\sqrt{\frac{\mu kT}{2\pi^3}}\right] + x\varepsilon_0, \qquad (10')$$

$$F'_3 = kT\left[-\frac{2I_{1/2}}{I_{-1/2}} + \ln A\right],$$

$$I_\alpha = \int_0^\infty \frac{x^\alpha}{e^x/A+1}\,dx, \quad A = e^{\nu'\,kT}.$$

From this we obtain for the entropy:[6]

$$s' = s'_3 + xk \ln\left[(m_3/\rho_3 x)(\mu k/2\pi\hbar^2)^{3/2} + 5/2\right]. \qquad (11)$$

$$s' = s'_3 + xk \ln\left[(m_3 p_0^2/\rho_3 x\hbar^3)(\mu kT/2\pi^3)^{1/2} + 3/2\right], \qquad (11')$$

$$s'_3 = k\left[3I_{1/2}/I_{-1/2} - \ln A\right].$$

For a rough evaluation let us set μ in the spectrum (9) equal to the mass of He^4, (11) then yields

$$s' = s'_3 + xk \ln(1.2T^{3/2}/x). \qquad (12)$$

In the case of the spectrum (9′), however, let us set for estimating purposes P_0 and μ equal to their values for rotons; (11′) then gives

$$s' = s'_3 + xk \ln(20\,T^{1/2}/x). \qquad (12')$$

From (12) and (12′) it is evident that the effect of impurities upon the entropy is more pronounced for the case $p_0 \neq 0$. The influence of the impurities upon the entropy of liquid He^3, however, (in contrast to the situation in liquid He^4) is negligibly small in the temperature region in which the impurities may be regarded as subject to classical statistics. This is explained by the fact that He^3, being a Fermi liquid, possess a very large entropy. The effect of the impurities upon the specific heat of He^3 is even weaker.

We turn now to consideration of liquid-solid phase equilibrium within the framework of the given model.

If one neglects the oscillatory term in the free energy (since $T \ll \Theta$), it is possible to write for the free energy of a weak solid solution of He^4 in He^3:

$$F'' = F''_3 + x\chi_4 + kT\ln(x/e), \qquad (13)$$

where χ_4 is the zero-point energy of a single dissolved He^4 atom.

From the condition of equality of the chemical potentials of the dissolved particles, we obtain for the ratio of the concentrations in the two phases, using (10), (10′), and (13):

$$\varkappa = \frac{x'}{x''} = \frac{m_3}{\rho_3}\left(\frac{\mu kT}{2\pi\hbar^2}\right)^{3/2} e^{q/kT}, \qquad (14)$$

$$\varkappa = \frac{x'}{x''} = \frac{m_3}{\rho_3}\frac{p_0^2}{\hbar^3}\left(\frac{\mu kT}{2\pi^3}\right)^{1/2} e^{q/kT}, \qquad (14')$$

where

$$q = \chi_4 - \varepsilon_0 + \int_0^P \{v''_4(P,\ T) - v'_4(P,\ T)\}\,dP. \qquad (15)$$

If μ is set equal to the mass of the He^4 atom, the factor preceding the exponential in (14) becomes $\sim 0.1\,T^{3/2}$. For $P = 30$ atmos we obtain from the experimental data[7] on pure He^4, $q/k \sim -0.1°$. For $T = 0.5°$, then, the concentration ratio $\kappa = x'/x'' \sim 1/30$. Thus for a spectrum of the type (9) with $T < T_0$ we will always have $x' < (T/T_d)^{3/2}$. The "impurity gas" is therefore subject to Boltzmann statistics down to $T = 0$, and it can readily be shown that $x' \to 0$ as $T \to 0$. In this case the liquidus curve will have a point of inflection, and will not reach the λ-transition curve. Such a conclusion, however, is not completely certain, since in the solution q/k may differ considerably from its value for pure He^4.

For the case of a spectrum of the type (9′), if we take p_0 and μ to be of the same order as for rotons, we have $x'/x'' \sim 1$ at $T \approx 0.5°$ and $P \approx 30$ atmos. Thus in this case the concentrations in the two phases increase rapidly with increasing $|\Delta T|$, and even for $\Delta T \gtrsim 0.1°K$ the model under consideration becomes unsuitable.

3. SOLUTIONS OF HIGH CONCENTRATION

At temperatures below 0.83°K liquid He^3-He^4 mixtures separate into two phases of differing He^3 concentration. This phenomenon must affect the form of the liquid-solid phase equilibrium diagram for He^3-He^4 solutions. In view of the fact that the solution separation has been experimentally investigated under the saturated vapor pressure of the solution,[9,10] while we are interested in pressures ~ 30 atmos, it is necessary to consider the influence of pressure upon this effect.

At the critical point the following conditions are fulfilled:[4]

$$\begin{aligned}\partial\mu'_3(\mathrm{T_c}(P), x', P)/\partial x' &= 0,\\ \partial^2\mu'_3(\mathrm{T_c}(P), x', P)/\partial x'^2 &= 0.\end{aligned} \qquad (16)$$

From this one readily obtains

$$\frac{d\mathrm{T_c}}{dP} = \frac{\partial v_3}{\partial x'}\Big/\frac{\partial s_3}{\partial x'}, \qquad (17)$$

where s_3 and v_3 are the entropy and volume associated with a single He^3 atom in the solution.

From the existing experimental data on the concentration dependence of the solution density[11] we

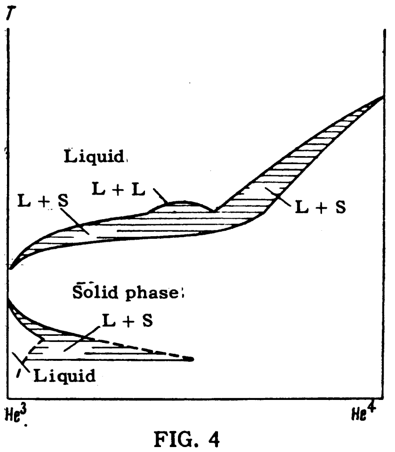

FIG. 4

may estimate that $dT_c/dp \sim 0.01 - 0.1$ deg/atmos.

It is not difficult also to evaluate the derivative $(dT/dP)_{x'}$ at any point on the separation diagram. We have:

$$(dT/dP)_{x'} = -(\partial T/\partial x')(\partial x'/\partial P). \qquad (18)$$

The derivative of the concentration with respect to pressure can readily be computed:

$$\left(\frac{dx'}{dP}\right) = -\left\{\frac{\partial v'(x_1')}{\partial x'} - \frac{v'(x_2') - v'(x_1')}{x_2' - x_1'}\right\} \Big/ \left(\frac{\partial^2 \varphi'}{\partial x'^2}\right)_{x_1'}, \qquad (19)$$

where x_2' and x_1' are the He^3 concentrations at the two separation points for a given temperature and $v'(x')$ is the volume per particle in a solution of concentration x'.

Using experimental data on the concentration dependence of the solution density, the value of $\partial\varphi/\partial x'^2$ calculated from the data on the concentration dependence of the saturated vapor pressure,[12] and the value of dT/dx' computed from the separation diagram, we obtain the estimate

$$(dT/dP)_{x'=0.07} \sim 10^{-2} \text{ deg/atmos}$$

As we observe, the separation of the solutions depends strongly upon pressure. For this reason it is impossible to state definitely whether or not limited solubility in the liquid phase will be observed for the pressures in which we are interested, on the order of 30 atmos. If the solubility remains limited at such high pressures, then a triple point will be observed on the upper part of the liquid-solid phase equilibrium diagram. The approximate form of such a diagram, for $P > P_0$, is shown in Fig. 4.

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