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This paper was prepared for submittal to the proceedings of the
International Conference on the Physics of Strongly Coupled Plasmas
Aug 17 – 21, 1992
Rochester, NY

November 1992

Lawrence Livermore National Laboratory

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ELECTRONIC STRUCTURE AND ENTHALPY OF HYDROGEN AND HELIUM MIXTURES

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1. INTRODUCTION

We have carried out the first local density approximation (LDA) calculations of the electronic structure, equation of state and enthalpy of mixing for a number of different compositions of hydrogen and helium in bcc and fcc lattices.[1] These are fully quantum mechanical, self-consistent calculations utilizing state of the art methods of electron band theory,[2] which make no assumptions regarding pressure ionization. The major approximation in the LDA method is that the exchange and correlation energy is given by a free electron functional in terms of the local electron density. LDA methods, which are well established, offer the possibility of accurately describing the electronic structure of both nearly free hydrogen electrons and more tightly bound helium electrons.

The majority of previous mixture calculations start with the assumption that both hydrogen and helium are pressure-ionized so that the electronic structure is approximately that of free or weakly screened electrons in the presence of positive ions. Stevenson[3] used a hard-sphere mixture model for the ions with an ion-ion pseudopotential to account for electron screening and predicted that a mixture containing 7% helium by number, the composition believed to be present in Jupiter and Saturn, would phase separate at a temperature of about 7000 K at 8 Mbar. Subsequent calculations carried out for the fully ionized mixture and for a mixture of screened ions[4] (linear response theory) have all arrived at predictions similar to those of Stevenson. MacFarlane and Hubbard[5] performed Thomas-Fermi-Dirac calculations for mixing enthalpies of hydrogen and helium in bcc and fcc lattices and predicted that phase separation would not occur at any temperature.

2. CALCULATIONS

The primary result of our calculations is given in Fig. 1 which shows the enthalpy of mixing per atom at a temperature of 0 K and a pressure of 10.5 Mbar,

$$\Delta H(x) = H(x) - xH(x=1) - (1-x)H(x=0), \tag{1}$$

where $H(x) = E(x) + PV(x)$ is the enthalpy per atom and x is the number fraction of helium atoms [E(x) is the total energy per atom, P is the pressure, which is held constant, and V(x) is the volume per atom]. The calculated ΔH is a very slowly varying function of pressure. For all of the alloys considered, $\Delta H(x)$ is virtually unchanged between 5 and 10 Mbar. In addition, we find that $\Delta H(x = 1/2)$ for the bcc structure is nearly constant between 5 and 20 Mbar and that above 20 Mbar it decreases very slowly with increasing pressure (it has dropped by only 35% at 1000 Mbar). In our calculations pure helium metallizes at 40 Mbar in the bcc structure (i.e., the energy gap between the 1s band and the 2p band goes to zero). However, we find that nothing striking happens to ΔH at 40 Mbar and it has dropped by only 10% from its value at 5 Mbar.

The large values of the mixing enthalpies in Fig. 1 stem from the fact that the helium-derived electrons are more tightly bound to the nucleus and therefore are at lower energies relative to the more itinerant hydrogen-derived electrons. This effect manifests itself in the electronic structure as two distinct features in the density of states (DOS). One feature is entirely below the Fermi level and is composed primarily of helium 1s orbitals. The other, which intersects the Fermi level, is composed primarily of

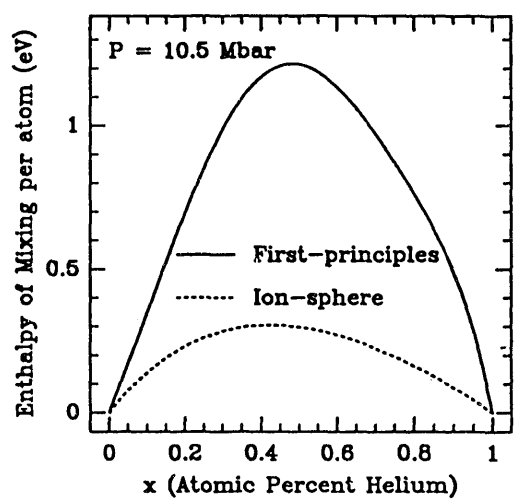

FIGURE 1
The enthalpy of mixing per atom in eV [defined in Eq. (1)] obtained from first-principles total energy calculations and the Ion-Sphere model at a pressure of 10.5 Mbar and a temperature of 0 K.

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hydrogen 1s orbitals. In Fig. 2 we plot the partial DOS for the helium 1s and hydrogen 1s orbitals in the bcc structure. Figure 2a corresponds to solid helium at 10.5 Mbar while Fig. 2b is for metallic hydrogen. The plot for hydrogen shows the parabolic curvature typical of a free electron metal. Figure 2c is a plot of the 1s partial DOS for the 50% mixture of hydrogen and helium. We clearly see that in this case the helium and hydrogen 1s electronic states are well separated in energy, with the hydrogen states lying near the Fermi level. This energy separation leads to the large, positive enthalpy of mixing and inhibits the formation of the alloy. In a pressure-ionized mixture of free electrons and ions there would be no distinction between helium and hydrogen electronic states. In view of the large deviations from free electron behavior illustrated in Figs. 2a and 2c, it is likely that any low order perturbation theory treatment starting with free electron states will break down for the helium-derived electronic states.

The relatively large, positive values of ΔH in Fig. 1 also imply that a high temperature must be reached before entropy dominates and the fully mixed phase becomes energetically favored over the coexistence of a helium-rich phase and a helium-poor phase. In order to directly address the question of phase separation, we construct a simple finite temperature model for the free energy. Since kT is much less than the Fermi energy we neglect the temperature dependence of ΔH. If we consider only the ideal entropy of mixing, the Gibbs free energy of mixing is then,

$$\Delta G(x) = \Delta H(x) + kT\,[x \ln x + (1-x)\ln(1-x)]\,. \quad (2)$$

Through a series of common tangent constructions we can determine the phase separation temperatures for all values of x. The results of this calculation, at a pressure of 10.5 Mbar, are shown as the solid curve in Fig. 3.

We can estimate the uncertainty arising from our simplified treatment of thermal effects by a comparison with well understood two-component plasma models, the OCP-Linear mixing[6] (OCP-LM) model and the Ion-Sphere model.[7] The linear-mixing excess Helmholtz free energy is written in terms of the OCP excess free energy and is known to be in excellent agreement with exact calculations for a two-component plasma.

The Ion-Sphere model makes the same approximations for the ion-ion interaction as in the OCP-LM calculation, but the calculated ΔH is for a solid mixture at 0 K. The Ion-Sphere model treats thermal effects exactly as we do in Eq. (2). The difference between the Ion-Sphere and OCP-LM curves at x = 0.07 in Fig. 3 is very close to 1000 K and the corresponding difference in the critical temperature is approximately 2000 K. We take these quantities to be estimates of the uncertainty due to the simplified treatment of thermal effects in our calculations. The total uncertainties listed in Fig. 3 also include the estimated uncertainty due to the limited number of crystal structures we considered. Both

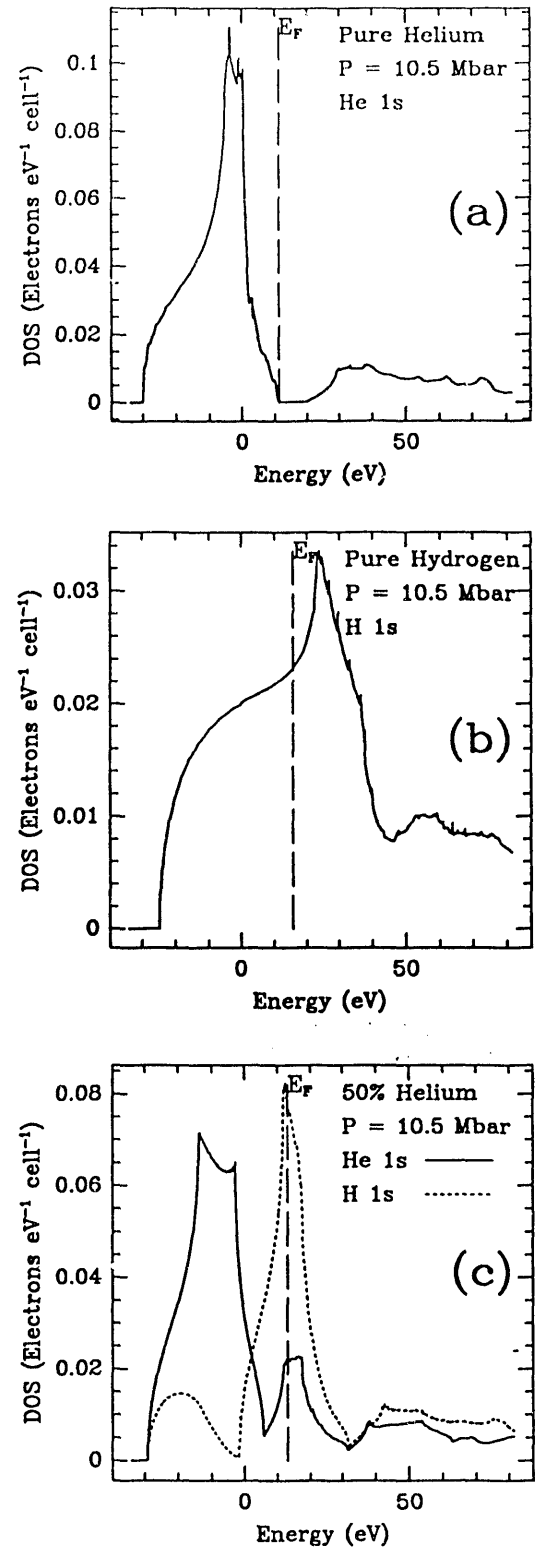

FIGURE 2 a), b) c)
Partial density of states (DOS) of the helium and hydrogen 1s orbitals at 10.5 Mbar in the bcc structure, a) for helium; b) for metallic hydrogen; c) for the 50% mixture.

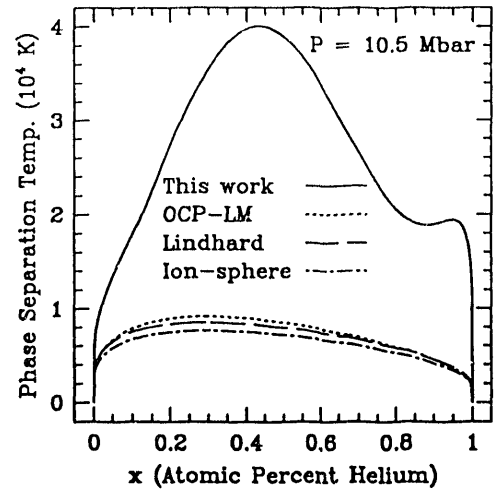

FIGURE 3

The solid curve is our calculation of the phase separation temperatures at a pressure of 10.5 Mbar [based on the results of total energy calculations and using Eq. (2)]. The critical (maximum) temperature is estimated to be T_c = 40,000 K ± 12,000 K at a critical concentration of x_c = 0.43. We also find the phase separation temperature at x = 0.07 (relevant to Jupiter and Saturn) to be T = 15,000 K ± 3000 K. The remaining curves are obtained from three different plasma models (see text).

plasma models may be compared to the Monte Carlo simulations of Hubbard and DeWitt[4] (at 10.5 Mbar) who used the Lindhard dielectric function to screen the bare Coulomb interaction between the ions (dashed curve in Fig. 3 — labeled Lindhard). The Lindhard results are very close to both the OCP-LM and Ion-Sphere curves, but very far from our calculations.

Our phase separation temperature of 15,000 K ± 3000 K for a 7% helium mixture is virtually independent of pressure in the range from 5 Mbar to 20 Mbar. This calculation confirms that the fluid interior of Saturn has phase separated, since the maximum temperature in the fluid is estimated to be only 10,000 K. The estimated temperatures in the fluid interior of Jupiter range from 10,000 K near the surface to 20,000 K at the central core. Thus our calculation also predicts that phase separation has begun in Jupiter.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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