are due to coupling between the CO and lattice modes in the Cu to yield a resonant mode.[16] The inelastic scattering from CO was independent of incident conditions similar to Xe (Ref. 6) and Kr.[4]

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Model for the Equation of State of Condensed Matter in the "Intermediate" Pressure (about 0.5–10 TPa) Region

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A model for the equation of state of condensed matter in the "intermediate" pressure region (0.5–10 TPa) is proposed. The dominant pressure and thermal ionization effects are simulated through a modification of Saha's ionization theory. The pseudopotential method which includes core ionization effects is used to obtain the cold and lattice thermal contributions. The model is applied to Al and Mo.

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Most P-V data from shock compression experiments are limited to pressures below about 0.5 TPa.[1,2] The various theoretical equation-of-state models are also adequate either for this "experimental" region[3,4] or for the high-density "Thomas-Fermi-Dirac" (TFD) region[5] involving pressures and temperatures greater than 10 TPa and 100 eV, respectively.

Recently, some experimental data have been generated in the "intermediate" region (about 0.5–10 TPa). Trainor *et al.*[6] have used laser energy deposition to achieve shock velocities corresponding to pressures up to 1.8 TPa in aluminum. By means of shocks produced by underground nuclear explosions, Hugoniot equation-of-state points have been measured by Ragan and co-workers[7,8] for molybdenum at 2.0 and 4.9 TPa and for uranium at 6.7 TPa and by Al'tshuler *et al.*[9] and Podurets *et al.*[10] for a number of materials in the range 1–5 TPa.

Some theoretical attempts have also been made recently to develop an equation-of-state model in the intermediate region by incorporating shell structure effects in TFD theory.[11,12] Liberman[13] has proposed a self-consistent spherical TFD model in which the potential is in the muffin-tin form. Ross[14] has extended Ashcroft's liquid perturbation theory[15] to dense, partially ionized

plasmas by including electronic excitation of conduction and core electrons; however, this theory neglects pressure ionization effects. In this paper, we propose a model which approaches the intermediate region from the experimental side[4] and is based on the pseudopotential formalism.

The valence charge on the atom in the presence of pressure and thermal ionization is estimated using the screened-Coulomb modified form of Saha's equation[16,17] (also called CSCP-IEEOS) which has been shown to be appropriate for both high and low densities.[18] The combined effect of pressure and thermal ionization is to raise the initial valence charge Z_0 to a final value Z_{PT}. It is interesting to note that Z_0 at normal density and 0 K for the two metals Al and Mo considered by us here are predicted by this theory to be 3.0 and 6.0, respectively—which are known to be the normal valence states.[19]

The total pressure in the final state (V,T,Z_{PT}) can be written as

$$P(V,T) = -(\partial F/\partial V)_T, \tag{1}$$

where the free energy $F(V,T)$ can be broken into the following parts:

$$F(V,T) = F_c(V) + F_{1T} + F_e + F_{ion}. \tag{2}$$

Here F_c is the free energy in the cold compressed state (V, $T_0 = 0$ K, Z_{PT}) and is calculated for the valence charge Z_{PT} rather than Z_0. This is equal to the corresponding E_c, the lattice internal energy, at 0 K. F_{1T} corresponds to the contribution of thermal vibrations of the nuclei. F_e corresponds to conduction-electron thermal excitations and F_{ion} to ionization and to the entropy arising from the presence of different ionic species with different core-excitation states. For computational purposes, the temperature T and the ionization state Z_{PT} are obtained in a self-consistent way; for example, for compression with use of single shocks, the Rankine-Hugoniot energy-conservation relation would be used.

E_c is calculated using the pseudopotential formalism with the core radius r_{PT} being fixed corresponding to the valence charge Z_{PT} following the procedure of Heine and Weaire[20]:

$$E_c = Z_{PT}(E_k + E_x + E_{co}) - \tfrac{9}{5}Z_{PT}^2/r_a + E_1 + \sum_{\vec{g}}{}' |S(\vec{g})|^2 |v(\vec{g})|^2 x(\vec{g}) \epsilon(\vec{g}). \tag{3}$$

Here E_k, E_x, and E_{co} represent the kinetic, exchange, and correlation energies of the homogeneous electron liquid of charge Z_{PT}. The second term is the electrostatic energy as a function of the atomic radius ($\frac{4}{3}\pi r_a^3 = V$). E_1 and the last term (E_2) are the first- and second-order band-structure terms.[21] The various quantities in E_2 have the same meaning as given by Heine and Weaire.[20]

For the lattice thermal contribution E_{1T}, the internal energy is taken as $3kT$ (per atom); the corresponding pressure term[22] is

$$P = \gamma E_{1T}/V, \tag{4}$$

and the nuclear Grüneisen parameter values γ are estimated from the phonon frequencies using the values of Z_{PT} and r_{PT} derived as above.[4] We also note that γ is essentially a function of V and does not depend significantly on the details of the structure.[23,24]

Following Landau and Lifshitz,[25] we write the pressure corresponding to the thermal excitation of conduction electrons as

$$P_e = \tfrac{2}{3}E_{ke}/V, \tag{5}$$

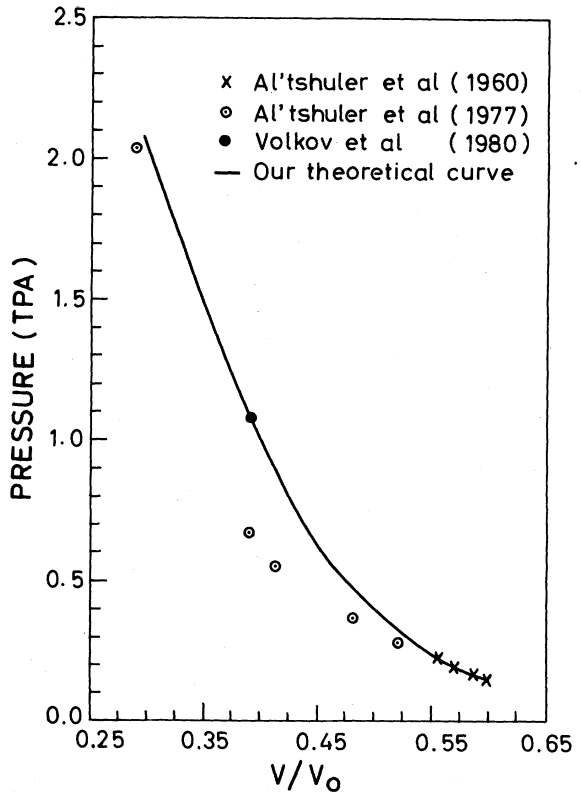

FIG. 1. The curve is the computed shock Hugoniot of Al. Also shown on it are the experimental points (crosses and solid circles) in which both shock and particle velocities were measured (Ref. 27) and the recent experimental point of Volkov *et al.* (Ref. 29), respectively. The points from Ref. 28 (circles with dots), in which only the shock velocities were measured, are also plotted.

TABLE I. Pressure and thermal ionization effects along the Hugoniot.

Element	V/V_0	Z_P [a]	Z_{PT}
Mo	0.331	6.1	8.1
	0.25 [b]	6.8	
	0.15	8.0	
	0.10	8.4	
	0.05	12.0	
Al	0.35	3.0	3.0
	0.30	3.0	3.2

[a] Z_P corresponds to pressure ionization only at $T = 0$ K.

[b] Higher compressions than this can be achieved only in multiple-shock situations.

where E_{ke} is the excess kinetic energy of the Z_{PT} electrons between the states (V, $T = 0$ K, Z_{PT}) and (V, T, Z_{PT}). For the ionization effects, we write

$$F_{ion} = E_{ion} + E_{excit} - TS_{ion}. \quad (6)$$

E_{ion} is the energy required for the ionization of the $Z_{PT} - Z_0$ electrons and E_{excit} corresponds to the ionic (bound-state) excitation energies in the final state (V,T); these two terms were computed following Rouse.[17] S_{ion} is the entropy due to the ionic charge disorder because of the presence of different ionic species at the various lattice sites. However, the ionization is sharply peaked around one ionic state at any given (V,T) and the contribution of S_{ion} to the pressure is therefore very small (e.g., for Mo at $V/V_0 = 0.331$ and $P = 4.97$ TPa in Table II, this term contributes only about 0.02 TPa). The pressure term from the various excitation states possible for each ionic species is also similarly negligible.

The above procedure has been applied to calculate the shock Hugoniot equation of state for aluminum and molybdenum. Ashcroft's empty-core pseudopotential[4] was used for Al and the Krasko-Gurskii type of pseudopotential[26] for Mo. The valence charge values for various compressions are given in Table I.

It is found that at the compression of $V/V_0 = 0.3$, the Al core remains intact up to a temperature of 7.7 eV and then Z_{PT} rises slowly. We also found that E_e rises rapidly along the Al Hugoniot and becomes comparable to lattice thermal contribution at $V/V_0 = 0.3$ ($E_T = 0.963 \times 10^{12}$ erg/g and $E_e = 1.05 \times 10^{12}$ erg/g at a Hugoniot temperature of 9 eV). The computed shock Hugoniot for Al is shown in Fig. 1. It can be seen that in the experimental region, it agrees well[4] with the data of Al'tshuler *et al.*[27] We have also compared our Hugoniot with the data of Al'tshuler *et al.* in the intermediate region[28] but here there is poor agreement. However, it may be added that the interpolation shock adiabat obtained by Al'tshuler *et al.*[28] based on their experimental data and the Thomas-Fermi model heavily overpredict the compression at 1.085 TPa compared to the experimental measurement of Volkov *et al.*[29] On the other hand, there is excellent agreement of this experimental point with our theoretical model as

TABLE II. The various contributions to the pressure and the Hugoniot temperatures for Al and Mo in the intermediate region.

Element	V/V_0	P_c (TPa)	P_{1T} (TPa)	P_e (TPa)	P (TPa)	T_H [a]	P' (TPa)
Al	0.45	0.29	0.28	0.04	0.61	3.5	0.6 [b]
	0.389	0.49	0.47	0.12	1.08	5.4	1.085 [c]
	0.32	0.92	0.65	0.24	1.81	7.9	1.8 [b]
Mo	0.41	1.25	0.53	0.19	1.97	6.1	2.0 [d]
	0.331	3.45	0.71	0.69	4.85	11.5	4.97 [e]

[a] This is defined as the value of T for which $E(V,T)$ and $P(V,T)$ satisfy the Rankine-Hugoniot relation.

[b] Pressures corresponding to experimentally measured shock velocities of Trainor *et al.* calculated by them using theoretical models (Ref. 6).

[c] Volkov *et al.*'s recent experimental point (Ref. 29).

[d] Ragan, Silbert, and Divon's experimental point in which both U_s and U_p were measured (see Ref. 7).

[e] Calculated pressure corresponding to a measured shock velocity of 27.0 km/s in an impedance-matching experiment (Ref. 8).

shown in Fig. 1 and Table II. Also, our computed pressure values shown in Table II corresponding to the experimentally measured shock velocities of Trainor *et al.*[6] agree well with the values calculated by these authors using their own (unreported) theoretical models. Also shown in the table are the various contributions to the total pressure.

Mo starts showing significant pressure ionization from $V/V_0 = 0.33$ (see Table I). Our computed pressures, corresponding to Ragan's 2.0-TPa point where both U_s and U_p were measured and his[8] 4.97-TPa value corresponding to a measured shock velocity of 27.0 km/s in a impedance-matching experiment, are shown in Table II. The reasonable agreement may be noted. Compared to this, the use of TFD theory for electronic thermal contribution in the absence of pressure and thermal ionization led to a pressure value of 4.2 TPa at $V/V_0 = 0.33$.

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