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# PHASE SEPARATION OF METALLIC HYDROGEN-HELIUM ALLOYS[*]

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## Abstract

Calculations are presented for the thermodynamic functions and phase separation boundaries of solid metallic hydrogen-helium alloys at temperatures between 0°K and 19,000°K and at pressures between 15 and 90 megabars. Expressions for the band structure energy of a randomly disordered alloy (including third order in the electron-ion interaction) are derived and evaluated. Short- and long-range order are included by the quasi-chemical method, and lattice dynamics in the virtual crystal harmonic approximation. We conclude that at temperatures below 4,000°K there is complete phase separation of hydrogen-helium alloys, and that a miscibility gap remains at the highest temperatures and pressures considered. The relevance of these results to models of the deep interior of Jupiter is briefly discussed.

# I. INTRODUCTION

Knowledge of the phase diagram of hydrogen-helium alloys at high pressures (4-40 megabars) is of importance in the study of the interior of the giant planets.[1-3] Phase separation of hydrogen and helium during the cooling process may partly account for Jupiter's excess emission of energy.[2] This paper presents a calculation of the thermodynamic functions and phase-separation boundaries of <u>solid</u> hydrogen-helium alloys at pressures between 15 and 90 megabars, and at temperatures between 0°K and 19,000°K. These metallic systems are also of intrinsic interest, since the particles carry point charges, and the bare electron-electron, electron-ion, and ion-ion interactions are given exactly by Coulomb's law.

The calculations reported here supplement earlier results of Stevenson[3] on hydrogen-helium phase separation in the <u>liquid</u> phase. Present estimates of the melting curves of these materials[4] and of the temperature in the deep interior of Jupiter[3] indicate that both hydrogen and helium may well be liquid in the planet's interior, at temperatures far below 19,000°K. However, since the uncertainties in the calculated melting temperatures are quite large[5], a solid-solid phase separation calculation remains of particular interest.

The phenomenon of solid-solid phase separation in alloys is, of course, not limited to the hydrogen-helium system, but is known to occur in many alloys.[6] For example, Li and Mg (both simple metals) form solid alloys at all concentrations except in the range of about 70%-85% Mg, where there exists a miscibility gap. An alloy formed in this concentration range will separate into two phases of different concentrations. It is noteworthy that the miscibility gap is still present at temperatures just below melting. The hydrogen-helium alloy is, however, different from many other alloys (such as Li and Mg) in one important respect.

Whereas the difference between the Mg and Li electron-ion interactions (pseudopotentials) is small, hydrogen and helium have electron-ion interactions of very different strengths, and this difference is expected to play an important role in the thermodynamic properties of their alloys.

In Sec. II we discuss the general approach taken in formulating the Helmholtz free energy F for hydrogen, helium, and their alloys. The static internal energy $\bar{E}_s$ is calculated in Sec. III for any given configuration of hydrogen and helium (confined, however, to an underlying lattice), and is subsequently evaluated for a randomly - disordered configuration. Contributions to F arising from long - and short-range order are treated in Sec. IV, and the free energy associated with lattice dynamics in Sec. V. In Sec. VI we present the equations of state and the Gibbs free energy G per ion of hydrogen-helium alloys. Writing G as a function of its natural variables (pressure p, temperature T , and the relative concentration by number of helium c), we compute $\Delta G$, which is defined by:

$$\Delta G = G(p,T,c) - [c\, G(p,T,1) + (1-c)\, G(p,T,0)] \ . \tag{1}$$

From $\Delta G$ we determine the curves describing solid-solid phase separation.

## II. HELMHOLTZ FREE ENERGY

For a system of volume $\Omega$, the free energy F can be written as

$$F(T,\Omega,c) = F_s(T,\Omega,c) + F_v(T,\Omega,c) \ , \tag{2}$$

where $F_s(T,\Omega,c)$ is the static free energy, and $F_v(T,\Omega,c)$ the vibrational free energy. In principle, F can be calculated from the partition function $\bar{Z}$, which is the sum of $e^{-\beta E}$ over all degrees of freedom, electronic and ionic, and in particular over all configurations of hydrogen and helium on the assumed underlying lattice. (Here $\beta = 1/k_B T$ and E is the total energy.) It is useful to introduce the following notation: Let $\langle A \rangle_s$ denote the ensemble average of the variable A for a static lattice. The electronic degrees of freedom and the configurational degrees of freedom remain summed over in obtaining $\langle A \rangle_s$ .

We use the symbol $\langle A \rangle_{s,o}$ to indicate the ensemble average of A for a static lattice in which the configurations summed over are restricted to be randomly disordered. We can now write $F_s(T, \Omega, c)$ of Eq. (2) as

$$F_s(T, \Omega, c) = \langle E \rangle_s - T \langle S \rangle_s , \tag{3}$$

where S is the entropy. We may also write Eq. (2) as

$$F = \langle E \rangle_{s,o} + \left[ F_s - \langle E \rangle_{s,o} \right] + F_v^o + \left[ F_v - F_v^o \right] , \tag{4}$$

where $F_v^o$ is the vibrational free energy of a randomly disordered alloy.

We will ignore the last term in Eq. (4), and in Sec. V calculate only $F_v^o$. The validity of this approximation will be discussed in the final section. The neglect of the term $[F_v - F_v^o]$, and the separation of the static free energy as shown in Eq. (4), are motivated by the fact that those temperatures for which hydrogen-helium alloys actually do form are sufficiently high as to favor such random disorder. (This point will be argued more fully in Sec. VI.) Thus we expect that at these temperatures $\langle E \rangle_{s,o}$ will be the major contribution to $\langle E \rangle_s$. Note that the second term of Eq. (4) includes the configurational entropy, as well as corrections to the static energy due to correlations of the positions of hydrogen and helium on the lattice.

## III. STATIC ENERGY

In this section we calculate $\langle E \rangle_{s,o}$ by writing a general expression for $\bar{E}_s$, the static energy of any configuration of the ions, and then computing its average over randomly disordered configurations. The approach is to consider an alloy as consisting of hydrogen and helium ions, located on a lattice, and immersed in a responding electron gas of compensating density. The ion-ion electron-electron, and electron-ion interactions are all given by Coulomb's law. The (divergent) long-wavelength limits of these interactions sum to zero, and are eliminated from the starting Hamiltonian.[7] One can then write $\bar{E}_s$ as

$$\bar{E}_s = E^{(o)} + E_M + E_b . \tag{5}$$

Here $E^{(o)}$ is the energy (per ion) of a homogeneous interacting electron gas (in the presence of a positive, uniform background charge), the Madelung energy $E_M$ is the electrostatic energy of the point ions (in the presence of a uniform negative background charge), and $E_b$ is the energy due to the electrons' response to the non-uniform component of the total ionic potential V. By treating V as relatively weak, $E_b$, which is known as the band structure energy, can be calculated by perturbation theory. What we are describing is conventional pseudopotential theory,[8] applied to a system for which the electron-ion interaction is known exactly. This approach has been used extensively in the context of metallic hydrogen,[7,9] and is an important element in the alloy calculation of Ref. 3.

In Eq. (5), $E^{(o)}$ is given by

$$E^{(o)} = Z^* \left(\frac{e^2}{2a_o}\right) \left[\frac{3}{5}\left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2} - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} + (-0.115 + 0.031 \ln r_s)\right], \quad (6)$$

where $Z^*$ is the average ionic charge in units of e ($e > 0$). Since $Z_{HE} = 2$ and $Z_H = 1$, $Z^* = cZ_{HE} + (1-c)Z_H = 1 + c$. Note that $r_s$ is the usual dimensionless electron spacing parameter:

$$\frac{4}{3}\pi\, (r_s a_o)^3 = \frac{\Omega}{Z^* N}, \quad (7)$$

where $a_o$ is the first Bohr radius. Since N is the number of ions (in $\Omega$), $NZ^*$ is the corresponding number of electrons. The first two terms in Eq. (6) are the kinetic and exchange energies. The last term is the correlation energy, and is only known approximately. We have used the approximation due to Nozieres and Pines,[10] which is expected to be quite satisfactory in the $r_s$ range considered here ($r_s \sim 1$). Note that $E^{(o)}$ is independent of both the configuration of hydrogen and helium ions on the underlying lattice, and of the lattice itself. Since we are interested in temperatures much less than the Fermi temperature

$$T_F = \frac{5.82 \times 10^5\ \mathrm{K}^\circ}{r_s^2}, \quad (8)$$

the electron system[11] is taken to be in its ground state.

The second term in Eq. (5) is the Madelung energy, and is given by[8]:

$$E_M = \frac{1}{2\Omega N} \sum_{(ij)}{}' \sum_{\underset{\sim}{k}}{}' \frac{4\pi}{k^2} e^{i\underset{\sim}{k}.(\underset{\sim}{R}_i-\underset{\sim}{R}_j)} Z_i Z_j \quad , \tag{9}$$

where $Z_i$ is the charge of the ion at site i whose position is given by $\underset{\sim}{R}_i$. The prime on the sum over i and j denotes the omission of the terms i = j. The prime on the $\underset{\sim}{k}$-sum denotes the omission of $\underset{\sim}{k} = 0$.

The Madelung energy is generally large and negative, and for a given family of structures often assumes its lowest value for the most symmetric structure.

Using perturbation theory[7,9] $E_b$ can be developed as a series in ascending orders of the electron-ion interaction:

$$E_b = E_b^{(2)} + E_b^{(3)} + \ . \ . \ . \ . \ , \tag{10}$$

with

$$E_b^{(2)} = \tfrac{1}{2} \frac{\Omega}{N} \sum_{\underset{\sim}{k}_1}{}' V(\underset{\sim}{k}_1)\ V(-\underset{\sim}{k}_1)\ \frac{k_1^2}{4\pi} \left[\frac{1}{\epsilon(q_1)} - 1\right] \quad , \tag{11}$$

and

$$E_b^{(3)} = \frac{1}{3}\frac{\Omega}{N} \sum_{\underset{\sim}{k}_1}{}' \sum_{\underset{\sim}{k}_2}{}' V(\underset{\sim}{k}_1)\ V(\underset{\sim}{k}_2)\ V(-\underset{\sim}{k}_1-\underset{\sim}{k}_2)\left[\frac{6}{k_F} \cdot \frac{1}{\epsilon(\underset{\sim}{q}_1)} \cdot \frac{1}{\epsilon(\underset{\sim}{q}_2)} \cdot \frac{1}{\epsilon(-\underset{\sim}{q}_1-\underset{\sim}{q}_2)}\right] 4H_s^{(3)}(-\underset{\sim}{q}_1,\underset{\sim}{q}_2), \tag{12}$$

where the primes denote the omission of $\underset{\sim}{k}_1 = 0$, $\underset{\sim}{k}_2 = 0$, <u>and</u> $\underset{\sim}{k}_1 = -\underset{\sim}{k}_2$ .

In Eq.s (11) and (12), V(k) is given by:

$$V(\underset{\sim}{k}) = \frac{1}{\Omega} \int d^3r\ e^{-i\underset{\sim}{k}.\underset{\sim}{r}} V(\underset{\sim}{r}) \ , \tag{13}$$

$$V(\underset{\sim}{r}) = - \sum_i \frac{Z_i}{|\underset{\sim}{r}-\underset{\sim}{R}_i|} \quad , \tag{14}$$

where V(r) is the total ionic potential as seen by the electrons. The restrictions on the sums in Eq.s (11) and (12) follow from the form of the Hamiltonian.[7] The vectors $\underset{\sim}{q}$ are defined by $\underset{\sim}{q} = \underset{\sim}{k}/2k_F$, where the Fermi wave-vector $k_F$ is given by the relation

$$k_F^3 = 3\pi^2\ \frac{Z^*N}{\Omega} \quad .$$

In Eq.s (11) and (12), $\epsilon(\underset{\sim}{q})$ is the zero-frequency limit of the dielectric function of the homogeneous interacting electron gas, and $H_s^{(3)}$ is given in Eq. (C3) of Ref. 7. We use Hartree atomic units in the equations above, (and throughout the rest of the paper).

It is important to note that Eq. (11) is an exact result for $E_b^{(2)}$, for $\frac{k_1^2}{4\pi}\left[\frac{1}{\epsilon(q_1)} -1\right]$ measures the exact linear response of the number density of the homogeneous interacting electron gas to an external potential, (in this case the potential due to the ions). In contrast, Eq. (12) is only approximate, as the corresponding second-order response function is not known exactly. The approximation used in Eq.(12) corresponds to treating the electrons as independent particles moving in a self-consistent potential constructed from a Hartree potential and the external potential, provided $\epsilon$ is taken to be the Lindhard dielectric function[7,12]. In the present calculations we have used the Geldart-Vosko[13] modified form of the Hubbard dielectric function, which includes effects due to exchange and correlation, and yields the correct $\underset{\sim}{q} \rightarrow 0$ limit. It is certainly preferable to use this form (rather than the Lindhard function) in $E_b^{(2)}$, but it technically inconsistent to use it in $E_b^{(3)}$ as written in Eq. (12). However, these two dielectric functions yield values of $E_b^{(3)}$ within 1% of each other, so that the effect on phase boundaries, which depend on differences of free energies, is inconsequential.

Although the hydrogen-helium alloys have been taken as metallic, the convergence of the perturbation series of Eq. (10) is not dependent on the existence of a metallic state, as discussed in Ref. 3. The point is that the perturbation series should be adequate as long as the one-electron band gaps are less than the band widths, which is the case for helium above 10 megabars. Since actual metallic conduction may only occur[3] in helium at 70 megabars, this distinction is of considerable importance. (Hydrogen, on the other hand, is expected[14] to be metallic at pressures of a few megabars.)

Considerable progress[7] has been made in calculating $E_b^{(4)}$, which however, we do not include here. For metallic hydrogen $E_b^{(4)}$ is smaller than $E_b^{(3)}$ by roughly a factor of ten, and it includes the effects of the change in the chemical potential of the electron gas due to the presence of the ions. To correctly calculate $E_b^{(4)}$, one must use finite-temperature perturbation theory, as discussed in Ref. 7.

The terms $E_M$, $E_b^{(2)}$, and $E_b^{(3)}$ are valid as written for <u>any</u> configuration of hydrogen and helium, and contain contributions that depend both on the configuration and on the structure of the underlying lattice. More specifically, since the total potential $V(\underset{\sim}{r})$ in Eq. (14) takes the form of a sum over sites, $E_b$ will contain the following classes of terms:

(i) <u>Structure Independent</u> terms, that is, terms independent of configuration and lattice structure. These arise from the terms in $E_b^{(2)}$ and $E_b^{(3)}$ in which all sites coincide.

(ii) <u>Two-Body</u>, or ion-ion terms. These comprise the remaining terms in $E_b^{(2)}$, and the terms in $E_b^{(3)}$ for which only two site labels coincide.

(iii) <u>Three-Body</u>, or ion-ion-ion terms. These arise from the terms in $E_b^{(3)}$ in which no site labels coincide.

There are, of course, four-body terms and terms involving more than four ions, but these originate in higher orders of perturbation theory. Recognizing that $E_M$ is also a sum over ion-ion terms, we can group together contributions to $\bar{E}_s$ in Eq. (5) by the classes (i)-(iii) above, and obtain:

$$\bar{E}_s = \bar{E}^{(0)} + \frac{1}{2N} \sum_{\underset{\sim}{R}_i,\underset{\sim}{R}_j}{}' \phi_{ij}^{(2)}(\underset{\sim}{R}_i - \underset{\sim}{R}_j) + \frac{1}{3N} \sum_{\underset{\sim}{R}_i,\underset{\sim}{R}_j,\underset{\sim}{R}_k}{}' \phi_{ijk}^{(3)}(\underset{\sim}{R}_i - \underset{\sim}{R}_k, \underset{\sim}{R}_j - \underset{\sim}{R}_k) + \ldots \quad . \qquad (15)$$

Here the primes denote restrictions forbidding the terms $i = j$ in the two body term, and the terms $i = k$ and $j = k$ (but not $i = j$) in the three body term. Note that the two- and three- body potentials depend on density and on the identity of the ions at sites i and j, (as well as on the separations $\underset{\sim}{R}_i - \underset{\sim}{R}_j$).

All terms in $\bar{E}_s$ which are independent of configuration and lattice structure are included in $\bar{E}^{(o)}$. The point about rewriting Eq. (5) as in Eq. (15) is simply that by summing over the electron degrees of freedom (at T=0°K), we have been able to write $\bar{E}_s$ as a sum over (density-dependent) effective pair and three-body potentials, plus a term dependent only on density. This recasting of Eq. (5) is clearly valid for any configuration of hydrogen and helium ions, and is a conceptually useful alternative to Eq. (5).

We now calculate the first term in Eq. (4), the static energy of a <u>randomly</u> <u>disordered</u> system:

$$\langle E\rangle_{s,o} = E^{(o)} + \langle E_M\rangle_o + \langle E_b^{(2)}\rangle_o + \langle E_b^{(3)}\rangle_o + \ldots \qquad (16)$$

To do this we must first give the definition of <u>randomly</u> <u>disordered</u>. To this end we introduce the quantity $p_i$:

$p_i = 1$, if site i is occupied by a helium ion, (17)

$p_i = 0$, if site i is occupied by a hydrogen ion.

From its definition,[15] one can see that $p_i$ obeys the following relations:

$$(p_i)^n = p_i, \qquad n = 2,3, \ldots \qquad (18a)$$

$$\langle p_i\rangle = c, \qquad (18b)$$

where the average in Eq. (18b) is over <u>all</u> configurations. Introducing the auxiliary variables $d_i$:

$$d_i = p_i - c, \qquad (19)$$

we have

$$\langle d_i\rangle = 0 \ . \qquad (20)$$

Since $p_i$ measures the probability that site i is occupied by a helium ion, $d_i$ measures the deviation of that probability from its average value. In Eq. (9) for $E_M$, we write $Z_i$ as

$$Z_i = p_i Z_{HE} + (1-p_i)Z_H \ . \qquad (21)$$

Thus $E_M$ will clearly involve averages of the type $\langle p_i p_j \rangle$ . In terms of these correlation functions we define a randomly disordered system as one for which the n-th order correlation function factors according to[16]:

$$\langle p_{i_1} p_{i_2} \; . \; . \; . \; p_{i_n} \rangle_o = \langle p_{i_1} \rangle_o \, \langle p_{i_2} \rangle_o \; . \; . \; . \langle p_{i_n} \rangle_o = \langle p_{i_1} \rangle \, \langle p_{i_2} \rangle \; . \; . \; . \; \langle p_{i_n} \rangle \; , \qquad (22)$$

where $i_1 \neq i_2 \neq \; . \; . \; . \neq i_n$

Thus for the two-site correlation function we obtain:

$$\langle p_i p_j \rangle_o = \langle p_i \rangle \, \langle p_j \rangle = c^2 \text{ if } i \neq j, \; \langle p_i p_j \rangle_o = \langle {p_i}^2 \rangle_o = \langle p_i \rangle_o = c \text{ if } i=j. \qquad (23)$$

Since i = j is excluded from Eq. (9), we immediately have:

$$\langle E_M \rangle_o = \frac{Z^{*2}}{2\Omega N} \sum_{i,j}{}' \; \sum_{\underset{\sim}{k}}{}' \; \frac{4\pi}{k^2} \, e^{i\underset{\sim}{k} \cdot \left( \underset{\sim}{R}_i - \underset{\sim}{R}_j \right)} \; . \qquad (24)$$

The Madelung energy of a randomly disordered alloy is that of a pure metal of ionic charge $Z^*$, (corresponding to the so-called "virtual crystal"),[16] and can be calculated by well-known techniques.[8]

To calculate $\langle E_b \rangle_o$ we must first use Eq.s (13) and (14) to write $V(\underset{\sim}{k})$ in terms of the variable $p_i$:

$$V(\underset{\sim}{k}) = \sum_i e^{-i\underset{\sim}{k} \cdot \underset{\sim}{R}_i} \left( p_i \left( \frac{-4\pi \, Z_{HE}}{k^2 \, \Omega} \right) + (1-p_i) \left( \frac{-4\pi \, Z_H}{k^2 \, \Omega} \right) \right) , \qquad (25)$$

where $\underset{\sim}{R}_i$ is again the position vector of site i. Introducing $d_i$ via Eq. (19), we obtain:

$$V(\underset{\sim}{k}) = \sum_i e^{-i\underset{\sim}{k} \cdot \underset{\sim}{R}_i} \left( \bar{U} \, (\underset{\sim}{k}) + d_i \, \Delta U(\underset{\sim}{k}) \right) , \qquad (26)$$

where

$$\bar{U} \, (\underset{\sim}{k}) = - \left[ c \, \frac{4\pi \, Z_{HE}}{k^2 \, \Omega} + (1-c) \, \frac{4\pi \, Z_H}{k^2 \, \Omega} \right] = \frac{-4\pi \, Z^*}{k^2 \, \Omega} \; , \qquad (27a)$$

and

$$\Delta U(k) = - \frac{4\pi}{k^2 \, \Omega} \left( Z_{HE} - Z_H \right) = \frac{-4\pi}{k^2 \, \Omega} \; . \qquad (27b)$$

From Eq.s (11) and (17), we find:

$$\langle E_b^{(2)}\rangle_o = \frac{1}{2}\frac{\Omega}{N}\sum_{\underset{\sim}{k}_1}{}' \langle V(\underset{\sim}{k}_1)\, V(-\underset{\sim}{k}_1)\rangle_o\, \frac{k_1^2}{4\pi}\left[\frac{1}{\epsilon(\underset{\sim}{q}_1)} - 1\right], \tag{28}$$

and

$$\langle V(\underset{\sim}{k}_1)\, V(-\underset{\sim}{k}_1)\rangle_o = \sum_i e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_i}\sum_j e^{+i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_j}\left\langle\left(\bar{U}(\underset{\sim}{k}_1) + d_i\Delta U(\underset{\sim}{k}_1)\right)\left(\bar{U}(-\underset{\sim}{k}_1) + d_j\Delta U(-\underset{\sim}{k}_1)\right)\right\rangle_o . \tag{29}$$

From Eq. (20) we see that the cross terms in Eq. (29) vanish. Using the relation

$$\sum_i e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_i} = N\,\delta_{\underset{\sim}{k},\underset{\sim}{K}}, \tag{30}$$

where $\underset{\sim}{K}$ is any vector of the reciprocal lattice, we have:

$$\langle V(\underset{\sim}{k}_1)\, V(-\underset{\sim}{k}_1)\rangle_o = N^2\delta_{\underset{\sim}{k}_1,\underset{\sim}{K}}\,\bar{U}(\underset{\sim}{k}_1)\,\bar{U}(-\underset{\sim}{k}_1) + \sum_i\sum_j e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_i}\, e^{+i\underset{\sim}{k}_1\cdot R_j}\left(\Delta U(\underset{\sim}{k}_1)\Delta U(-\underset{\sim}{k}_1)\right)\langle d_i d_j\rangle_o . \tag{31}$$

In the Appendix, we prove the relationship:

$$\sum_i\sum_j e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_i}\, e^{+i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_j}\,\langle d_i d_j\rangle_o = N(c-c^2) . \tag{32}$$

Substituting Eq.s (31) and (32) into (28), and using

$$\lim_{\Omega\to\infty}\frac{1}{\Omega}\sum_{\underset{\sim}{k}} \to \frac{1}{(2\pi)^3}\int d^3k ,$$

we have the final second-order result:

$$\langle E_b^{(2)}\rangle_o = \frac{NZ^{*2}}{2\Omega}\sum_{(\underset{\sim}{K})}{}'\frac{4\pi}{K^2}\left[\frac{1}{\epsilon(\underset{\sim}{Q})} - 1\right] + \frac{1}{2}(Z_{HE}-Z_H)^2\,(c-c^2)\int\frac{d^3k}{(2\pi)^3}\,\frac{4\pi}{k^2}\left[\frac{1}{\epsilon(q)} - 1\right], \tag{33}$$

where $\underset{\sim}{Q} = \underset{\sim}{K}/2k_F$ . In Eq. (33), the first term is just the second order band structure energy[17] of a pure metal of ionic charge $Z^*$. This virtual crystal result is not correct for a randomly-disordered system, because in Eq. (29) the terms in which the sites i and j coincide must be handled separately. However, it is worth noting that the virtual crystal result correctly gives the structural-dependence of $\langle E_b^{(2)}\rangle_o$, since the second term in Eq. (33) is clearly independent of both the lattice structure and the configuration of hydrogen and helium on the lattice.

We have written $\langle E_b^{(2)}\rangle_o$ in a form that is quite similar to other expressions in the literature,[8,18] and have used a rather indirect method to do so. This method, however, avoids much of the confusion that would otherwise arise in the calculation of $\langle E_b^{(3)}\rangle_c$, to which we now turn.

Equation (12) for $\langle E_b^{(3)}\rangle o$ can be written in the following form:[12]

$$\langle E_b^{(3)}\rangle o = \frac{\Omega}{N} \sum_{\underset{\sim}{k}_1}{}' \sum_{\underset{\sim}{k}_2}{}' \sum_{\underset{\sim}{k}_3}{}' \langle V(\underset{\sim}{k}_1)\, V(\underset{\sim}{k}_2)\, V(\underset{\sim}{k}_3)\rangle_o \quad \chi_2(\underset{\sim}{q}_1,\underset{\sim}{q}_2,\underset{\sim}{q}_3)\; \delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3,o} \quad , \tag{34}$$

where the function $\chi_2$ is defined by direct comparison of Eq.s (34) and (12). However, we shall never need the explicit expression for $\chi_2$, but only its symmetry properties. The form of the function $H_s^{(3)}(-\underset{\sim}{q}_1,\underset{\sim}{q}_2)$ in Eq. (12) guarantees that $\chi_2$ is symmetric with respect to the interchange of any two arguments.[7,12] Using Eq.s (27) and (30), we have

$$\begin{aligned}\langle V(\underset{\sim}{k}_1)V(\underset{\sim}{k}_2)V(\underset{\sim}{k}_3)\rangle_o &= N^3\, \delta_{\underset{\sim}{k}_1,\underset{\sim}{K}_1}\, \delta_{\underset{\sim}{k}_2,\underset{\sim}{K}_2}\, \delta_{\underset{\sim}{k}_3,\underset{\sim}{K}_3}\, \bar{U}(\underset{\sim}{k}_1)\, \bar{U}(\underset{\sim}{k}_2)\, \bar{U}(\underset{\sim}{k}_3)\\ &+ N\, \delta_{\underset{\sim}{k}_3,\underset{\sim}{K}_3}\, \bar{U}(\underset{\sim}{k}_3)\, S_2(\underset{\sim}{k}_1,\underset{\sim}{k}_2)\, \Delta U(\underset{\sim}{k}_1)\, \Delta U(\underset{\sim}{k}_2) + N\, \delta_{\underset{\sim}{k}_1,\underset{\sim}{K}_3}\, \bar{U}(\underset{\sim}{k}_1)\, S_2(\underset{\sim}{k}_2,\underset{\sim}{k}_3)\, \Delta U(\underset{\sim}{k}_2)\, \Delta U(\underset{\sim}{k}_3)\\ &+ N\, \delta_{\underset{\sim}{k}_2,\underset{\sim}{K}_2}\, \bar{U}(\underset{\sim}{k}_2)\, S_2(\underset{\sim}{k}_3,\underset{\sim}{k}_1)\, \Delta U(\underset{\sim}{k}_3)\, \Delta U(\underset{\sim}{k}_1)\\ &+ S_3(\underset{\sim}{k}_1,\underset{\sim}{k}_2,\underset{\sim}{k}_3)\, \Delta U(\underset{\sim}{k}_1)\, \Delta U(\underset{\sim}{k}_2)\, \Delta U(\underset{\sim}{k}_3),\end{aligned} \tag{35}$$

where we have defined

$$S_2(\underset{\sim}{k}_1,\underset{\sim}{k}_2) = \sum_i \sum_j e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_i}\; e^{-i\underset{\sim}{k}_2\cdot\underset{\sim}{R}_j}\; \langle d_i d_j\rangle_o \quad , \tag{36a}$$

and

$$S_3(\underset{\sim}{k}_1,\underset{\sim}{k}_2,\underset{\sim}{k}_3) = \sum_\ell \sum_m \sum_n e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_\ell}\; e^{-i\underset{\sim}{k}_2\cdot\underset{\sim}{R}_m}\; e^{-i\underset{\sim}{k}_3\cdot\underset{\sim}{R}_n}\; \langle d_i d_j\rangle_o \quad . \tag{36b}$$

These functions are shown in the Appendix to be

$$S_2(\underset{\sim}{k}_1,\underset{\sim}{k}_2) = N\, \delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2,\underset{\sim}{K}}\, (c-c^2) \quad , \tag{37a}$$

and

$$S_3(\underset{\sim}{k}_1,\underset{\sim}{k}_2,\underset{\sim}{k}_3) = N\ \delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3,\underset{\sim}{K}}\ (c-3c^2+2c^3)\quad . \tag{37b}$$

Substituting Eq.s (35), (36) and (37) into Eq. (34), and making use of the symmetry of $\chi_2$ we obtain:

$$\langle E_b^{(3)}\rangle o = \frac{\Omega}{N}\sum_{\underset{\sim}{k}_1}{}' \sum_{\underset{\sim}{k}_2}{}' \sum_{\underset{\sim}{k}_3}{}' \Big[N^3\ \delta_{\underset{\sim}{k}_1,\underset{\sim}{K}_1}\ \delta_{\underset{\sim}{k}_2,\underset{\sim}{K}_2}\ \delta_{\underset{\sim}{k}_3,\underset{\sim}{K}_3}\ \bar{U}(\underset{\sim}{k}_1)\ \bar{U}(\underset{\sim}{k}_2)\ \bar{U}(\underset{\sim}{k}_3)$$

$$+3N\ \delta_{\underset{\sim}{k}_3,\underset{\sim}{K}_3}\ \bar{U}(\underset{\sim}{k}_3)\ N\ \delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2,\underset{\sim}{K}}\ (c-c^2)\ \Delta U(\underset{\sim}{k}_1)\ \Delta U(\underset{\sim}{k}_2)$$

$$+ N\ \delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3,\underset{\sim}{K}}\ (c-3c^2+2c^3)\ \Delta U(\underset{\sim}{k}_1)\ \Delta U(\underset{\sim}{k}_2)\ \Delta U(\underset{\sim}{k}_3)\Big]\ \chi_2\ (\underset{\sim}{q}_1,\underset{\sim}{q}_2,\underset{\sim}{q}_3)\ \delta_{\underset{\sim}{q}_1+\underset{\sim}{q}_2+\underset{\sim}{q}_3,o}\quad . \tag{38}$$

The first term in Eq. (38) is the third order band structure energy[17] of the virtual crystal. As before, there are corrections to the virtual crystal result which have their origin in the coincidence of sites in Eq. (34). However, now the corrections are <u>structure-dependent</u>. To see this more explicitly, we recast $\langle E_b^{(3)}\rangle_o$ in terms of the function $H_s^{(3)}$ of Eq. (12). By using the symmetry properties of $H_s^{(3)}$ with respect to interchange of arguments (see Ref. 7), we can rewrite Eq. (38) as:

$$\langle E_b^{(3)}\rangle o = -\frac{8}{9\pi}\left(\frac{4}{9\pi}\right)^{1/3} r_s\Big[Z^* \sum_{\underset{\sim}{Q}_1,\underset{\sim}{Q}_2}{}' \left(\frac{1}{Q_1^2\ \epsilon(\underset{\sim}{Q}_1)}\cdot\frac{1}{Q_2^2\ \epsilon(\underset{\sim}{Q}_2)}\cdot\frac{1}{|\underset{\sim}{Q}_1-\underset{\sim}{Q}_2|^2\epsilon(\underset{\sim}{Q}_1-\underset{\sim}{Q}_2)}\right)H_s^{(3)}(\underset{\sim}{Q}_1,\underset{\sim}{Q}_2)$$

$$+\frac{9}{\pi}\ (c-c^2)\quad (Z_{HE}-Z_H)^2\sum_{\underset{\sim}{Q}}{}'\int d^3q\left(\frac{1}{q^2\epsilon(\underset{\sim}{q})}\cdot\frac{1}{Q^2\epsilon(\underset{\sim}{Q})}\cdot\frac{1}{|\underset{\sim}{q}-\underset{\sim}{Q}|^2\epsilon(\underset{\sim}{q}-\underset{\sim}{Q})}\right)H_s^{(3)}(\underset{\sim}{q},\underset{\sim}{Q})$$

$$+\frac{9}{\pi^2}(c-3c^2+2c^3)(Z_{HE}-Z_H)^3\int d^3q_1\int d^3q_2\left(\frac{1}{q_1^2\epsilon(\underset{\sim}{q}_1)}\cdot\frac{1}{q_2^2\epsilon(\underset{\sim}{q}_2)}\cdot\frac{1}{|\underset{\sim}{q}_1-\underset{\sim}{q}_2|^2\epsilon(\underset{\sim}{q}_1-\underset{\sim}{q}_2)}\right)H_s^{(3)}(\underset{\sim}{q}_1,\underset{\sim}{q}_2)\Big]\ . \tag{39}$$

As before, $\underset{\sim}{Q} = \underset{\sim}{K}/2k_F$, and the prime in the double sum means we omit $\underset{\sim}{Q}_1 = 0$, $\underset{\sim}{Q}_2 = 0$, and $\underset{\sim}{Q}_1 = \underset{\sim}{Q}_2$. Since the second term in Eq. (39) involves a sum over the reciprocal lattice, it is clearly structure-dependent. Eq. (39) is our final result for $\langle E_b^{(3)}\rangle o$ .

The polynomials in c that appear in Eq.s (33) and (39), (the basic results of this section), are cumulant polynomials $P_s(c)$, familiar from the theory of electron states in the tight-binding model of randomly disordered alloys.[19] They are defined by the generating function

$$\sum_{s=1}^{\infty} P_s(c) \frac{x^s}{s!} = \ln(1 - c + ce^x) \; , \tag{40}$$

which gives,

$$\begin{aligned} P_1(c) &= c, \\ P_2(c) &= c - c^2 , \\ P_3(c) &= c - 3c^2 + 2c^3 , \; . \; . \; . \; . \quad . \end{aligned} \tag{41}$$

The cumulants arise in both problems for the same reason, namely that the decoupling of the correlation functions, illustrated in Eq. (22), does not hold when two or more sites coincide. This point has been stressed previously in Ref.s 20 and 21.

## IV. LONG AND SHORT RANGE ORDER

We now turn to the second term in Eq. (4), namely $F_s - \langle E \rangle_{s,o}$ . In the previous section we have summed over the electronic degrees of freedom to obtain an effective Hamiltonian for the ions (Eq. (15)). The static partition function (and hence the static free energy) can be obtained by summing $e^{-E/k_BT}$ over all (static) configurations of hydrogen and helium ions on the underlying lattice. To carry out this sum, we need a convenient language with which to describe the configurations. At high temperatures, this is acheived through the use of the correlation functions[22,23] $\langle p_i p_j \rangle$, $\langle p_i p_j p_k \rangle$, etc. introduced in Sec. III. In general, a helium ion may be more likely to have a hydrogen ion as a nearest neighbor than another helium ion (or vice-versa), but the probability (at high temperatures) of a very distant neighbor of the helium ion being another helium ion will depend <u>only</u> on the mean concentration of helium.

The correlation functions $\langle p_i p_j \rangle$ etc. are ideally suited to describe such short-range order,[24,25] for we expect the quantity $\langle p_i p_j \rangle - \langle p_i \rangle \langle p_j \rangle$ to become very small as $\underset{\sim}{R}_i$ and $\underset{\sim}{R}_j$ become increasingly well separated. On the other hand, at very low temperatures, and particularly for stoichiometric compositions, the alloy, if it forms at all, is expected to take up an almost completely ordered state. (For example, if c= 0.5, the alloy may have the CsCl structure at T = 0°K.) It is clearly inappropriate to attempt to describe this situation with the correlation functions of the type $\langle p_i p_j \rangle$, since $\langle p_i p_j \rangle - \langle p_i \rangle \langle p_j \rangle$ is expected to be infinitely long-ranged. Instead, it is convenient to introduce the notion of long-range order,[24,25] which for the example quoted above would be defined by the number of helium ions on "right sites", i.e. the number of He ions on the "helium ion" sublattice. The point is, of course, that this number is 1.00 at T = 0°K. It also approaches rather abruptly the disordered value of 0.5 at the critical temperature ($T_c$), above which there is <u>no</u> long-range order.

Thus, any theory used to calculate $F_s - \langle E \rangle_{s,o}$ must be capable of describing these two very different types of behavior at low and high temperatures. More specifically, at low temperatures we have:

$$\lim_{T \to 0} (F_s - \langle E \rangle_{s,o}) = \Delta E \; , \tag{42}$$

where $\Delta E$ is the energy difference between the completely ordered phase and its completely random counterpart. At extremely high temperatures we have[24]

$$\lim_{T \to \infty} (F_s - \langle E \rangle_{s,o}) = -T \langle S \rangle_{s,o} = k_B T \left[ c \ln c + (1-c) \ln(1-c) \right] , \tag{43}$$

where the expression on the RHS of Eq. (43) is simply the negative of the entropy of a randomly disordered alloy, weighted by the temperature.

The first step in formulating such a theory is drastically to simplifiy Eq. (15), and replace it by a nearest-neighbor model, viz:

$$\bar{E}_s = \frac{1}{2N} \sum_{\ell,m}^{n.n.} \left[ p_\ell p_m \, \Phi_{HE-HE} + 2p_\ell (1-p_m) \, \Phi_{HE-H} + (1-p_\ell)(1-p_m) \, \Phi_{H-H} \right] , \tag{44}$$

where the sum is over nearest neighbors only, and the pair interactions $\Phi_{HE-HE}$, $\Phi_{HE-H}$, and $\Phi_{H-H}$ will be <u>chosen</u> to satisfy Eq.s (42) and (43). Note that since we are computing only the <u>difference</u> between energies, the structure-independent term in Eq. (15) may be neglected. The appeal of the simple form in Eq. (44) is that it allows an exact mapping of the problem onto the antiferromagnetic Ising model.[26,27] In addition, the Hamiltonian of Eq. (44) has received a great deal of attention as a model Hamiltonian of an alloy.[24] Since we only need keep terms dependent on configuration, it is easy to show that the pair interactions do not enter separately, but only in the standard combination,

$$v = \Phi_{HE-H} - \tfrac{1}{2}(\Phi_{H-H} + \Phi_{HE-HE}) \ , \tag{45}$$

where v is assumed to be negative.[28]

The energy difference $\Delta E$, as calculated from the Hamiltonian of Eq. (44), is proportional to $-v$, with the proportionality constant depending on the (stoichiometric) composition and the assumed underlying lattice. It is therefore compelling to <u>choose</u> v so that the energy difference $\Delta E$ between ordered and disordered alloy will be the <u>true</u> static energy difference,[29] as calculated by the methods of Sec. III, i.e. with no restrictions to nearest neighbors. Providing our methods of solving the model problem defined by Eq.(44) satisfies the limit in Eq.(43), the resulting function $F(T, \Omega, c) - \langle E \rangle_{s,o}$ will then exhibit both the correct high and low temperature behavior.

Such a method of solution of the model problem is provided by the quasi-chemical approximation.[25,30] The basic idea of the method is to treat clusters of ions as independent units, subject only to the conservation of the number of each type of ion consistent with a <u>given</u> long-range order. The probability of a cluster having a certain configuration of hydrogen and helium ions is then simply given by the standard Boltzmann factor.

If the cluster is chosen to be the whole crystal, the result is exact. For smaller clusters, (in particular for a few atoms), error is introduced because the fact that a given site may be part of two (or more) clusters is ignored in assigning a probability that the site is occupied by (say) a helium atom. Nevertheless, the method does take into account correlation effects in a manner reminiscent of classical liquid theory. The free energy can be written down as a function of temperature and long-range order only, and is to be minimized with respect to the latter. The quasi-chemical approximation is thus able approximately to describe both long- and short-range order within one context.

The approximation is related to more accurate methods[31] in that it is the first of a hierarchy of approximation[32] which can be substantially developed, although the calculations become extremely involved. It is most readily applied in the following cases:

(i) $c = 0.5$, where the underlying lattice is bcc, and the assumed ordered state is the CsCl structure.

(ii) $c = 0.75$ (or $c= 0.25$), where the underlying lattice is fcc, and the assumed ordered state is the $Cu_3Au$ structure.

The method correctly predicts that for $c = 0.25$ alloys (ii), the order-disorder transition is of first-order,[25] that is, the long-range order drops discontinuously to zero at $T_c$. It also correctly predicts that the transition for alloys of type (i) is of second order, with the long-range order vanishing continuously at $T_c$. The existence of short-range order above the transition temperature, and hence a configurational contribution to the specific heat, is also described by the method,[33] but the details of the experimental specific heats are reproduced only qualitatively.[25,27]

When compared to more accurate solutions of the Ising model, the quasi-chemical method's prediction of $T_c$ is only very roughly correct.[34,35] However, calculation shows that in the very low temperature region the quantity $F_s - \langle E \rangle_{s,o}$ for c = 0.5 agrees fairly well with the low temperature Ising model series expansion.[26]

We have used the quasi-chemical approximation to calculate $F_s - \langle E \rangle_{s,o}$ for c = 0.25, c = 0.50, and c = 0.75 alloys by using the solutions corresponding to the categories (i) and (ii) above. The parameter v was chosen to yield the true static energy difference $\Delta E$ between ordered and disordered phases, as previously described. However, the assumed structures for the ordered and disordered phases in the calculation of $\Delta E$ were chosen by criteria to be explained in Sec.s V and VI, and were not consistent with the structures for which the quasi-chemical method was evaluated (see (i) and (ii) above). In addition, the contributions of lattice vibrations and the third order band structure energy to $\Delta E$ were neglected.[36] These approximations are expected to have a serious effect near $T_c$, but should make little difference well above or below $T_c$.[37] Since $\Delta E$ is a function of $r_s$, we have constructed an approximate form for $F_s(T,r_s,c) - \langle E \rangle_{s,o}$ which has the correct high and low temperature limits. We have not assumed that the order-disorder transition occurs at constant volume, for the actual behavior of the alloys is determined in Sec. VI from the Gibbs energy G computed at constant pressure and temperature.

## V. LATTICE VIBRATIONS

To calculate the contribution to the free energy of the lattice vibrations we first assume that the alloy is randomly disordered. The "phonon" spectrum of the random alloy is then calculated by replacing each ion with one of charge $Z_{eff}$ and mass $M_{eff}$. The values of $Z_{eff}$ and $M_{eff}$ are chosen so that the long-wavelength limit of the phonon spectrum is given correctly.[38,39]

This is readily seen to require

$$M_{eff} = M^{*} = cM_{HE} + (1 - c)\, M_{H}, \tag{46}$$

and

$$Z_{eff} = Z^{*} = cZ_{HE} + (1 - c)\, Z_{H} \quad .$$

The force constants for an alloy of arbitrary configuration are defined (to second order in the electron-ion interaction)from Eq. (15):

$$\tilde{\Phi}^{ij}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j) = \nabla_\alpha \nabla_\beta\, \phi^{(2)}_{ij}\,(\underset{\sim}{R}) \Big|_{\underset{\sim}{R} = \underset{\sim}{R}_i - \underset{\sim}{R}_j} \qquad (i \neq j) \tag{47}$$

There are three types of force constants (corresponding to hydrogen-hydrogen, hydrogen-helium, and helium-helium pairs), and from Eq.s (11)-(14) these are

$$\begin{aligned} &\tilde{\Phi}^{H-H}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j) = Z_H^{2}\, \tilde{\Phi}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j), \\ \text{and} \qquad &\tilde{\Phi}^{H-HE}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j) = Z_H\, Z_{HE}\, \tilde{\Phi}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j), \\ &\tilde{\Phi}^{HE-HE}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j) = Z_{HE}^{2}\, \tilde{\Phi}_{\alpha\beta}\,(\underset{\sim}{R}_i - \underset{\sim}{R}_j) \quad . \end{aligned} \tag{48}$$

Here $\tilde{\Phi}_{a\beta}(\underset{\sim}{R})$ depends on $r_s$ and may be written as:

$$\tilde{\Phi}_{\alpha\beta}(\underset{\sim}{R}) = \nabla_\alpha \nabla_\beta \int \frac{d^3k}{(2\pi)^3} \cdot \frac{4\pi}{k^2}\, \frac{1}{\epsilon(\underset{\sim}{k})}\, e^{-ik.\underset{\sim}{R}} \quad . \tag{49}$$

In terms of force constants, Eq. (46) is equivalent to the replacement of the three types of force constants with a particular type of "average" force constant.

The concept of phonons in disordered systems in general, and more specifically the use of average masses and force constants, has met with some success when applied to alloys whose constituent elements have similar masses or force constants.[20,40,41] Clearly the masses and force constants of pure hydrogen and helium are <u>not</u> close to each other, but some justification for the replacement of an alloy by an "equivalent" pure system is given by the "virtual crystal approximation" for the phonon Green function.[20] More specifically, if we start with a pure system of point ions having mass and charge given by Eq. (46), and introduce the difference between the physical charges and masses and the "average" ones as a perturbation,[42] then within this approximation the perturbation causes no change in the phonon Green function.

We have evaluated the dynamical matrix of the pure system defined by Eq. (46) in the adiabatic and harmonic approximations, with the electron-ion interaction taken into account up to second order. This has been repeated for a variety of crystal structures and concentrations, including pure hydrogen and helium. From the phonon frequencies, we calculate[43] the vibrational free energy $F_v^o$:

$$F_v^o = k_B T \sum_{\underset{\sim}{q}j}^{B.Z} \ln\left(2\sinh\left[\tfrac{1}{2}\beta\hbar\,\omega(\underset{\sim}{q}j)\right]\right) , \tag{50}$$

where $\beta = 1/k_B T$, $\omega(\underset{\sim}{q}j)$ is the phonon frequency of wave number $\underset{\sim}{q}$ and branch index j, and the sum is over the first Brillouin zone. This zone sum was carried out using the special-point technique[44,45] with a modest number ($\sim 10$) of special points.

Note that by using the harmonic approximation, the frequencies appearing in Eq. (50) depend on $r_s$ but <u>not</u> on temperature. In order for them to acquire a temperature dependence, a more sophisticated approximation, such as the self-consistent phonon theory,[43] would be needed. However, some thermal expansion <u>is</u> included by using the harmonic frequencies, for the contribution of $F_v^o$ to the pressure is <u>not</u> negligible (see Fig.s (1) and (2)).

The calculation of the phonon frequencies of the (randomly disordered) alloys and of hydrogen and helium was used as a guide in the choice of the lattice structure chosen for the calculations of Sec. III. The point is that these Coulomb systems (in the virtual crystal phonon approximation) are very often harmonically unstable, as discussed by Beck and Straus.[29]

(By an instability, we refer to the occurrence of imaginary phonon frequencies.) The lattice structures used in the calculations of Sec. III, as described in detail in Sec. VI, were chosen to give real frequencies. It should be noted, however, that the relationship between instabilities in the virtual crystal approximation and those in the real (randomly disordered) alloy is not clear. We shall assess the effect of our approximate treatment of the phonons on the phase boundaries in Sec. VI.

## VI. RESULTS AND DISCUSSION

### A. Choice of Lattice Structures.

Here we discuss the lattice structures chosen to calculate the various contributions to Eq. (4). The static energy differences between lattices are in general very small,[7,9] especially when compared to the energy in the phonon system. (However, these energy differences may not be small compared to the differences in phonon energies between lattices.) This raises the question of whether these materials can ever solidify in the conventional sense. It should be noted that the energy differences are also not necessarily small when compared to the difference $\Delta G$ of the Gibbs energies between the alloy and the pure hydrogen and helium systems, as Fig. 3 illustrates. An extensive search in Bravais lattice space for the structure of lowest energy (as carried out in Ref. 9) is not feasible for this problem: we limited ourselves to the consideration of the bcc, fcc, and hcp (with variable c/a ratio) lattices in the calculations of $\langle E \rangle_{s,o}$ and $F_v^o$ in Eq. (4). (Simple cubic lattices are harmonically quite unstable for these systems.)

For the randomly disordered alloys (and for pure hydrogen and helium), either fcc or bcc proved to be stable for all $Z^*$ except in the range $1.20 \leqslant Z^* \leqslant 1.30$, and the stable lattice was chosen for the calculations. At $Z^* = 1.25$, hcp (with $c/a = 1.7$) was stable, and this structure was therefore chosen in the concentration range near $Z^* = 1.25$. The lattices used to compute

$\langle E \rangle_{s,o}$ and $F_v^{\,o}$ are summarized in Table I. The absence of an entry for a particular contribution to the energy indicates that the value of that contribution was obtained by interpolation from its values at other concentrations. Note that $\langle E_b^{(3)} \rangle_o$ was calculated for fcc, not hcp, in the region $1.10 \leq Z^* \leq 1.35$. It is not expected that this procedure will cause any significant error in the phase separation curves. In addition, the designated phases for $Z^* = 1.00$ and 1.25 are harmonically unstable[46] at low densities (corresponding to pressures of less than 20 and 30 megabars, respectively). Previous calculations[46] show that such instabilities will only occur at much higher values of $r_s$ (lower pressures) when the phonon spectrum is calculated in the self-consistent harmonic theory. Thus we adopted the procedure of extrapolating the phonon frequencies to lower density to calculate $F_v^{\,o}$ at low pressure.

We now discuss the lattice structure of the ordered alloys used in calculating $F_s - \langle E \rangle_{s,o}$ by the methods described in Sec. IV. The energy difference $\Delta E$ between ordered and randomly disordered states was calculated for $c = 0.25$, 0.50, and 0.75. (For pure hydrogen and helium, $\Delta E$, as well as $F_s - \langle E \rangle_{s,o}$, clearly vanishes.) For the alloy of $c = 0.50$, we have considered two types of lattices:

(i) Simple tetragonal (st), with a basis of one helium and one hydrogen ion, situated so that when $c/a = 1.0$, this lattice has the CsCl structure.[47]

(ii) Face-centered tetragonal (fct), with a basis of one helium and one hydrogen ion, situated so that when $c/a = 1.0$, this lattice has the NaCl structure.

As the fct lattice proved unstable for a wide range of $c/a$ values, we used the st lattice at $c/a = 1.0$, where it is stable.

We considered two structures for the ordered $c = 0.25$ ($c = 0.75$) alloys:

(i) Simple tetragonal (st) lattice of helium (hydrogen) ions with a four-point basis. The helium (hydrogen) ion resides at the lattice point, and three hydrogen (helium) ions sit at the face centers. If all the ions were identical, the lattice would be face-centered tetragonal. (This is the generalization of the $Cu_3Au$ structure to $c/a \neq 1.00$)

(ii) Body-centered tetragonal (bct) lattice of helium (hydrogen) ions with a four-point basis. The helium (hydrogen) ion resides at the lattice point, and three hydrogen (helium) ions sit at the face-centers and edge midpoints. If all the ions were identical, the lattice would be simple tetragonal, with half the original lattice constant.[48]

Of these two structures, the st lattice with $c/a = 0.7$ proved, for $c = 0.75$, to have the lowest static energy (to second order in the electron-ion interaction). Since this structure is harmonically stable, the difference between its static energy and that of the corresponding disordered alloy of Table I (bcc) was set equal to $\Delta E$, as required in the application of the quasi-chemical theory of Sec. IV. For $c = 0.25$, neither of the two structures are harmonically stable (over a wide range of $c/a$ values). This may be a dynamic indication[49] of immiscibility at $T = 0°K$, or alternatively it may indicate that these structures are energetically quite far from the structure an ordered alloy actually assumes. Of these two structures, the bct lattice with $c/a = 1.0$ has the lowest static energy for $r_s \geq 0.920$ ($p \leq 28.9$ megabars at $T = 0°K$), but the st lattice with $c/a = 1.0$ has the lowest energy for $r_s < 0.920$. The static energy differences between these structures and the corresponding random alloy (hcp) were used for $\Delta E$ in the calculation of Sec. IV. In Table II we present the critical temperature $T_c$ as a function of pressure for the order-disorder transition, as calculated from Sec. IV.

In order to determine how serious an error was made in neglecting lattice vibrations in the computation of $\Delta E$, we computed $F_v$ for the CsCl-structure alloy at $T = 0°K$ and $r_s = 0.99$. The result is within 7% (0.001 a.u. per ion) of the corresponding random alloy (bcc) result. The difference is small, even on the scale of $\Delta G$. This also shows that our neglect of the term $[F_v - F_v^o]$ in Eq. (4) is quite justified.

## B. Phase Separation.

The equations of state of pure hydrogen and helium are presented in Fig.s 1 and 2. For hydrogen, at T = 0°K, they agree well with Caron's results (see Ref. 29).

Under conditions of constant temperature and pressure, the free energy to be minimized is the Gibbs free energy G:

$$G(p,T,c) = F(p,T,c) + p\,\Omega_o \,, \qquad (51)$$

where p is the pressure and $\Omega_o$ the volume per ion. Stability of mixed phases is determined by $\Delta G$:

$$\Delta G = G(p,T,c) - [c\,G(p,T,1) + (1-c)\,G\,(p,T,0)] \;. \qquad (52)$$

Here c = 1 refers to pure helium and c = 0 to pure hydrogen. In order for there to be any mixing, $\Delta G$ must be negative. A miscibility gap occurs when $\Delta G$ is negative but the system can lower its Gibbs energy by separating into a helium-rich phase and a hydrogen-rich phase.[50] This is demonstrated in Fig. 3, where we present typical results for $\Delta G(p,T,c)$ at fixed p and T. At any concentration between $c = c_1$ and $c = c_2$ the system can lower its Gibbs energy by separating into a helium-rich phase at $c = c_1$ and a hydrogen-rich phase at $c = c_2$, with the relative amounts of the two phases being given by number conservation. For such a partially separated system, the Gibbs function is given by the dashed line in Fig. 3. The error bars in Fig. 3 refer to the estimated computational error,[51] not the error due to the various physical approximations made. We have also shown typical static energy differences (to second order) between lattice structures in Fig. 3, from which the sensitivity of the phase boundaries to lattice structure can be estimated.

The phase separation curves themselves are presented in Figs. 4-8. Note that the temperatures for which mixing occurs are generally well above the order-disorder transition temperatures listed in Table. II. Thus, as we have mentioned, the details of this transition are not very important in the calculation of the phase boundaries. The uncertainties in Δ G are the cause of the uncertainties in the phase boundaries, indicated by the cross-hatched regions. regions. The most striking features of the results are (i) are the persistence of a large miscibility gap at the highest temperatures and pressures, and (ii) the large temperatures necessary for <u>any</u> mixing to occur.[52] The occurrence of large mixing temperatures is not dependent upon the approximations we have used to take into account short-range order and lattice vibrations, although the precise values of the mixing temperatures clearly are. The prediction of <u>complete</u> phase separation at temperatures below some temperature $T_m$ reflects the large positive values of Δ G for the static alloys ($\Delta G \sim k_B T_m$). In contrast, the large miscibility gap is primarily due to the "pinning" of the phase boundary near c = 0.25. This is caused by the exceptionally <u>low</u> values of Δ G for c = 0.25 (see Fig. 3) at high temperatures, an effect for which the lattice dynamics is entirely responsible.

The relatively low phonon frequencies predicted by the virtual crystal approximation for the c = 0.25 randomly <u>disordered</u> alloys should be compared with the imaginary frequencies found for the c = 0.25 <u>ordered</u> alloys. In both cases the alloy exhibits phonons whose frequencies-squared are low. This results, in one case, in a true instability, and in the other case the low energy and high entropy resulting from these low frequencies greatly favor mixing. In respect of the c = 0.25 alloys, it appears that the treatment of the lattice dynamics may be quite crucial.

A more correct treatment of the disordered alloy (within the harmonic theory), and the application on the *temperature-dependent* self-consistent (harmonic) phonon theory for example, may produce qualitative differences in the phase boundaries. One such difference might be the disappearance of the miscibility gap at temperatures below 19,000°K.

In conclusion, the calculation predicts that until the temperature has reached a fairly high value, which will certainly depend upon pressure, there is essentially *complete* phase separation in solid alloys of metallic hydrogen and helium. This may be regarded as a fairly firm result, since it is not dependent in any crucial way upon the approximations used to compute $\Delta G$. If hydrogen and helium are solid in some region of the interior of Jupiter, these conclusions have a direct bearing on any phase separation model of energy emission.

We also predict a large miscibility gap that persists to $T = 19{,}000$°K and $p = 90$ megabars. However, this prediction depends upon the approximations we have used in treating the lattice dynamics of the alloys, and might well be substantially modified by a more detailed treatment of the phonon spectrum. The third-order terms in the band-structure energy have little effect, tending to raise $\Delta G$ by only a small amount. Thus the approximate response function used in $\langle E_b^{(3)}\rangle_0$, as well as the neglect of $\langle E_b^{(4)}\rangle_0$, is not expected to have any important effect on the phase boundaries. The same is true of the use of the quasi-chemical approximation.

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## APPENDIX

The calculation of $\langle E_b{}^{(2)}\rangle_o$ and $\langle E_b{}^{(3)}\rangle_o$ in Sec. II! requires the evaluation of the following averages:

$$S_2\,(\underset{\sim}{k}_1,\underset{\sim}{k}_2) \equiv \sum_i \sum_j e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_i}\; e^{-i\underset{\sim}{k}_2\cdot\underset{\sim}{R}_j}\;\langle d_i d_j\rangle_o \quad , \tag{A-1}$$

and

$$S_3\,(\underset{\sim}{k}_1,\underset{\sim}{k}_2,\underset{\sim}{k}_3) \equiv \sum_\ell \sum_m \sum_n e^{-i\underset{\sim}{k}_1\cdot\underset{\sim}{R}_\ell}\; e^{-i\underset{\sim}{k}_2\cdot\underset{\sim}{R}_m}\; e^{-i\underset{\sim}{k}_3\cdot\underset{\sim}{R}_n}\;\langle d_\ell d_m d_n\rangle_o \quad . \tag{A-2}$$

We will freely make use of the definitions and properties of the variables $p_i$ and $d_i$ as presented in Sec. III. Expressing $d_i$ in terms of $p_i$, we have

$$\langle d_i d_j\rangle_o = \langle(p_i - c)(p_j - c)\rangle_o = \langle p_i p_j\rangle_o - c^2 = \delta_{ij}(c - c^2) \quad , \tag{A-3}$$

Similarly,

$$\langle d_\ell d_m d_n\rangle_o = \langle(p_\ell - c)(p_m - c)(p_n - c)\rangle_o$$

$$= \langle p_\ell p_m p_n\rangle_o - c\,\langle p_m p_n\rangle_o - c\,\langle p_\ell p_n\rangle_o - c\,\langle p_\ell p_m\rangle_o + 3c^3 - c^3 \quad . \tag{A-4}$$

Note that if $\ell \neq m \neq n$ in Eq. (A-4), Eq. (22) guarantees that the average will vanish. If only two of the sites are equal, we use Eq. (18) and again the average vanishes. Thus

$$\langle d_\ell d_m d_n\rangle_o = \delta_{\ell,m}\,\delta_{m,n}\,(c - 3c^2 + 2c^3) \quad . \tag{A-5}$$

Substituting Eq.s (A-3) and (A-5) into (A-1) and (A-2), and using Eq. (30),

$$S_2(\underset{\sim}{k}_1,\underset{\sim}{k}_2) = N\delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2,\underset{\sim}{K}}\,(c - c^2) \quad , \tag{A-6}$$

and

$$S_3(\underset{\sim}{k}_1,\underset{\sim}{k}_2,\underset{\sim}{k}_3) = N\delta_{\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3,\underset{\sim}{K}}\,(c - 3c^2 + 2c^3) \quad , \tag{A-7}$$

where $\underset{\sim}{K}$ is any vector of the reciprocal lattice.

# REFERENCES

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1. W. B. Hubbard and R. Smoluchowski, Space Sci. Rev. 14, 599 (1973).
2. E. E. Salpeter, Astrophys. J. Lett. 181, L83 (1973).
3. D. J. Stevenson, Phys. Rev. B12, 3999 (1975).
4. D. J. Stevenson and N. W. Ashcroft, Phys. Rev. A9, 782 (1974).
5. For instance, two different methods of calculating the melting temperature of hydrogen predict temperatures different by a factor of 4 at about 40 megabars. See Ref. 4.
6. M. Hansen, Constitution of Binary Alloys, (McGraw-Hill, 1958), 2nd Ed.
7. J. Hammerberg and N. W. Ashcroft, Phys. Rev. B9, 409 (1974).
8. W. A. Harrison, Pseudopotentials in the Theory of Metals, (Benjamin, NY, 1969).
9. E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. 61, 2429 (1971) [Sov. Phys. JETP 34, 1300 (1972)].
10. P. Nozieres and D. Pines, Nuov. Cim. 9, 470 (1958); P. Nozieres and D. Pines, Phys. Rev. 111, 442 (1958); P. Vashishta and K. S. Singwi, Phys. Rev. B6, 875 (1972).
11. The first low temperature correction to the free energy F of the free electron gas can be shown to contribute negligibly to the phase separation boundaries.
12. P. Lloyd and C. A. Sholl, J. Phys. C 1, 1620 (1968).
13. D. J. W. Geldart and S. H. Vosko, Can. J. Phys. 44, 2137 (1966).
14. A. K. MacMahan, H. Beck, and J. Krumhansl, Phys. Rev. A9, 1852 (1974).
15. None of our final results depends upon the definition of $p_i$ in terms of helium. It might just as well have been defined in terms of hydrogen.

16. D. Stroud and N. W. Ashcroft, J. Phys. F **1**, 113 (1971).

17. Since the calculation is valid for all c, the c = 0 (or c = 1) limits of $\langle E_M \rangle_o$, $\langle E_b^{(2)} \rangle_o$, and $\langle E_b^{(3)} \rangle_o$ recover the pure crystal result.

18. V. Heine and D. Weaire, in *Solid State Physics*, ed. by H. Ehrenreich, F. Seitz and D. Turnbull (Academic, N.Y., 1970), Vol. 24.

19. F. Yonezawa and T. Matsubara, Prog. Theor. Phys. **35**, 357 (1966); R. Kubo, Jour. Phys. Soc. Jap. **17**, 1100 (1962).

20. R. J. Elliott, J. A. Krumhansl and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).

21. F. Yonezawa and K. Morigaki, Prog. Theor. Phys. Suppl. **53**, 1 (1973).

22. C. G. Shirley and S. Wilkins, Phys. Rev. **B6**, 1252 (1972).

23. B. Taggart and R. A. Tahir-kheli, Phys. Rev. **46**, 1690 (1971); R. A. Tahir-kheli, Phys. Rev. **188**, 1142 (1969).

24. T. Muto and Y Takagi, in *Solid State Physics*, ed. by F. Seitz and D. Turnbull (Academic, N.Y., 1955), Vol. 1.

25. L. Guttman, in *Solid State Physics*, ed. by F. Seitz and D. Turnbull (Academic, N.Y., 1956), Vol. 3.

26. C. Domb, in *Phase Transitions and Critical Phenomena*, ed. by C. Domb and M. S. Green (Academic, N.Y., 1974), Vol. 3.

27. A. Bienenstock and J. Lewis, Phys. Rev. **160**, 393 (1967).

28. If Eq. (44) is taken to define the complete Hamiltonian of the system, then positive v implies the occurrence of phase separation at $T = 0^\circ$K (and zero pressure). Since we are using the Hamiltonian of Eq. (44) only to describe the free energy involved in the ordering of an assumed alloy, it is necessary to take v as being negative.

29. If only two-body interactions are kept in Eq. (15), then such a choice of v is exact within mean-field theory (known as the Bragg-Williams approximation in the alloy context). Since mean-field theory is expected to be valid for very long-range interactions (H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Oxford University Press, 1971), p. 91), and since the pair interactions in these alloys have a range of at least 10 neighbors (H. Beck and D. Straus, Helv. Phys. Act. 48, 655 (1975); L. G. Caron, Phys. Rev. B9, 5025 (1974)), mean-field theory should be a reasonable approximation.

30. R. H. Fowler and E. A. Guggenheim, Proc. Roy. Soc. A174, 189 (1940); C. N. Yang and Y. Y. Li, Chi. Jour. Phys. 7, 59 (1947); Y. Y. Li, Jour. Chem. Phys. 17, 447 (1949).

31. R. Kikuchi, Phys. Rev. 81, 988 (1951); M. Kurata and R. Kikuchi, Jour. Chem. Phys. 21, 434 (1953).

32. Each higher approximation consists of taking a larger group of ions as the basic cluster.

33. This is not true of mean-field theory.

34. Domb, Adv. Physics 9, 245 (1960).

35. D. M. Burley, in Phase Transitions and Critical Phenomena, ed. by C. Domb. and M. S. Green (Academic, N.Y., 1972), Vol. 2.

36. A more subtle assumption made is that at every concentration, there is only one ordered phase. For examples of other possibilities, see N. S. Golosov and A. M. Tolstik, Jour. Phys. Chem. Sol. 36, 899, 903 (1975); N. S. Golosov, A. M. Tolstik, and L. Ya. Pudan, Jour. Phys. Chem. Sol. 37, 273 (1976); N. S. Golosov and A. M. Tolstik, Jour. Phys. Chem. Sol. 37, 279 (1976).

37. One should note that the quasi-chemical approximation itself is least accurate in the critical region.

38. The long wavelength limit of the vibrational spectrum will yield a compressibility which agrees with that calculated from the static energy (up to second order in the electron-ion interaction) only if some terms of third and fourth order in the electron-ion interaction are included in the dynamical matrix. (C. J. Pethick, Phys. Rec. B2,1789 (1970).) Since we only keep second order terms in the dynamical matrix, the replacement of Eq. (46) is not exact, even in the long wavelength limit. The resulting error in the compressibility is of order 10%. (E. Stoll, P. Meier, and T. Schneider, Il. Nuovo Cimento 23B, 90 (1974).) This discrepancy is also present in the case of pure hydrogen and helim.

39. H. Beck and D. Straus (see Ref. 29) define the "average mass" incorrectly. However, since the mass of a pure system enters the dynamical matrix only as a multiplicative prefactor, none of their results are affected.

40. W. A. Kamitakahara and B. N. Brockhouse, Phys. Rev. B10, 1200 (1974). Note that the "average" force constants used in this reference do not correspond to the average defined by Eq.s (46) and (48).

41. E. C. Svensson, B. N. Brockhouse, and J. M. Rose, Sol. State Comm. 3, 245 (1965); S. C. Ng and B. N. Brockhouse, Sol. State Comm. 5, 79 (1967).

42. This procedure is necessary to keep $r_s$ constant.

43. P. Choquard, The Anharmonic Crystal (Benjamin, N.Y., 1971).

44. A. Baldereschi, Phys. Rec. B7, 5212 (1973); D. J. Chadi and M. L. Cohen, Phys. Rev. B8, 5747 (1973).

45. D. M. Straus and N. W. Ashcroft, Phys. Rev. B14, 448 (1976).

46. The type of "Kohn anomaly" instability shown by these two substances is discussed in Beck and Straus (see Ref. 29). The self-consistent phonon theory might well stabilize these substances at low density.

47. In the context of cubic lattices, c/a is the ratio of the distance between equivalent planes to the distance between equivalent ions in a plane.

48. F. Dyson, Ann. Phys. 63, 1 (1971).

49. Instabilities occur at long wavelength for both structures.

50. We describe the criterion for global instability.

51. The large error bars at higher temperatures and low concentrations of helium are largely due to the (estimated) error in only using a few special (hcp) points to calculate $F_v^o$ for c = 0.25. The fractional error $\Delta F_v^o/F^o$ is usually less than 5%, but $F_v^o$ can be large, on the scale of $\Delta G$. ($F_v^o$ for c = o.25 in Fig. 3 is of order 0.1 a.u. per ion.)

52. These features should be contrasted with the phase separation curves of Ref. 3.

## FIGURE CAPTIONS

**Figure 1:** Equation of state of metallic hydrogen.

**Figure 2:** Equation of state of helium.

**Figure 3:** Typical results for $\Delta G$ vs. c. The dashed line determines the phase-separated region. ($c_2 \leqslant c \leqslant c_1$). The dotted line shows another possibility for the phase-separated region consistent with the error bars. Typical static energy differences between lattices of randomly-disordered alloys are also shown. (FCT refers to face-centered tetragonal.)

**Figure 4:** Phase separation curve at 15 megabars. x is the relative concentration (by number) of helium. The cross-hatched regions show the uncertainty in the phase separation boundary.

**Figure 5:** Phase separation curve at 21 megabars.

**Figure 6:** Phase separation curve at 30 megabars.

**Figure 7:** Phase separation curve at 60 megabars.

**Figure 8:** Phase separation curve at 90 megabars.

## TABLE I

Lattices used in Computations for Randomly Disordered Alloys, and for Pure Hydrogen and Helium

| Z | 1.00 | 1.05 | 1.10 | 1.15 | 1.20 | 1.25 | 1.30 | 1.35 | 1.40 | 1.45 | 1.50 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\langle E_M\rangle_o + \langle E_b^{(2)}\rangle_o$ | fcc | fcc | hcp* | hcp | hcp | hcp | hcp | hcp | fcc | bcc | bcc |
| $\langle E_b^{(3)}\rangle_o$ | fcc | fcc | fcc | fcc | fcc | fcc | --- | --- | --- | --- | bcc |
| $F_V$ | fcc | --- | --- | --- | --- | hcp | --- | --- | --- | --- | bcc |

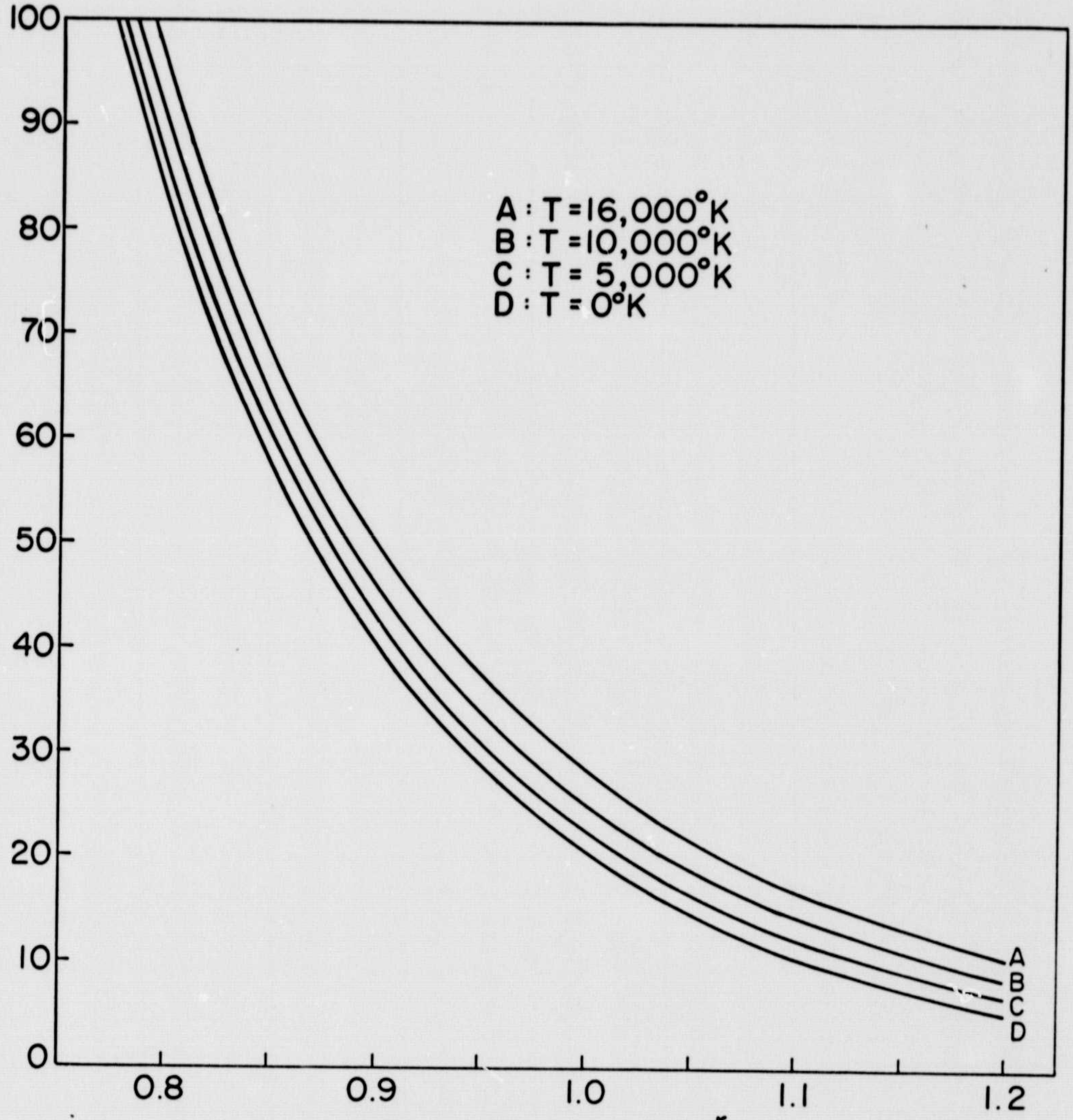
| Z | 1.50 | 1.55 | 1.60 | 1.65 | 1.70 | 1.75 | 1.80 | 1.85 | 1.90 | 1.95 | 2.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\langle E_M\rangle_o + \langle E_b^{(2)}\rangle_o$ | bcc | bcc | bcc | bcc | bcc | bcc | bcc | bcc | bcc | bcc | bcc |
| $\langle E_b^{(3)}\rangle_o$ | bcc | --- | --- | --- | --- | bcc | --- | --- | --- | --- | bcc |
| $F_V$ | bcc | --- | --- | --- | --- | bcc | --- | --- | --- | --- | bcc |

*hcp refers to the hexagonal close-packed lattice with c/a = 1.70.

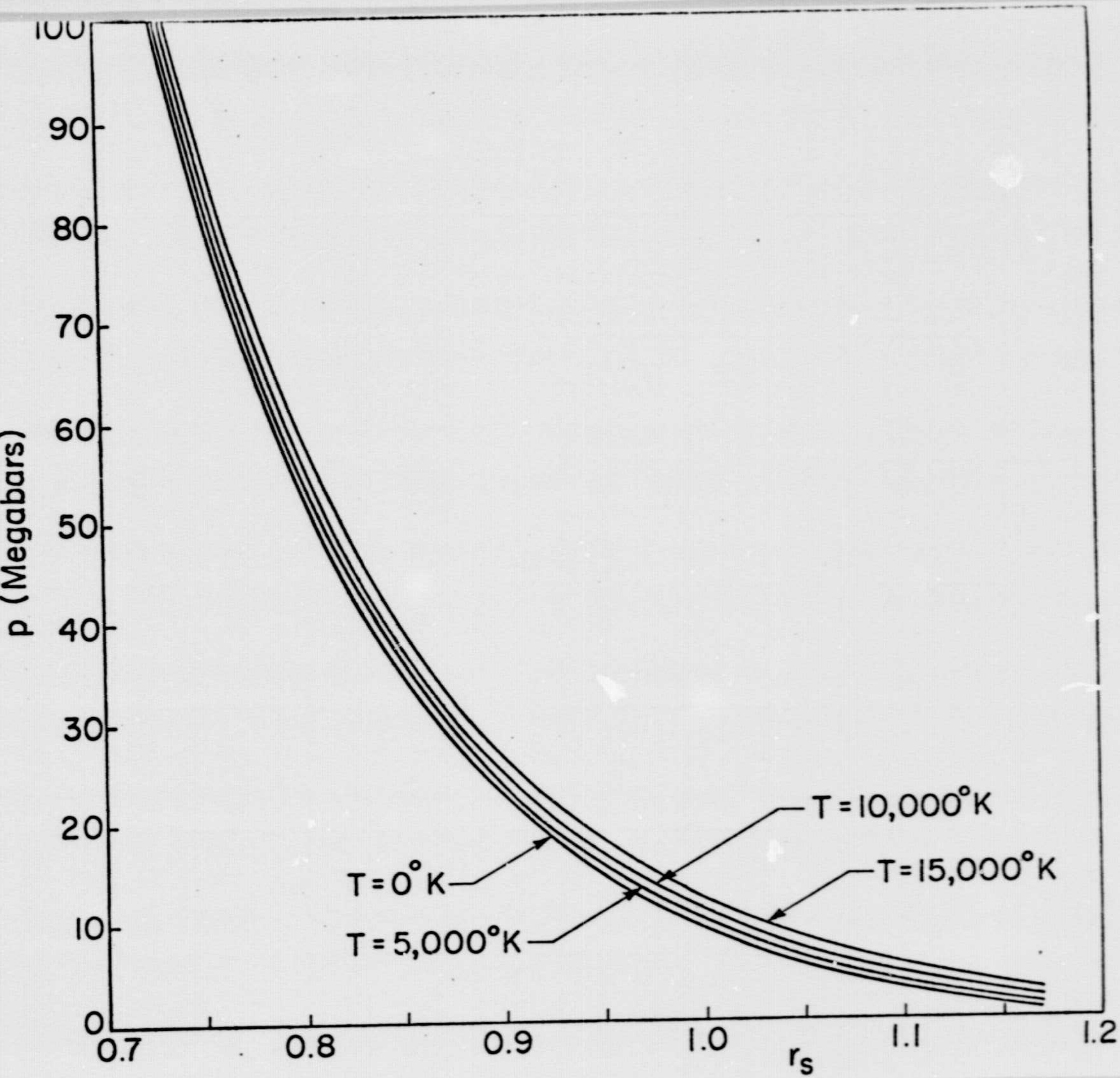
## TABLE II

Order - disorder critical temperature $T_c$ (in units of $10^3$ °K) as a function of pressure p (in units of megabars). (Pressures are approximate only).

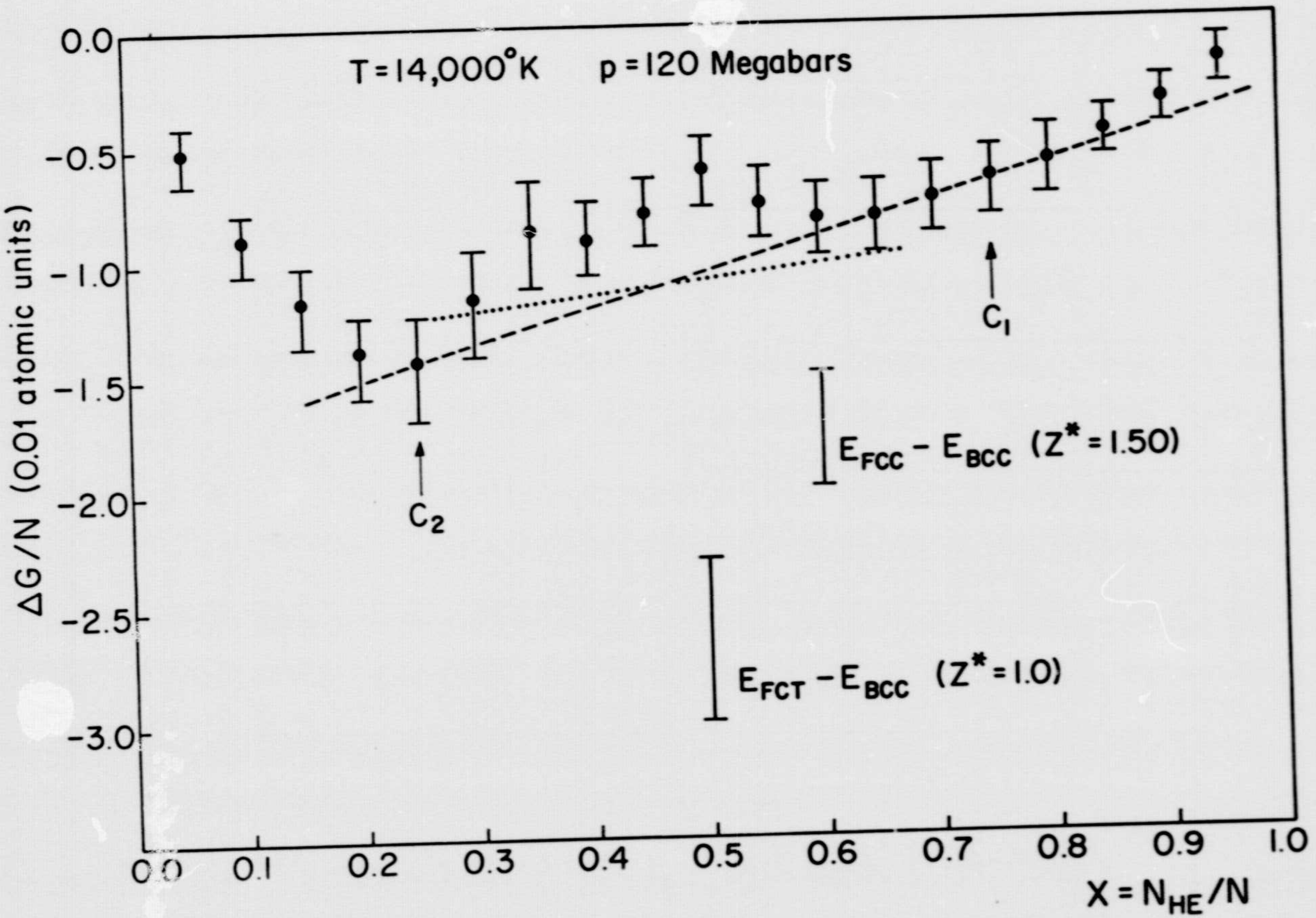
| c = 0.250 | | c = 0.500 | | c = 0.750 | |
|---|---|---|---|---|---|
| $T_c$ | p | $T_c$ | p | $T_c$ | p |
| 5.06 | 2.0 | 3.45 | 3.0 | 0.79 | 2.5 |
| 4.82 | 4.5 | 4.40 | 7.0 | 1.21 | 7.0 |
| 4.65 | 7.5 | 5.63 | 13.5 | 1.70 | 14.5 |
| 4.45 | 13.0 | 6.67 | 21.0 | 2.16 | 23.5 |
| 4.40 | 20.5 | 7.92 | 34.0 | 2.73 | 39.0 |
| 4.37 | 31.0 | 9.19 | 50.0 | 3.07 | 49.5 |
| 5.35 | 47.5 | 10.05 | 63.5 | 3.46 | 64.0 |
| 5.94 | 59.5 | 11.03 | 80.5 | 3.89 | 82.5 |
| 6.61 | 74.5 | 12.10 | 102.5 | 4.21 | 98.5 |
| 7.35 | 94.5 | 12.68 | 116.0 | 4.47 | 111.5 |
| 7.90 | 111.0 | 13.31 | 131.5 | 4.75 | 127.0 |
| 8.33 | 125.0 | | | | |



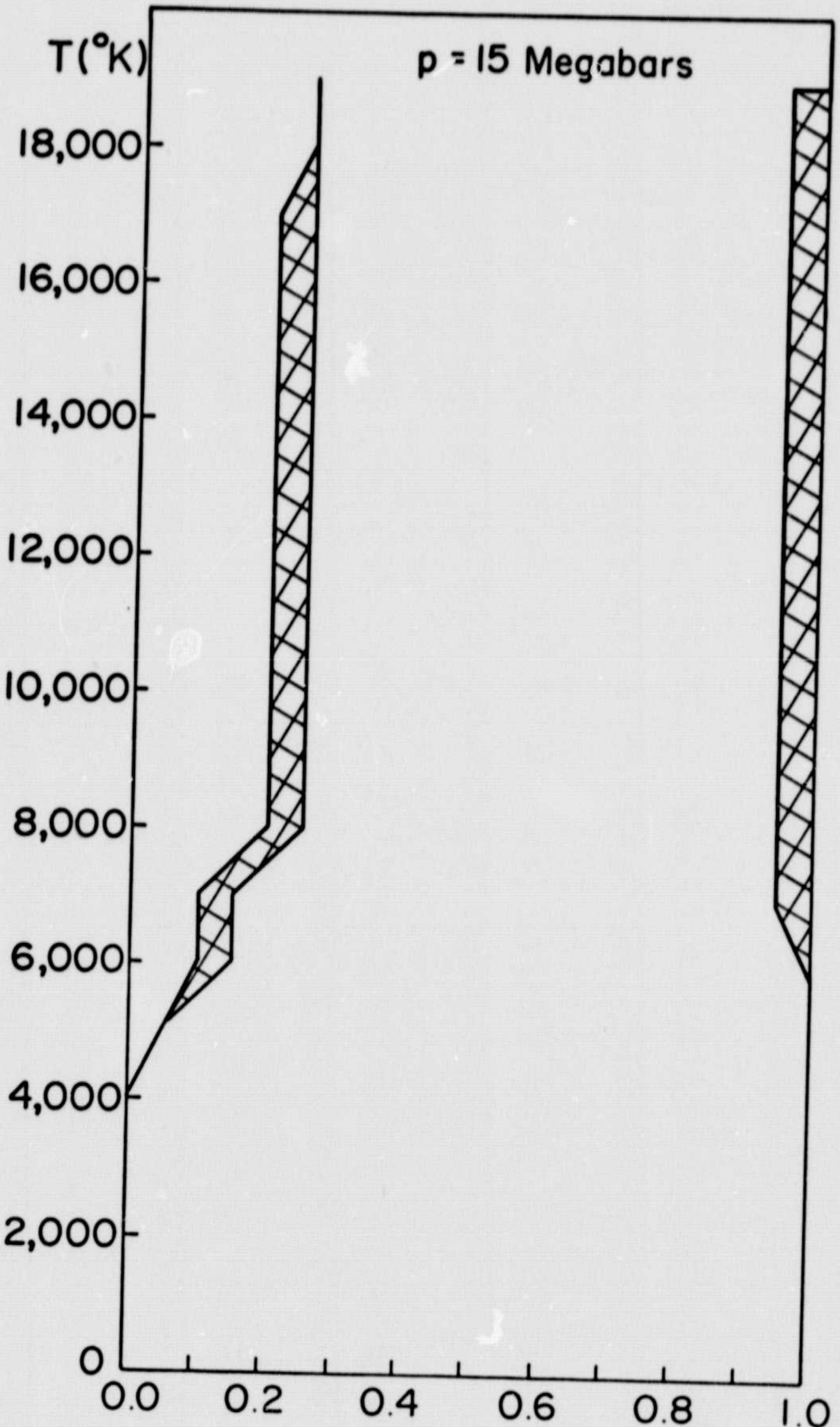
100
90
80
70
60
50
40
30
20
10
0
p (Megabars)
A : T = 16,000°K
B : T = 10,000°K
C : T = 5,000°K
D : T = 0°K
A
B
C
D
0.8
0.9
1.0
1.1
1.2
$r_s$



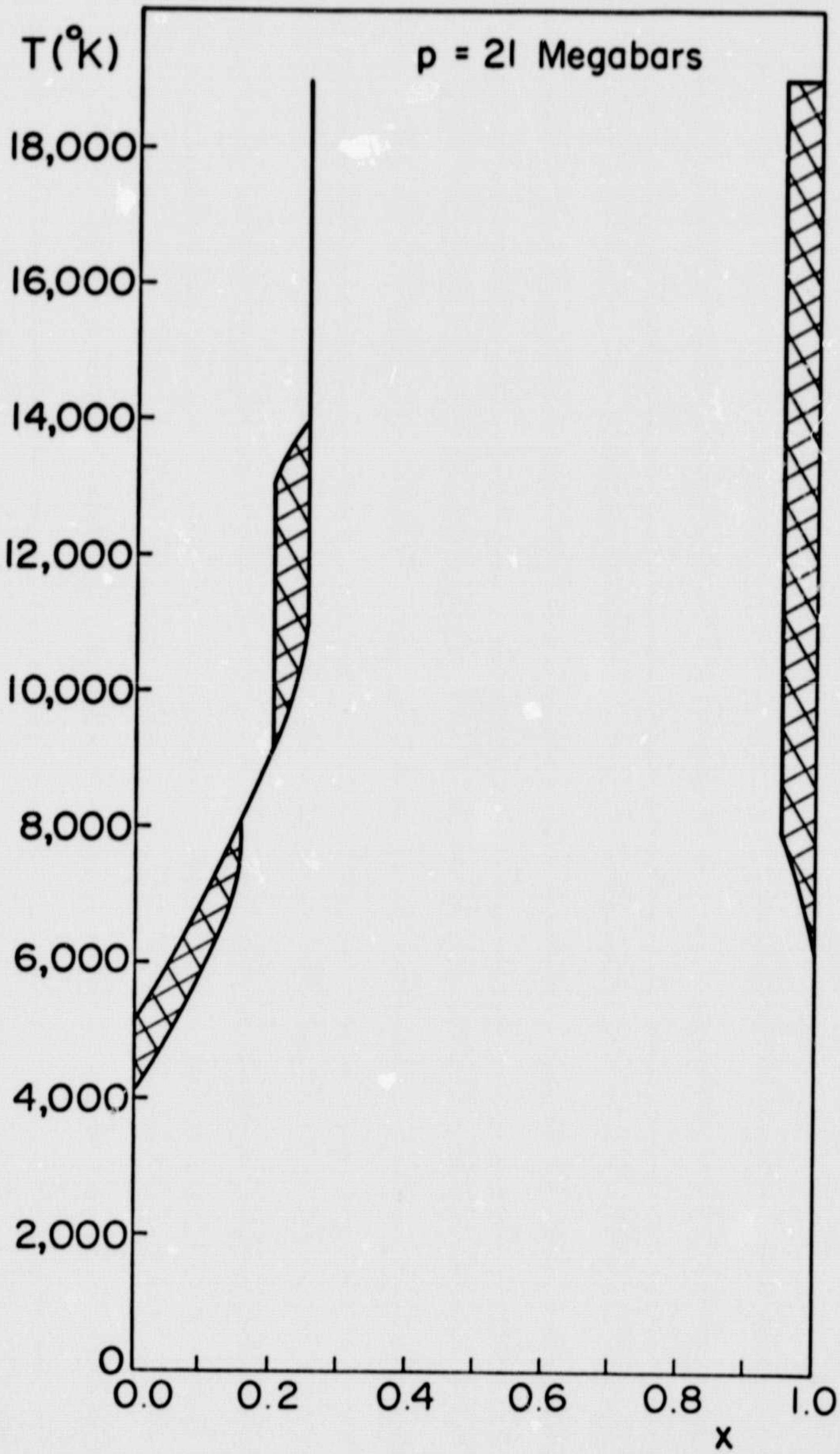
100
90
80
70
60
50
40
30
20
10
0
p (Megabars)
0.7
0.8
0.9
1.0
1.1
1.2
$r_s$
T = 10,000°K
T = 15,000°K
T = 0° K
T = 5,000°K

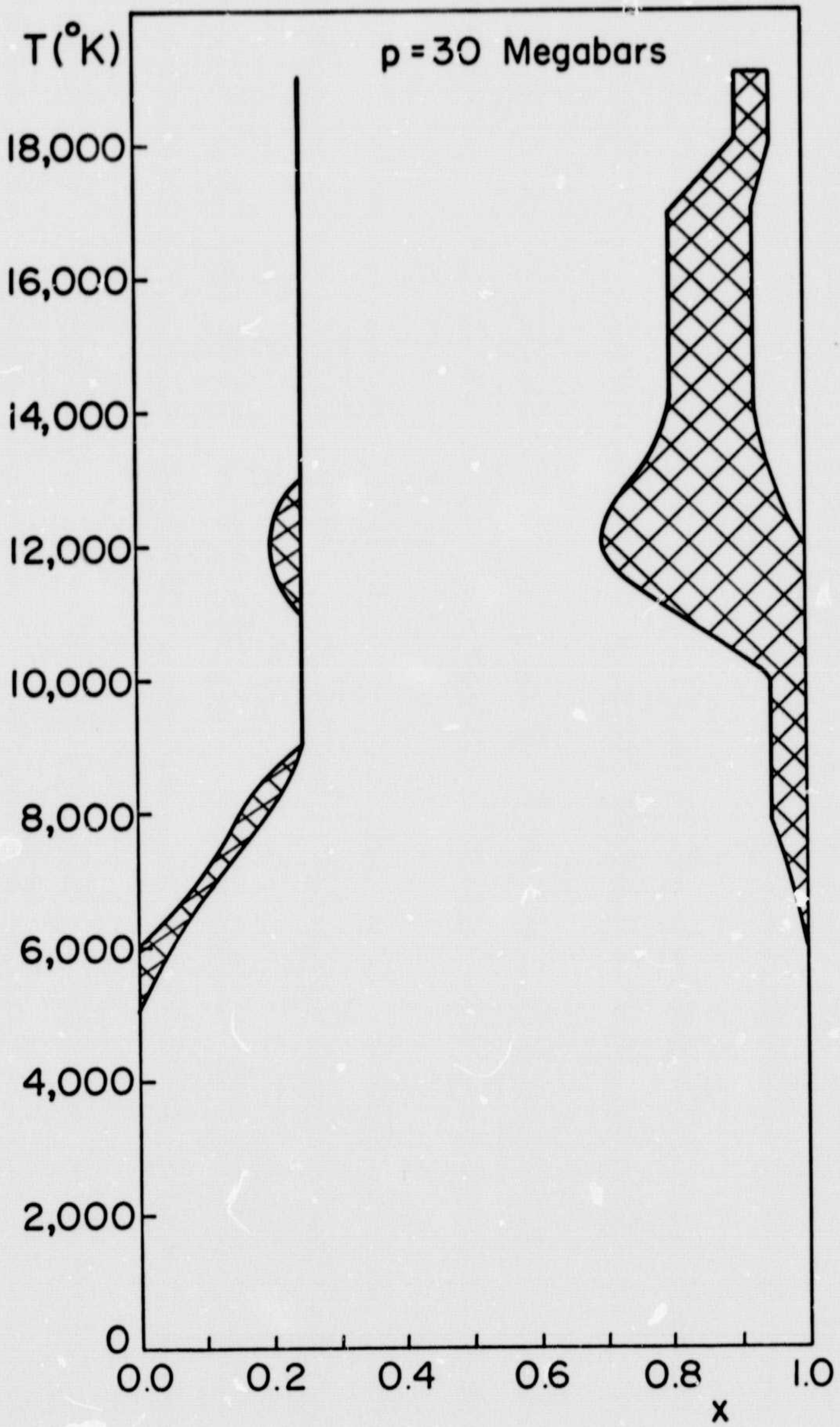


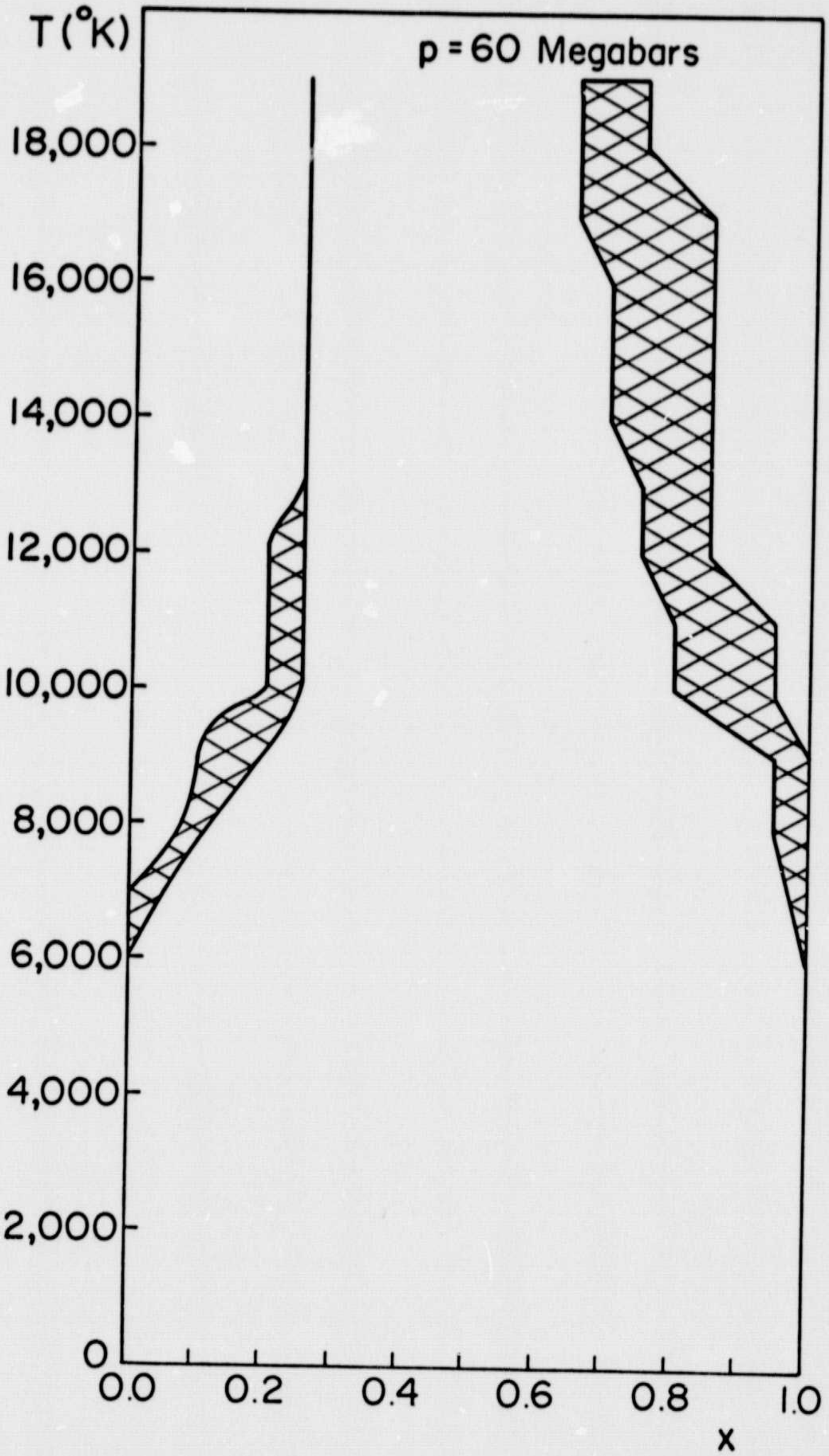
T = 14,000°K p = 120 Megabars
ΔG/N (0.01 atomic units)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X = N_HE/N
C_1
C_2
E_FCC − E_BCC (Z* = 1.50)
E_FCT − E_BCC (Z* = 1.0)

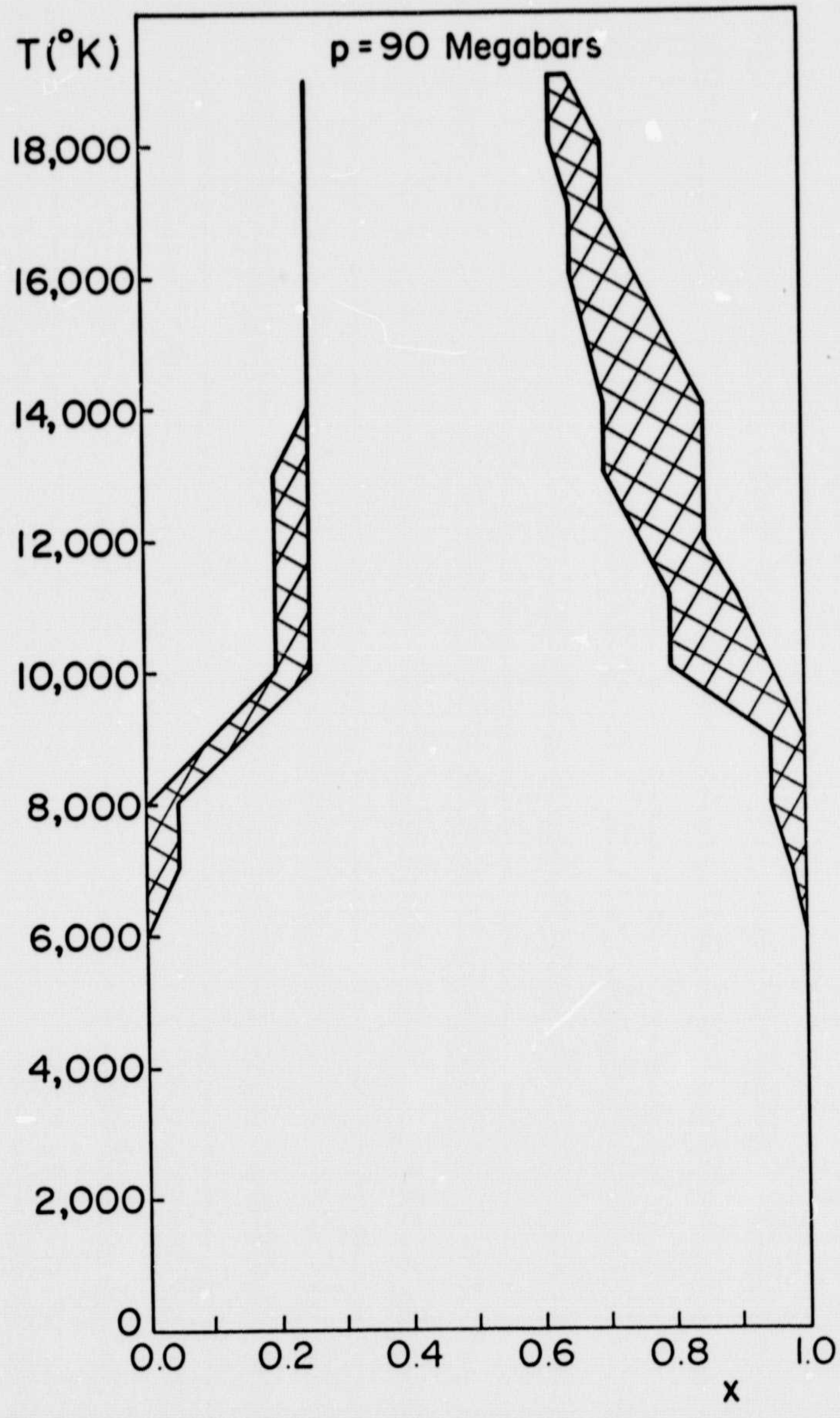


T(°K)
p = 15 Megabars
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
0.0
0.2
0.4
0.6
0.8
1.0
x


T(°K)
p = 21 Megabars
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
0.0
0.2
0.4
0.6
0.8
1.0
x


T(°K)
p = 30 Megabars
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
0.0
0.2
0.4
0.6
0.8
1.0
x


T(°K)
p = 60 Megabars
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
0.0
0.2
0.4
0.6
0.8
1.0
x


T(°K)
p = 90 Megabars
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
0.0
0.2
0.4
0.6
0.8
1.0
x