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ABSTRACT

By using recent Pade approximations for the thermodynamic functions in the region of high temperatures and high densities, a second critical point for xenon ($T_c \sim 14000$ K, $p_c \sim 50$ GPa, $\rho_c \sim 4$ gcm^{-3}) is predicted. Further the coexistence line for the corresponding first order transition (weakly ionized plasma - strongly ionized plasma) at $T < T_c$ and the lines of soft transitions to a high degree of ionization at $T > T_c$ are given.

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1. INTRODUCTION

Xenon is the leading candidate for the transition to highly ionized phases among the rare gases. As well known, Xe has a filled 5p band and empty 6s and 5d - conduction levels; the band gap is about 6 eV. Under compression, the energy levels of the d-like band will overlap with those of the 5p core and the system will become metallic. Static compression experiments at lower temperatures /1/ indicate that the insulator - to - metal - transition occurs at pressures in the Mbar region /2/. Ross and Mc Mahan /3/ presented calculations of this transition based on the APW method with a Hedin-Lundquist exchange correlation potential. These authors predicted that the transition from an insulator to a metal will occur at a pressure of about 130 GPa. This transition is a discrete first order phase transition. The exact phase diagram of Xe at high pressures and higher temperatures is still unclear and is still subject of many discussions /4,5/. The present authors believe in accordance with Dienemann et al. /6/, that for general theoretical reasons the transition to a conducting state should occur at lower pressures with increasing temperatures T/7/. The general theory which was worked out so far only for hydrogen /8/ predicts that the line at which the transition occurs ends in a critical point at $T_c = 10000 - 20000$ K and is continued by a soft transition line at $T > T_c$. The available shock compression experiments are approaching already the region of the predicted high-temperature transitions /4,9,10,11/. Therefore one might expect that an experimental test of the theoretical predictions will be possible in near future.

2. PADE APPROXIMATIONS FOR THE FREE ENERGY

According to our earlier work /8/ the free energy density is given by the following contributions

$$f(\varrho,T) = f_{id} + f_e + f_i + f_{ie} + f_a \quad (1)$$

The ideal part is

$$f_{id} = 2k_BT\Lambda_e^{-3}\{\alpha_e I_{1/2}(\alpha_e) - I_{3/2}(\alpha_e)\} + nk_BT\left[\ln(n\Lambda_i^3)-1\right] + n_a k_BT\left[\ln(n_a\Lambda_e^3\Lambda_i^3/K(T))-1\right],$$

$$\alpha_e = I_{1/2}^{-1}\left(\tfrac{1}{2}n\Lambda_i^3\right) ; \quad \Lambda_k = h\left[2\pi m_k k_B T\right]^{-1/2} \quad (2)$$

Here n is the free electron density, n_a the free atom density and K(T) the mass action constant /8/. The nonideal contribution of the electrons is approximated by

$$f_e = \frac{(c_1+r_s^3)f_e(\varrho,T=0) - \left[1.633\,r_s^{11/2}\tau^{5/2} + 1.5\,r_s^4\tau^2\right]n\,Ry}{(c_1+r_s^3) + c_2 r_s^4\tau^2 + 1.9493\,r_s^{9/2}\tau^2 + r_s^6\tau^3} .$$

$$\tau = \frac{k_BT}{Ry}, \quad r_s = \left(\frac{3}{4\pi n a_B^3}\right)^{1/3}, \quad c_1 \approx 50, \quad c_2 \approx 2.3 \quad (3)$$

The interactions of the ions contribute

$$f_i = -nk_BT \, \frac{1.1816\,\tilde n^{1/2} + c_3 \tilde n^{3/2} B_f^{(I)} \tilde n^{1/3}}{1 + q\tilde n^{1/2} + c_3 \tilde n^{3/2}} \qquad (4)$$

$$q = \frac{3\pi}{16}(1+\ln 2)(2\gamma\tau)^{1/2}, \quad c_3 \approx 1000,$$

$$\tilde n = n(e^2/k_BT)^3, \quad \gamma = m_e/m_i,$$

$$B_f^{(I)} = 1.4474 - 4.2944\,\tilde n^{-1/4} + 0.6712\,\tilde n^{-5/12} + (0.2726 \ln \tilde n + 2.983)\,\tilde n^{-1/3}.$$

Finally the ion-electron interactions are approximated by /8/

$$f_{ei} = -nk_BT \, \frac{0.9789\,\bar n^{1/2} + c_4 \bar n^{3/2} B_f^{(II)} \bar n^{1/3}}{1 + p\bar n^{1/2} + c_4 \bar n^{3/2}[1+(\frac{r_s}{3})^3]} \qquad (5)$$

$$c_4 \approx 1, \quad \bar n = n\Lambda_e^3, \quad \xi = 2\tau^{-1/2},$$

$$p = \frac{3\pi\tau^{1/2}}{8(\sqrt{2}-1)}\left\{1 + \frac{1}{\sqrt{\pi}\,\xi}\exp\left\{\frac{(\sqrt{\pi}/2)}{\ln(\xi/3)-\xi}\right\} - \frac{1}{4}\sqrt{2}(1+\ln 2)(1+\sqrt{\gamma})\right\}; \quad B_f^{(II)} = 0.073 r_s + 0.016 r_s^2$$

Modelling the atoms as hard spheres the atomic contribution is (R_a - atomic radius, which might be density- and temperature-dependent)

$$f_a = n_a k_BT \, \frac{4\eta_a - 3\eta_a^2}{(1-\eta_a)^2} - 2nk_BT \ln(1-\eta_a), \qquad (6)$$

$$\eta_a = \frac{4\pi}{3} n_a R_a^3 .$$

3. DISCUSSION

Let us underline first that the given approximation for the free energy is quite elaborated with respect to the electrical interactions, but it is only a rough approximation with respect to the atom-atom and to the charge-atom interactions. Since we are however here interested more in the ionized phases we simply took the hard sphere model for the atoms. The atomic radius might be considered as a free parameter which could be fitted to more evolved equations of state for the atomic phase /1,3,10/. The ionization equilibrium is obtained by minimization of the free energy at fixed mass density

$$\varrho = (m_e + m_i)(n + n_a) \;.$$

The phase transitions are investigated by checking the convexity of the minimized free energy density. The results obtained for Xe are summarized in Figs. 1 - 2 . The critical point we obtain is located at

$$T_c = 13700\,\mathrm{K}, \quad p_c = 46\,\mathrm{GPa}, \quad \varrho_c = 3.2\,\mathrm{g\,cm^{-3}} .$$

The degree of ionization is about 23% near to the critical point. In order to check the accuracy of our prediction we have made other runs with an atomic radius changed by about 20%. This influences the critical temperature by about 5%, the critical pressure by 50% and the critical density by 70%. This sensitivity shows us that the numbers predicted above are to be considered only as first estimates. However the qualitative picture should be correct and the true critical data are expected to be in the region

$$T_c = 13000\text{-}15000\,\mathrm{K}, \quad p_c = 20\text{-}80\,\mathrm{GPa}, \quad \varrho_c = 2-8\,\mathrm{g\,cm^{-3}}.$$

This is in accordance with a qualitative estimate by Hess /12/. An earlier estimate by Dienemann et al. /6/ seems to be too low with respect to the pressures. The coexistence line which starts in the critical point and should connect it with the known line for the dielectric-metal transition was also calculated and is shown in Fig. 1. The values given for the triple point are only a guess. At the phase transition line one expects the coexistence of two phases: (i) a weakly ionized gas, (ii) a strongly ionized plasma which is metal-like at lower temperatures. In dynamic experiments crossing the coexistence line one expects either a decrease in the pressure due to a van der Waals loop or the appearance of droplets of the conducting phase which are imbedded into a weakly ionized gas. At overcritical temperatures the transition is continuous.

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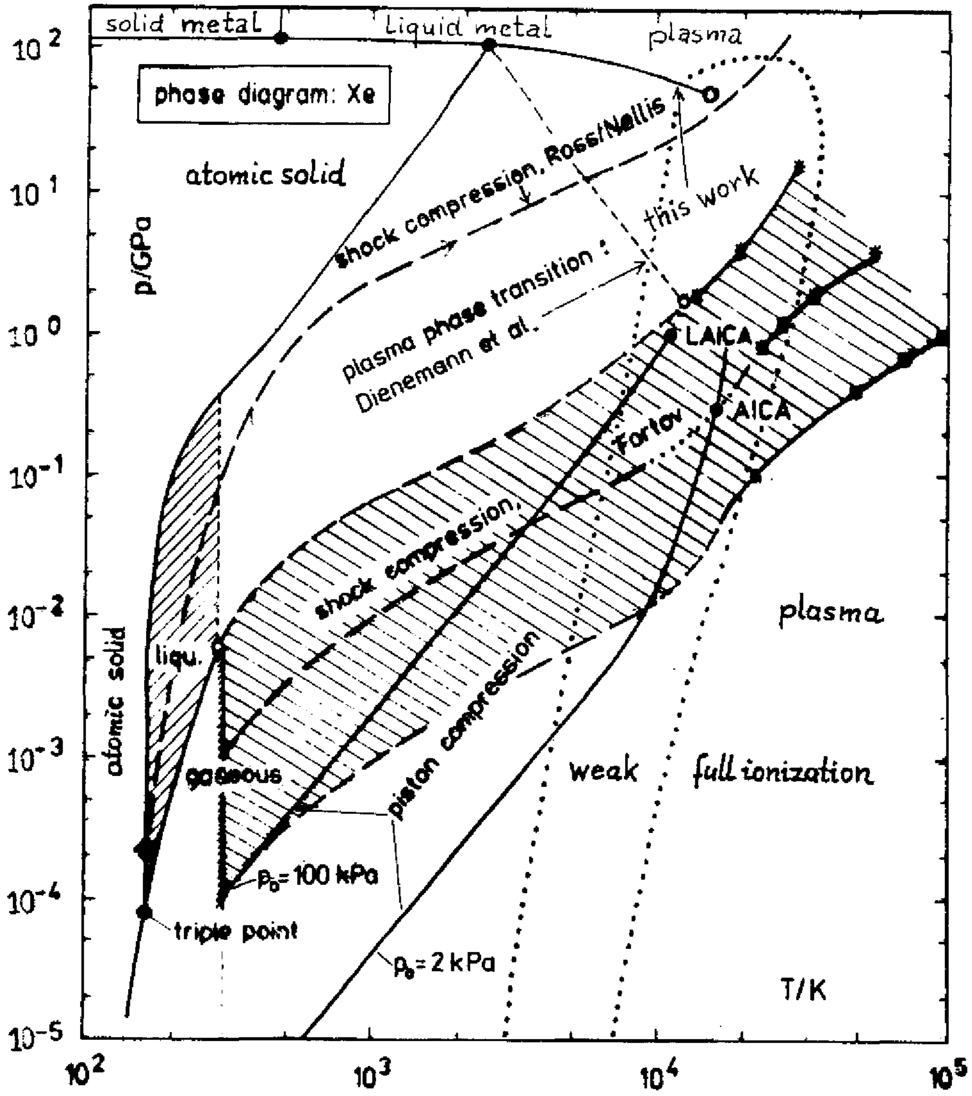
FIGURE CAPTIONS

Fig. 1 The phase diagram of Xe in the p - T - plane. The critical point T_c = 13700 K, p_c = 46 GPa was calculated in this work. For comparision the critical point obtained by Dienemann et al. and the corresponding coexistence line is given too (dashed line). The triple points are a guess. The two dotted lines correspond to continuous transitions from the weakly ionized atomic gas (left) to the fully ionized plasma (right). Further the regions of experimental studies are demonstrated /5/.

Fig. 2 The phase diagram in the p - v - plane. At higher volumes and temperatures the dielectric - metal transition goes continuously over into the plasma phase transition which was first predicted by Norman and Starostin. Further several experimental points are given. Evidently the transition pressures are reached so far only at lower temperatures.


solid metal
liquid metal
plasma
phase diagram: Xe
atomic solid
shock compression, Ross/Nellis
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plasma phase transition :
Dienemann et al.
LAICA
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shock compression
piston compression
plasma
atomic solid
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gaseous
weak
full ionization
p_0=100 kPa
triple point
p_0=2 kPa
T/K
p/GPa

Fig. 1

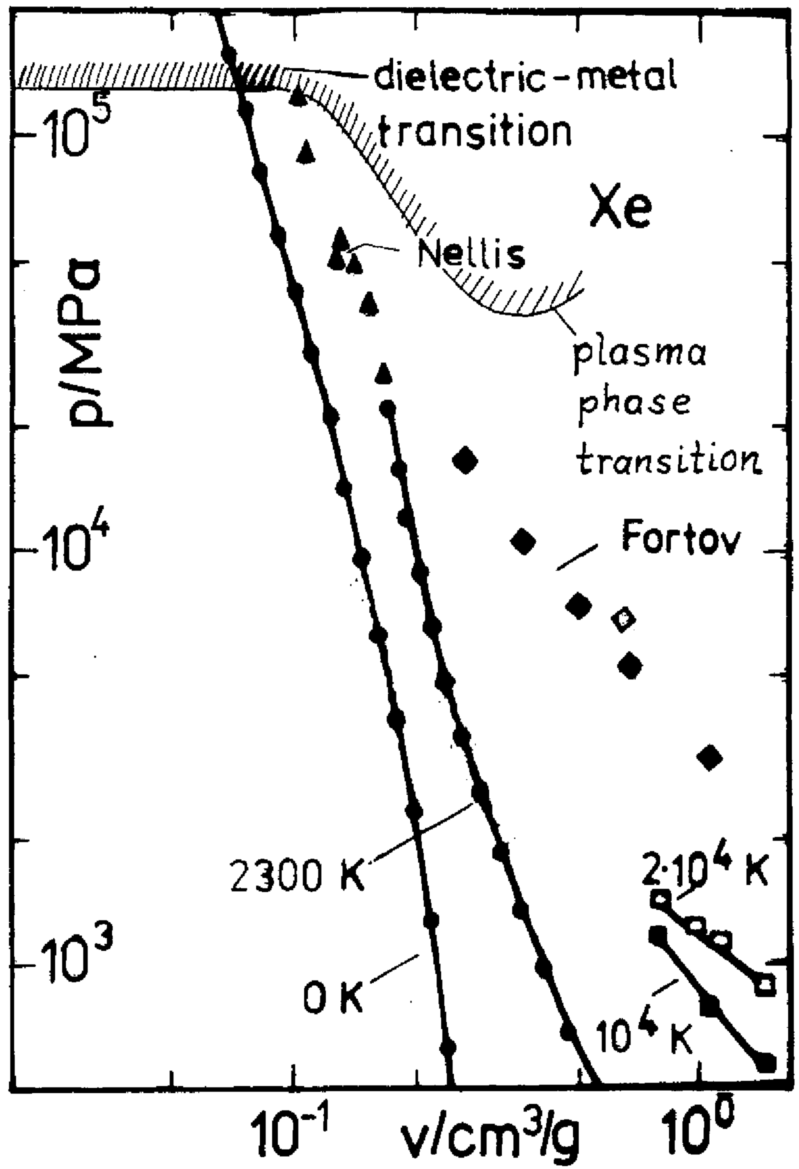
dielectric-metal transition
Xe
Nellis
plasma phase transition
Fortov
p/MPa
2300 K
0 K
2·10⁴ K
10⁴ K
v/cm³/g

Fig. 2