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THEORY OF PHASE SEPARATION IN SOLID ^{3}He-^{4}He MIXTURES*

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It was found by Edwards, McWilliams, and Daunt[1] (EMD) that upon cooling, a solution of solid ^{3}He and ^{4}He separates into a ^{3}He-rich phase and a ^{4}He-rich phase. This phenomenon was identified by a discontinuity in the specific heat at the phase-separation temperature. In this article we describe a theoretical analysis of the phase separation.[2]

The thermodynamic treatment of phase separation[3] is based on the excess Gibbs energy per mole defined as a function of the ^{3}He concentration x, temperature T, and pressure P as

$$g^E(x,T,P) = g(x,T,P) - xg_3^{(0)} - (1-x)g_4^{(0)} + Ts_m(x), \tag{1}$$

where $g_3^{(0)}$ and $g_4^{(0)}$ are the Gibbs energies per mole for pure ^{3}He and pure ^{4}He, respectively; that is, $g_3^{(0)} = g(1,T,P)$ and $g_4^{(0)} = g(0,T,P)$. The entropy of mixing per mole is

$$s_m = -R[x\ln x + (1-x)\ln(1-x)]. \tag{2}$$

A "regular" solution[3] has

$$g^E = x(1-x)\alpha(P) \tag{3}$$

with α independent of temperature. Such an excess function gives rise to a critical temperature

$$T_c = \alpha/2R \tag{4}$$

with a symmetrical phase-separation curve. In EMD it is shown that a ^{3}He-^{4}He mixture apparently forms a regular solution. A simple analysis, valid for classical static lattice models, can be given[4] to show how such a g^E can come about. Our model of a solid helium solution will show that it is expected to be nearly regular, however, for far different reasons than the classical model.

We base our calculations on a generalization of the Nosanow theory[5] of the pure phases of solid helium. Thus, for the ground state of the mixtures we choose a trial wave function of the form

$$\psi_0 = \Pi_i \varphi_3(i) \Pi_j \varphi_4(j) \times \prod_{k<l} f_{33}(kl) \prod_{m<n} f_{44}(mn) \prod_{p,q} f_{34}(pq). \tag{5}$$

The first product is over all ^{3}He atoms in the lattice with

$$\varphi_3(i) = \exp\{-\tfrac{1}{2}A_3(\vec{r}_i - \vec{R}_i)^2\}; \tag{6}$$

that is, we localize ^{3}He atoms about their lattice sites with single-particle Gaussians whose width is determined by A_3. The second product is over all ^{4}He atoms with a relation analogous to (6) holding. The functions $f_{ab}(kl)$ account for the short-range correlation effects which are due to the large zero-point motion of the atoms and the repulsive core of the potential.[5] We choose the Nosanow analytic form for $f(r)$,

$$f_{ab}(r) = \exp\{-K_{ab}[(\sigma/r)^{12} - (\sigma/r)^6]\}, \tag{7}$$

where $\sigma = 2.56$ Å, and where there are three K parameters: one for ^{3}He-^{3}He correlation functions, one for that of ^{4}He-^{4}He, and one for the ^{3}He-^{4}He functions. Thus the last three products in (5) are over the three kinds of pairs in the solid. To reduce the number of variational parameters we do not minimize the energy with respect to the K_{ab}'s but set K_{33} equal to the value of the K parameter of pure ^{3}He; similarly for K_{44}; K_{34} is taken as an average of K_{33} and K_{44}. Thus we have only two variational parameters, A_3 and A_4, for each volume and x value. We have checked the assumption concerning the K_{ab}'s by minimizing with respect to all five variables in one case with negligible further lowering of the energy.

As in the pure-phase theory, the energy is evaluated by a cluster expansion truncated after the two-body terms. There is a one-body energy term, associated with the $\varphi^{(a)}$, given by

$$N_a t_a = x_a N \tfrac{3}{4} A_a \hbar^2/m_a, \tag{8}$$

where N is the total number of particles, and x_a, N_a, and m_a are the concentration, number, and mass of the a-type atoms, respectively. Further, the two-body term associated with the interactions of (a, b) pairs is given by

$$\begin{aligned} & x_a x_b N w_{ab} \\ & \quad = N x_a \sum_{R_{ij}} n_b(R_{ij}) \\ & \qquad \times \frac{\int [\varphi_a(i)\varphi_b(j)f_{ab}(ij)]^2 V_{ab}(ij)\,d\vec{r}_i\,d\vec{r}_j}{\int [\varphi_a(i)\varphi_b(j)f_{ab}(ij)]^2\,d\vec{r}_i\,d\vec{r}_j}, \end{aligned} \tag{9}$$

where $V_{ab}(ij) = V(ij) - [\hbar^2/2m_{ab}]\nabla_i^2 \ln f_{ab}(ij)$, $V(ij)$ is the Lennard-Jones potential, m_{ab} is the reduced mass of the (a, b) pair, and $n_b(R_{ij})$ is the number of b-type particles in a shell at distance R_{ij} from a particle taken as origin. [If a and b particles are identical, a factor of $\frac{1}{2}$ should appear in (9).] We assume that ^{3}He and ^{4}He particles are randomly distributed throughout a perfect bcc lattice. Thus there is no short-range order and

$$n_b(R_{ij}) = x_b n(R_{ij}), \tag{10}$$

where $n(R_{ij})$ is the total number of particles in a shell at distance R_{ij}. Because of (10), x_b factors out as shown on the left of Eq. (9). Any effects of lattice distortion are neglected and will be shown to be small later. The effects on the energy of an hcp structure in the ^{4}He-rich phase are certainly small and will be neglected since the hcp and bcc lattices have almost the same energy at a given pressure.[5]

From (8) and (9) we can write the mixture ground-state energy per mole $e(x, P)$ as

$$\begin{aligned} & e(x, P) \\ & \quad = x t_3 + (1-x)t_4 + \tfrac{1}{2}x^2 w_{33} + \tfrac{1}{2}(1-x)^2 w_{44} + x(1-x)w_{34} \\ & \quad = x e_3(x, P) + (1-x)e_4(x, P) + x(1-x)\Delta w(x, P), \end{aligned} \tag{11}$$

where $e_a(x, P) = t_a + \frac{1}{2}w_{aa}$ is the energy per mole of the a atoms, but at the mixture molar volume. Also

$$\Delta w \equiv w_{34} - \tfrac{1}{2}w_{33} - \tfrac{1}{2}w_{44}. \tag{12}$$

By computation with an effective Debye temperature, or by examination of the specific-heat data of EMD, we find that the effect of the excited phonon states on the Gibbs energy of the mixture is negligible, such terms being smaller than the other terms by three orders of magnitude or more. Thus, by using (1) and (11) we can write the excess Gibbs energy as

$$g^E(x, P) = x\Delta e_3 + (1-x)\Delta e_4 + x(1-x)\Delta w + P v^E, \tag{13}$$

where

$$\Delta e_a = e_a(x, P) - e_a^{(0)}(P), \tag{14}$$

$$v^E = v(x, P) - x v_3^{(0)}(P) - (1-x)v_4^{(0)}(P) \tag{15}$$

with $e_a^{(0)}(P)$ and $v_a^{(0)}(P)$, the pure-phase ground-state internal energy and volume per mole for the a system at pressure P. To find the equilibrium value of $v(x, P)$ we minimize the total enthalpy of the system as a function of v at fixed P and x.

In a classical static lattice solid[4] it is sometimes assumed that $v_3^{(0)} = v_4^{(0)} = v$, so $\Delta e_a = 0$ and g^E is of the regular solution form (3) with $\alpha = \Delta w$. However, we find that such a model is quite incorrect for helium. Indeed, Δw is very small and negative. The important feature of solid helium solutions is the large difference between $v_3^{(0)}(P)$ and $v_4^{(0)}(P)$, the former being ~24.4 cm^3/mole and the latter ~20.4 cm^3/mole at $P \cong 36$ atm, this difference being caused by zero-point effects. Thus for, say, small ^{3}He concentrations, $v(x, P) \approx v_4^{(0)}(P)$ and each ^{3}He atom finds itself in a much smaller volume than it would find in a pure ^{3}He phase. Hence $e_3(x, P) > e_3^{(0)}(P)$. Similarly, $e_4(x, P) < e_4^{(0)}(P)$. It is the strong dependence of Δe_3 and Δe_4 on x, through the changes in volume with x at constant pressure, which determines g^E (since Δw and v^E nearly vanish). These results are in agreement with some general considerations given by Prigogine, Bringen, and Bellemans.[2]

In Fig. 1 we plot the theoretical values of $v(x, P)$, Δe_3, and Δe_4 vs x. We see that $v(x, P)$ is very nearly linear, but we can express the small departure from linearity as

$$P v^E \cong -\sigma x(1-x) \tag{16}$$

with $\sigma/P \cong 0.4$ cm^3/mole. Further, in a rough approximation we can fit the energy curves

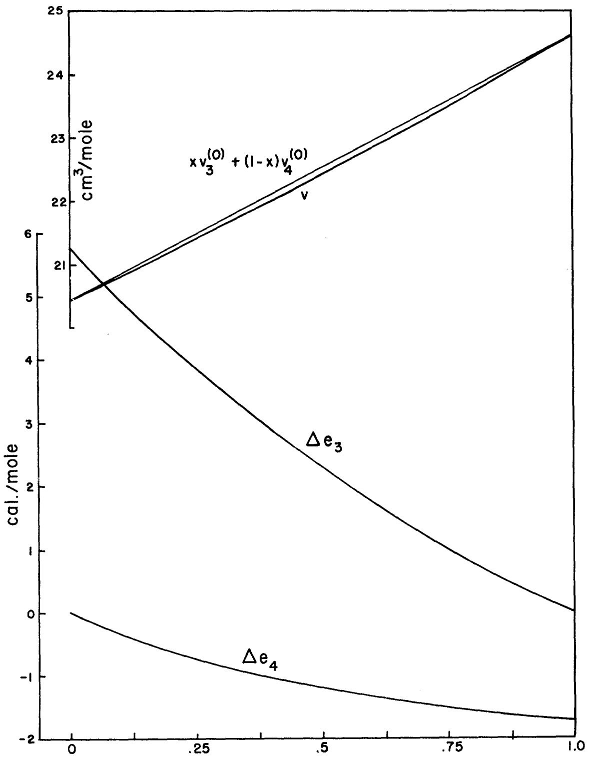

FIG. 1. Upper curve is plot of mixture volume v vs ^{3}He concentration x. Curve Δe_3 is a plot of the difference between ^{3}He energy in the mixture and in the pure state versus x at constant pressure $P = 35.8$ atm. Δe_4 is a similar curve for ^{4}He.

by the convenient polynomial forms

$$\Delta e_3 \approx \beta(1-x) - \gamma x(1-x), \qquad (17)$$

$$\Delta e_4 \approx -\mu x + \nu x^2,$$

with $\beta, \gamma, \mu, \nu > 0$. These forms have not been used in our numerical calculations, but they are convenient here for qualitative arguments. Since v and x are almost linearly related, the slope of a Δe curve is related to the partial pressure; and the second derivative is related to the compressibility. Putting (16)-(18) and the small quantity

$$\Delta w \cong -\lambda, \quad \lambda > 0, \qquad (19)$$

into (13), we get[6]

$$g^E(x, P) = x(1-x)[(\beta - \mu - \lambda - \sigma) - (\gamma - \nu)x]. \qquad (20)$$

For $P = 35.8$ atm (the pressure of the EMD experiment) we find $(\beta - \mu - \lambda - \sigma) \cong 2.0$ cal/mole and $(\gamma - \nu) \cong 0.2$ cal/mole. If in the factor in square brackets in (20) we take $x \approx \frac{1}{2}$, then we have an excess function of the form of Eq. (3) with a critical temperature $T_c = 0.47$°K by Eq. (4).

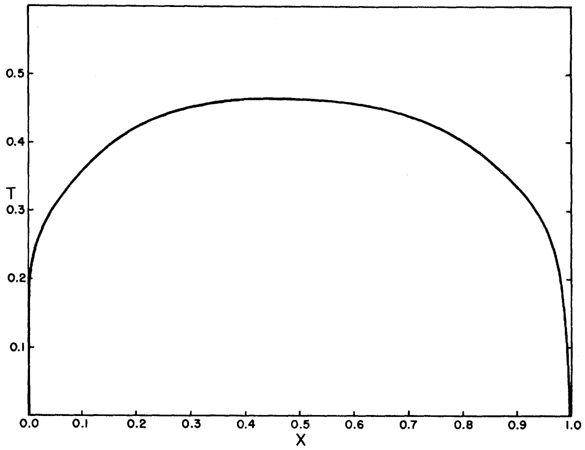

FIG. 2. Theoretical phase-separation curve for $P = 35.8$ atm. Note that the curve is slightly unsymmetrical.

The effect of the x dependence within the square brackets is to make the T-x curve unsymmetrical with the maximum shifted below $x = \frac{1}{2}$. Our more precise numerical treatment bears out the above crude calculations as shown in Fig. 2. Indeed we find that $T_c \cong 0.47$°K with the critical concentration $x_c \cong 0.45$. The experimental curve of EMD is symmetrical with $T_c = 0.38$°K. We feel the agreement of the theory with the experimental value of T_c is reasonable since the variational energies of the pure states with trial functions of the form we have used are too high.[5] It is likely that any improvement in the basic pure-state wave function will provide an equivalent or greater improvement (hence a lowering of T_c) in the mixture calculation. However, the fact that the EMD T-x curve is symmetrical is surprising since the symmetry-destroying term in (2), $(\gamma - \nu)x$, while it may be small, is expected to be present on the rather general grounds that the compressibilities of the two components differ at equal pressures.

We have also computed the T-x curve for a higher pressure. We find for $P = 55$ atm that this curve is still unsymmetrical and that T_c is decreased slightly to $T_c \cong 0.45$°K. Thus the phase separation curve is rather pressure independent. However, the excess volume v^E is smaller by an order of magnitude at this pressure. This decrease of T_c with increasing pressure has been observed by Zimmerman.[7]

If experiments were done at truly constant pressure, we see from the v-x curve of Fig. 1 that upon phase separation, there would be a small increase in volume. In a blocked capillary experiment it is actually the volume which is constant; so there is an increase in pressure upon phase separation. There are at least two groups[8,9] preparing experiments which detect the phase separation by noting this pressure change with sensitive strain gauges. We find that the pressure increase is

$$\Delta P \approx 0.2 \text{ atm}$$

for $x = \frac{1}{2}$, independent of initial pressure.

In order to estimate the effect of lattice distortion on our calculations, we considered a single ^{3}He atom embedded in a ^{4}He bcc lattice. We fixed the A parameter for all ^{4}He atoms beyond the second neighbors at the pure-phase value and minimized the difference between pure ^{4}He energy and the energy with this single impurity, with respect to the ^{3}He A parameter, the distances of the first and second neighbors from the ^{3}He, and the A parameters for the first- and second-neighbor ^{4}He atoms. In all, then, there were five parameters. A single correlation-function parameter, K, was used for all pairs of particles and fixed at the value appropriate to pure ^{4}He. Some numerical tricks made this calculation quite simple and will be described in a future publication. The result is that the near neighbors of the ^{3}He impurity increase their distance from the ^{3}He by 0.4 % of the undistorted nearest-neighbor distance and the energy is lowered by the lattice distortion by $\delta_3 \cong 0.08$ cal/mole of ^{3}He impurities at $P \cong 36$ atm. If we have a small concentration x of ^{3}He impurities, we expect the energy to be lowered by $\sim x\delta_3$. We can calculate a similar quantity for a ^{4}He atom in a bcc ^{3}He lattice at $P \cong 36$ atm. The ^{4}He impurity neighbors decrease their distance from the ^{4}He by ~0.7 %. Here the energy is lowered by the distortion by $\delta_4 \cong 0.24$ cal/mole of ^{4}He impurities. For small ^{4}He concentration, $1-x$, the lowering is $\sim\delta_4(1-x)$. The simplest guess at an interpolation formula for the distortion contribution to g^E for all concentrations is

$$g_{\text{dist}}^{E} \approx -x(1-x)[\delta_3 + (\delta_4 - \delta_3)x]. \qquad (22)$$

Assuming (22), the critical temperature is lowered by this effect by only 0.02°K and the lack of symmetry in the phase separation curve is reinforced.

In summary it seems that solid-helium solutions can be understood on the basis of volume effects. Future experiments may clarify the question of the symmetry of the phase-separation curve, and perhaps give further confirmation to the prediction of a decrease in T_c with increasing pressure.

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