Metals Physics at Ultrahigh Pressure: Aluminum, Copper, and Lead as Prototypes

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New shock compression data for Al, Cu, and Pb in the pressure range 0.3–1 TPa (3–10 Mbar) have been combined with first-principles theory and earlier equation-of-state data to give the first self-consistent description of the thermodynamic states of metals at ultrahigh pressures. No evidence is found for a break in the slope of the shock Hugoniot of Al near 0.5 TPa, as claimed by Al'tshuler.

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The physics of condensed matter at ultrahigh pressures is of considerable current interest. The first optical and x-ray-diffraction data in the 0.1–0.2-TPa (1–2 Mbar) range have been published recently for H_2 and D_2,[1] N_2,[2] and Si.[3] These *static* high-pressure data were obtained with diamond-anvil cells, and there are currently prospects for the extension of such measurements up to 0.5 TPa.[4] At the same time, high *dynamic* shock pressures generated by chemical and nuclear explosives have also been used to measure equation-of-state (EOS) data for metals up to 1 TPa.[5–14] Densities at these extremes of pressure can be several times those at ambient conditions, leading to significant changes in atomic, electronic, and chemical structure. In metals, a pressure-induced $s \rightarrow d$ or $d \rightarrow s$ transfer of electrons is expected to occur over a wide portion of the periodic table and this transfer is expected to modify physical properties in the 0.1–1-TPa range.

While it is of intrinsic interest to study various phenomena at ultrahigh pressures, it is also important to study prototypical systems in detail as a foundation for physical understanding in this rapidly expanding regime of experimentation. The metals Al, Cu, and Pb are especially noteworthy for study in the 0.1–1-TPa range because of the following: (i) The s-d transfer can influence the properties of these materials, yet their position outside of the normal transition metals in the periodic table makes them more amenable to an accurate theoretical description. (ii) The behavior of Al above 0.5 TPa is currently controversial.[7,9] Al'tshuler[9] contends that there is a break in the slope of the shock Hugoniot near 0.5 TPa and a softening above, the anomaly possibly being driven by an $s \rightarrow d$ transition. (iii) Previous EOS data on these metals,[6–8,10–14] when combined with the present experimental results, lead to the most extensive data base available for any materials in the 0.1–1-TPa pressure range. (iv) The suitability of Al, Cu, and Pb as high-pressure EOS standards can now be objectively considered for the first time.

In discussing experimental high-pressure EOS data, it is essential to distinguish between absolute and relative measurements. Absolute EOS data are independent of any theoretical model; relative EOS data, such as are obtained from shock-impedance-match experiments, depend on the EOS of a reference material, and often in a sensitive way. In the present paper, we utilize all previously published *absolute* data on Al,[6,8,10–12] Cu,[10–13] and Pb.[12–14] We also report here new absolute double-shock data on Al and new nuclear-driven shock-impedance-match (NIM) data on Cu and Pb. All of these results are summarized in Figs. 1 and 2.

Our new double-shock EOS data for Al up to 0.425 TPa (Fig. 1) were obtained with a two-stage light-gas gun. Double shocking achieves states closer to the room-temperature isotherm than single shocking, which yields the higher-temperature Hugoniot curve. The experiments are similar to the single-shock class,[10] except that the target is a composite Al specimen and Ta or Pt anvil. Velocities for the impactors of up to 8 km/s are used: Both the impactor velocity and the shock velocity

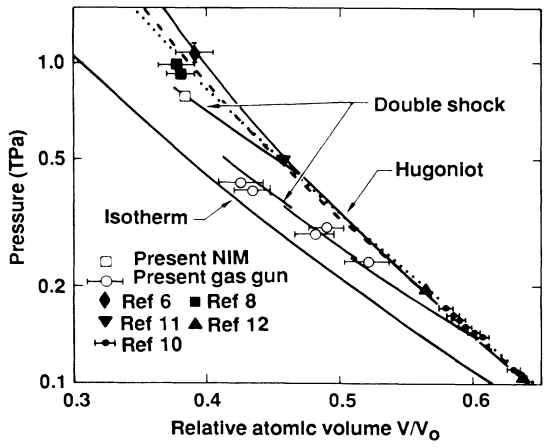

FIG. 1. Pressure-volume relations in Al. The filled and open circles are experimental single-shock (Hugoniot) and double-shock data, respectively, while the solid, dashed, and dotted curves represent the theoretical results derived from EOS 1, EOS 2, and EOS 3, respectively (1 TPa = 10 Mbar).

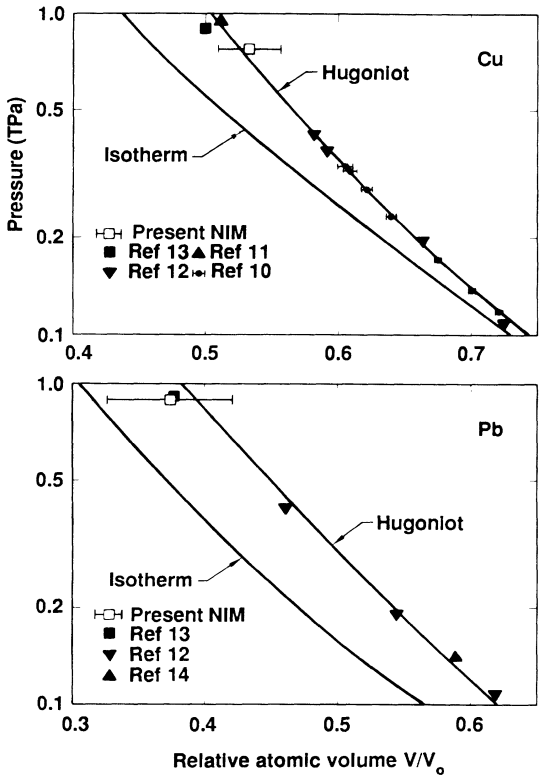

FIG. 2. Pressure-volume relations in Cu and Pb. The points are experimental Hugoniot data, while the solid curves represent the theoretical results derived from EOS 1.

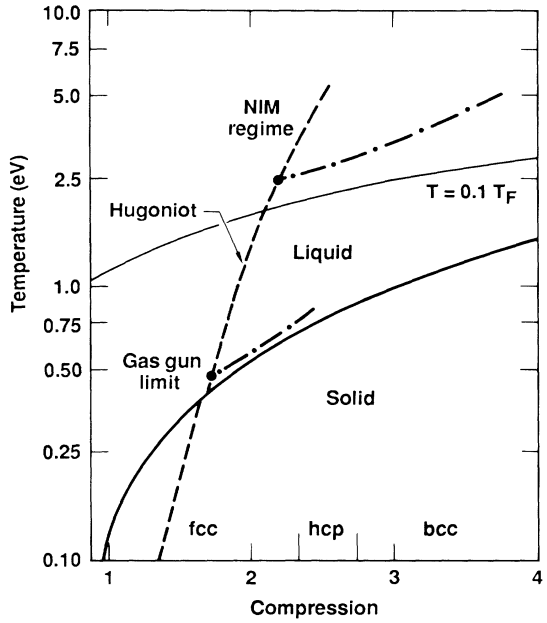

FIG. 3. Temperature along shock-compression curves in Al from EOS 1. The dot-dashed curves represent double-shock paths.

in the anvil are measured, and the measured Hugoniots of Al, Ta, and Pt are then used to reduce the data to thermodynamic states through the Rankine-Hugoniot equations. Our new NIM data, on the other hand, were obtained by use of a nuclear explosive for Al-Cu and Al-Pb pairs. Shock velocities are measured[15] in Al and in the adjacent Cu and Pb specimens. Al was single shocked to near 0.5 TPa and then double shocked to near 1 TPa (Fig. 1), the same single-shock pressure achieved in Cu and Pb (Fig. 2). The relative data obtained are checked for self-consistency both with the absolute data for these metals and with theory. Hugoniot points are derived for Cu and Pb by impedance matching with a theoretical EOS for Al; in turn this EOS is validated by the absolute data for Al. The agreement between our Cu and Pb NIM data relative to Al and the absolute data is very good, as can be seen in Fig. 2. The absolute Cu and Pb data near 1 TPa of Komer *et al.*[11] and Al'tshuler, Bakanova, and Trunin[13] were obtained by an underscribed shock generation system and until now never reproduced. Above 0.1-TPa shock pressure, the shear strength of these metals is either zero or negligible compared to the pressure itself, so that all of the experimental data can also be compared directly with thermodynamic calculations.

In the range 0.1–1 TPa, shock temperatures of metals can reach several electronvolts, but in the results reported here they never exceed about $\frac{1}{3}$ of the Fermi temperature T_F, as shown in Fig. 3 for Al. The electrons, therefore, remain substantially degenerate and the usual low-temperature expansions of condensed-matter physics describe their behavior. On the other hand, the onset of *melting* on the shock Hugoniot is observed and/or predicted to occur at 0.12 TPa in Al,[16] at 0.23 TPa in Cu,[17] and at 0.05 TPa in Pb.[18,19] Accordingly, the energetics of ion motion in both the solid and the hot liquid metal must be included. We have developed three closely related theories which satisfy these requirements. In the first approach[17,18] (EOS 1), the large zero-temperature component of the pressure P_0 is separated explicitly from the total:

$$P(V,T)=P_0(V)+P_{\text{therm}}(V,T), \tag{1}$$

where P_{therm} is the thermal pressure from ion motion and the excitation of electrons above the Fermi level. This separation allows us to utilize directly first-principles energy-band calculations for $P_0(V)$.[18,20–22] The ion-thermal contribution to P_{therm} is obtained from a complementary first-principles nonlocal pseudopotential approach,[16–18] generalized to accommodate both simple nearly free-electron metals, with little or no s-d electron transfer, and d-band metals, with arbitrary s-d transfer. In real space, this latter theory leads to a structure-independent interatomic potential which applies equally to the solid or the liquid state at a given fixed volume. Ion thermal pressures and energies are then calculated

from these potentials by use of quasiharmonic lattice dynamics in the solid and variational perturbation theory based on a soft-sphere reference system[23] in the liquid. The electron thermal contributions are obtained from the usual T^2 correction terms below $0.1T_F$ and from the parameter-free, average-atom model[24] above $0.1T_F$.

In both the second[16,25] and third[26,27] approaches (EOS 2 and EOS 3, respectively), all components of the pressure and energy are calculated from a parametrized local pseudopotential model, valid for nearly free-electron metals. To the extent that any s-d transfer is weak, these models should describe *both* Al and Pb, but have only been developed here in detail for Al. Direct contact is made with P_0 in Eq. (1) by our fitting the pseudopotential parameters, in whole or in part, to the same energy-band result used in EOS 1. The ion thermal contributions are calculated in a manner similar to that described for EOS 1, with the principal difference residing in the choice of pseudopotential used. In addition, EOS 3 explicitly treats the temperature dependence of the electron screening, whereas EOS 1 and EOS 2 do not. Also unlike EOS 1, the remaining electron thermal contributions in EOS 2 and EOS 3 are calculated directly from the thermodynamic functions implicit in the pseudopotential models themselves.

Figure 1 compares the principal Hugoniots calculated from our three theories for Al against available absolute data in the 0.1–1-TPa pressure range. Also illustrated in Fig. 1 are the 300-K isotherm and the reflected Hugoniots relevant to the double-shock and NIM experimental data for Al, as calculated from EOS 1. Corresponding pressure-volume relations for Cu and Pb are shown in Fig. 2. Our new NIM data displayed in Figs. 1 and 2 have been impedance matched with EOS 1 for Al. Impedance matching with EOS 2 or EOS 3 gives quite similar results. The overall agreement between theory and experiment for all three metals is good and within the error bars of the experimental data. Moreover, neither the absolute data nor the theory for Al suggest any break in the slope of the Hugoniot. While the $s \rightarrow d$ transition is fully included for Al in EOS 1, and has been shown to drive more subtle effects such as solid-solid phase transitions,[28] it is too weak in this metal to alter the Hugoniot qualitatively.

The qualification of the 300-K isotherms in Figs. 1 and 2 represents an additional major conclusion of this work. An upper-bound estimate on the uncertainty in these results is $\pm 10\%$. Table I provides the calculated isotherms for Al, Cu, and Pb in the 0.1–1-TPa pressure range. These are offered here as possible pressure-calibration scales for future static high-pressure experiments. Only one note of caution needs to be added. While Cu is predicted to remain stable in the fcc structure up to at least 2.5 TPa,[18] Al and Pb are predicted and/or observed to exhibit structural phase transitions below 1 TPa. In Al the predicted sequence is fcc → hcp → bcc,[28] all of these occurring in the 0.1–1-TPa pressure range. Lead is known to undergo an fcc → hcp transition at 0.014 TPa (140 kbar),[29] and at least one additional transition is possible below 1 TPa.[18] On the other hand, the volume changes associated with these phase changes are very small, so that the fcc isotherms for Al and Pb should still be good approximations to the actual compression curves.

TABLE I. Room-temperature (300 K) isotherms for fcc Al, Cu, and Pb, as calculated from EOS 1. The respective equilibrium atomic volumes V_0 are the observed values of 112.0, 79.68, and 204.7 a.u.

	Pressure (TPa)[a]		
V/V_0	Al	Cu	Pb
0.304	1.018	···	1.000
0.337	0.754	···	0.700
0.370	0.568	···	0.500
0.403	0.435	···	0.364
0.436	0.338	1.004	0.270
0.469	0.265	0.728	0.204
0.502	0.211	0.542	0.156
0.535	0.168	0.414	0.121
0.568	0.135	0.324	0.094
0.601	0.108	0.255	···
0.634	0.086	0.201	···
0.667	···	0.158	···
0.700	···	0.124	···
0.733	···	0.095	···

[a]1 TPa = 10 Mbar.

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