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SUBMITTED TO APS Topical Conference on the Shock Compression of Condensed Matter
June 17-20, 1991
Williamsburg, VA.

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QUANTUM MECHANICAL EFFECTS ON THE SHOCK HUGONIOT

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Calculations of the locus of shock Hugoniot states of aluminum, using two equations of state that either omit or include a quantum mechanical treatment for the material's electronic excitations, will be presented. The difference between the loci will be analyzed in the context of a comparison between an ab initio quantum mechanical model and a semiclassical treatment of the electronic states. The theoretical results are compared with high pressure (4 - 300 Mbars) data.

INTRODUCTION

The effect of the specific spatial arrangement of the electrons in a material has well known effects on the strength of a solid and its response to modest compressive forces. It was expected that once a material was significantly compressed the electrons that participated in the atomic bonding would be more or less uniformly distributed over an atomic cell and the Thomas-Fermi model for atoms would be an accurate description for computing equations of state. A similar line of reasoning was invoked to use the model at high temperatures since it was expected that thermally excited electrons would be in "free-electron" like states.

Bandtheoretic calculations of the high pressure, zero temperature equation of state of aluminum have demonstrated that Thomas-Fermi theory was not applicable unless the material was compressed beyond eight times the normal crystalline density[1]. These calculations have two fundamental differences when compared with basic Thomas-Fermi theory: They determine the charge density from quantum mechanical calculations of electron wavefunctions and they impose boundary conditions on these wavefunctions that explicitly account for the influence of neighboring atoms and their electrons. However, bandtheory calculations at elevated temperatures have not born fruit because of computational difficulties.

The question about when Thomas-Fermi theory is appropriate at high temperatures began to be resolved when experimental data at extremely high pressures on the principle Hugoniot were measured[2,3,4]. Aluminum enjoys a large collection of data at pressures of a few to hundreds of megabars that form a basis against which different theories can be tested.

The purpose of this work is two fold. First, a comparison is made of the predictions of the principle shock Hugoniot for pressures that range between one Mbar and 5×10^4 Mbars for two theoretical models; one quantum mechanical, the atom-in-a-jellium model[5] (sometimes referred to as "INFERNO"); and one semiclassical, the TFD or Thomas-Fermi-Dirac theory. The second purpose is to compare these predictions with experimental data that have been obtained from experiments driven by nuclear explosions.

THE THEORETICAL MODELS

Both models have the common feature that they are self-consistent field theories whose electronic states are populated according to Fermi-Dirac statistics. The electronic charge density is computed for a spherically symmetric potential that includes the coulombic electron-electron and electron-nucleus interactions along with a local density approximation for the exchange-correlation potential. Each assumes the potential is contained in a sphere with the material density given by the mass of the atom divided by the sphere volume. The sphere is required to contain exactly enough electrons so that their charge cancels the nuclear charge. Neither model accounts for the detailed arrangement of neighboring atoms except in the sense that the atomic sphere is surrounded by a neutral background of uniform positive and negative charges.

From this common starting point, the task is to evaluate the contribution to the equation of state from the thermal and compressional excitation of the electrons computed classically a la Thomas-Fermi theory or quantum mechanically by explicitly finding wave solutions of the Dirac equation. The computed charge density is used in the self-consistent field procedure to minimize the atom's Helmholtz free energy.

In the case of the TFD model all electronic states form a continuum ranging over both negative and positive energies. For the quantum mechanical theory, negative energy states are discrete (bound states). The positive energy states form a continuum but they differ from those in the TFD model in that they are solutions of the Dirac equation and are not free-electron like but can exhibit resonance structure in the electron density of states.

Calculations of Helmholtz free energy for both theories were carried out for compressions $1/1000 \leq \eta \leq 100$ and for temperatures $0 \leq T \leq 10$ keV. The thermal part of the electronic free energy was obtained by subtracting from them from the model's zero Kelvin result.

Each of these sets of calculations were then added to a common zero Kelvin isotherm and a nuclear motion contribution. The zero Kelvin contribution is essentially that obtained from bandtheory, and the nuclear motion contribution is based on the Debye model for solids at low temperatures and extrapolates to an ideal gas of particles at high temperatures. At the lowest pressures, these two contributions dominate the Hugoniot but they become less important as the temperature increases. The total pressures and energies are then given by the usual superposition.

$$P(\rho,T) = P_c(\rho) + P_n(\rho,T) + P_e(\rho,T), \text{ and } E(\rho,T) = E_c(\rho) + E_n(\rho,T) + E_e(\rho,T),$$

where the subscripts "c" and "n" label the zero Kelvin and nuclear motion contributions respectively. The subscript "e" denotes the electronic contribution from either the INFERNO or the TFD theories.

THE RESULTS

Figure 1 shows the locus of shock Hugoniot pressures versus compression for the theories along with data (with their estimated uncertaintes). The difference between the theories begins to show for P > 3 Mbar. The quantum mechanical pressures have the feature that they oscillate about those from the TFD theory. Both theories reach the same asymptote (four times the initial density of 2.7 gm/cm^3) when the temperatures reach about 10 keV.

The quantum mechanical theory gives higher pressures for $2.0 < \eta < 3.4$ by as much as 17 percent. The INFERNO pressures are in excellent agreement with the experimental data, whereas the TFD-based pressures are too low.

For $\eta > 3.4$, the situation is reversed with the quantum mechanical theory giving lower pressures than the TFD result. Although the data for these higher compressions has large uncertainties, the agreement is best for the INFERNO model. For $4.6 < \eta < 4.9$, the theories show a "turnaround" with the INFERNO results showing an additional strong oscillation.

The pressure differences from the quantum mechanical theory along with the oscillatory feature at the "turnaround" density, can be explained by examining the heat capacity predicted by the two theories along the Hugoniot path. Figure 2 shows the electronic heat capacity at constant volume as a function of Hugoniot temperature. At low temperatures, the electronic heat capacity depends on the number of electrons that can be excited within an energy band of a few kT width about the Fermi energy. The TFD theory predicts a smooth increase since its density of electronic states is a simple monotonic function of energy. The

quantum mechanical theory's more complicated density of states function ties up electrons in continuum resonances and in discrete bound states separated from the continuum by energy gaps. This causes the heat capacity to rise more slowly than TFD theory until the temperature rises above various threshold values. At extremely high temperatures, when the thermal energy is sufficient to remove all the electrons from the negative energy states, both theories give an ideal gas result for 13 independent particles.

Between these temperature extremes, both theories show the effect of the coulomb potential of the nucleus binding the electrons, indicated by the peak in the heat capacity for temperatures in the neighborhood of 300 eV (for TFD theory) and 100 eV (for the quantum mechanical theory).

The quantum mechanical results exhibit additional features that are indicative of the discrete nature of the bound states. After peaking at about 100 eV. the heat capacity behaves as though it would like to asymptote to a value appropriate to a gas of 11 electrons. However, there are two remaining electrons residing in the 1s bound state that is separated from the rest of the states by about 1.5 keV. The presence of this "energy gap" produces the large peak in the heat capacity at about 500 eV, commonly known as a Schottky anomaly. The increase in the heat capacity between 10 eV and 100 eV is a manifestation of the same sort of phenomenon involving the eight electrons residing in the 2s and 2p bound states. It is not as dramatic since their energy levels are not as well separated from the continuum (about 78 and 40 eV respectively).

Both of these features are true quantum mechanical effects caused by the discrete nature of the states at negative energies. These oscillations in the heat capacity are replicated in the Hugoniot pressures through the Rankine-Hugoniot energy conservation condition: $E - E_i = (P + P_i)(v_i - v)/2$.

CONCLUSIONS

From these results for pressure and heat capacity, one concludes that in the case of compressed aluminum, quantum mechanical calculations for the equation of state are necessary to reproduce the experimental data and that temperatures of several kilovolts are required before a Thomas-Fermi theory can be considered appropriate.

*This work was performed under the auspices of the U.S. Department of Energy.

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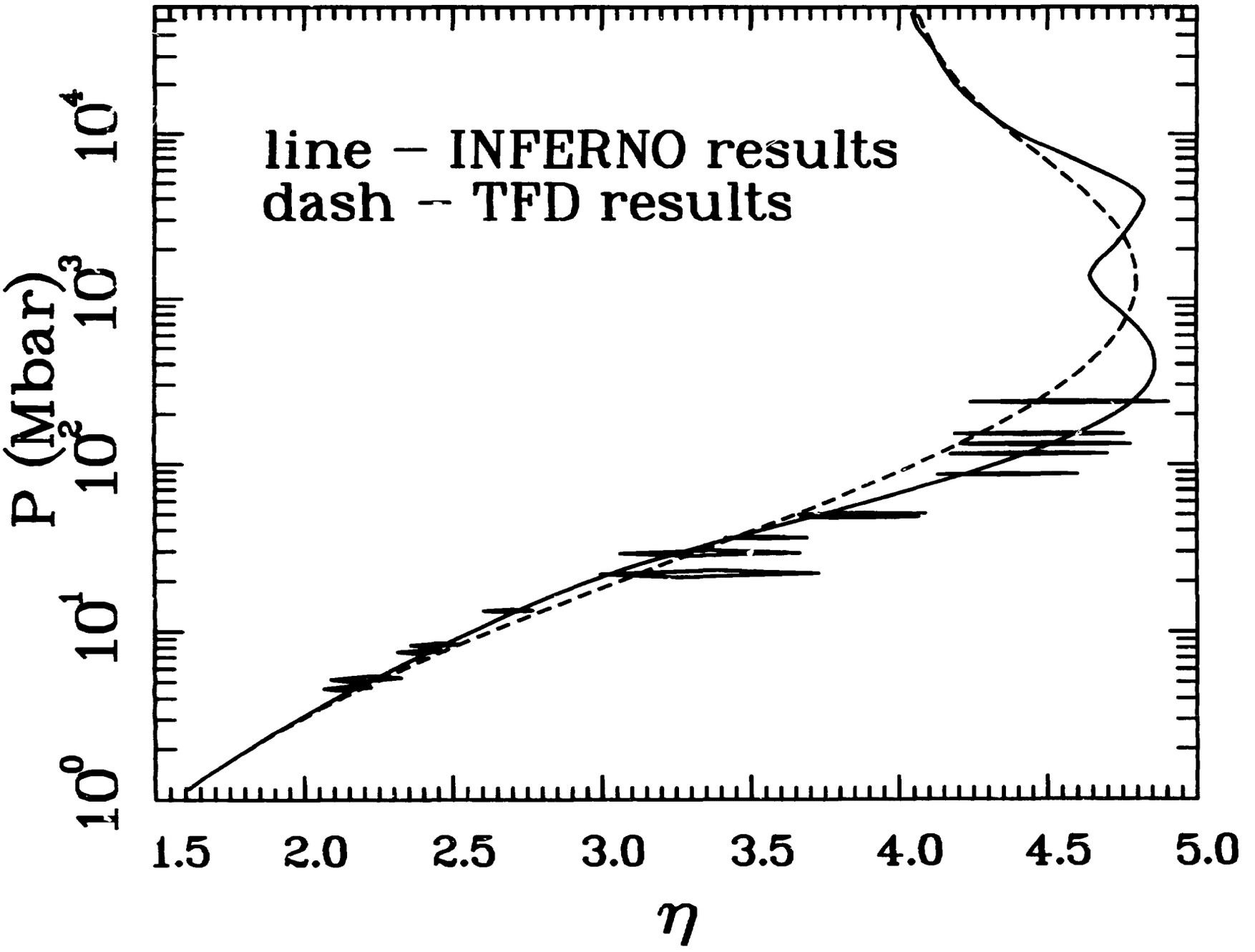
FIGURE CAPTIONS

FIGURE 1: Hugoniot Pressures vs Compression

FIGURE 2: Electronic Heat Capacity vs Temperature


line – INFERNO results
dash – TFD results
P (Mbar)
10^0
10^1
10^2
10^3
10^4
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
η

FICURE 1

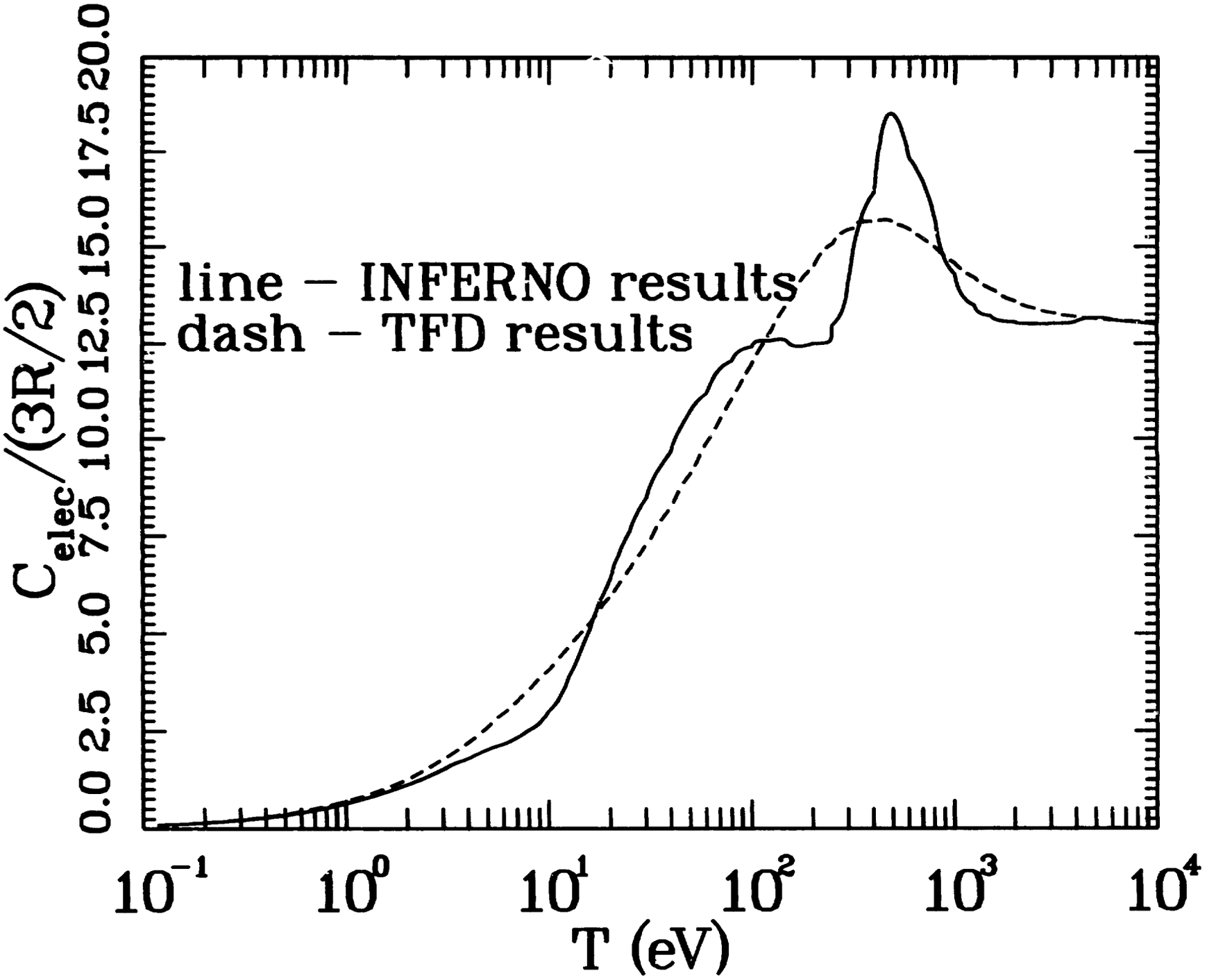

line – INFERNO results
dash – TFD results
$C_{elec}/(3R/2)$
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0
10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}
T (eV)

FIGURE 2