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INTRODUCTION

SHELL STRUCTURE EFFECTS IN COMPRESSED ALUMINUM*

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ABSTRACT

Self-consistent augmented-plane-wave (APW) calculations of the $T = 0$ aluminum pressure-volume isotherm are reported from normal density to essentially the free-electron limit, and are compared to predictions based on statistical models. Two distinct density regimes are observed in which the APW and statistical model results differ fundamentally. In the first the L shell electrons are pressure ionized and in the second the K shell electrons are pressure ionized. The first of these occurs in the range 5-75 TPa, and the second in the range $2.3 \times 10^3 - 1.1 \times 10^5$ TPa.

It is now possible to make equation of state measurements on compressed matter up to pressures in excess of 1 TPa, by carrying out shock compression studies on samples placed in the vicinity of underground explosions.¹ While these shock wave experiments measure very hot samples, current research in laser implosion techniques is aimed at reaching comparable compressions with much lower final temperatures.² This increasing experimental access to TPa and higher pressures provides the theoretician with an impetus to examine the problem of calculating very high pressure equations of state. To date, almost all theoretical determinations in this range have been based on statistical, Thomas-Fermi models.³⁻⁵ The Soviet shock compression work, for example, uses a comparative measurement technique which depends critically on a simplistic extrapolation of experimental data below 1 TPa over an order of magnitude in pressure to the predictions of statistical models above 10 TPa. The major disadvantage of the statistical models is that they ignore the electron shell structure of the atoms. Attempts to correct these models⁶ must be considered tentative. A more satisfactory treatment of electrons in solids rigorously including shell structure is the self-consistent augmented-plane-wave (APW) method. This method has become widely used in recent years to calculate $T = 0$ isotherms and cohesive energies of metals.

In the present work the APW method has been used to compute the $T = 0$ isotherm for aluminum from 0 - 10^6 TPa. Aluminum has been used as a standard in shock compression work,⁷ is amenable to pseudopotential calculations for additional comparison, and has a simple enough shell structure to permit a complete study. The present calculations show two well defined deviations

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in pressure from predictions of the statistical models for the aluminum isotherm. These occur as first the L and then the K electron shells are pressure ionized. The pressure deviation due to shell effects in the first case corresponds to an oscillation of about 13% amplitude about the statistical model pressures, and occurs over the range 5 - 75 TPa. This is precisely the pressure range over which the Soviet workers based their experimental analysis on the theoretical predictions of the statistical models, presuming them to be correct. The present work thus illustrates the need for improved equation of state calculations utilizing electron band theory. Nevertheless, because of their numerical simplicity, statistical theories remain extremely useful models of compressed matter. The major objective of this paper is to better define the range of validity of these models in comparison to a more rigorous theory.

METHOD

The self-consistent APW method has been described at length elsewhere.⁸ In these fcc calculations, the bands were treated with the equivalent of 256 points in the full Brillouin zone, the muffin-tin approximation was assumed, and the Kohn-Sham ($\alpha = 2/3$) exchange potential was used. Selected tests with 2048 points in the zone generally yielded pressures in excellent agreement with those obtained with 256 points.⁹ Estimates of the non-muffin-tin corrections to the pressure were made using the Thomas-Fermi charge density and appear to be quite small. In previous work¹⁰ on aluminum it was found that the percentage difference between pressures as calculated with the Kohn-Sham potential, the X_α potential ($\alpha = 0.72853$), and the Hedin-Lundqvist

exchange-correlation potential¹¹ decrease rapidly with compression. The latter two give pressures in very close agreement, with the Kohn-Sham pressures being somewhat larger. However even the largest difference amongst the three was seen to be only a few percent at 2 TPa. Thus all but the very lowest pressure results given in this paper should be insensitive to the choice of the exchange-correlation potential. In any case, since the statistical models do not include correlation effects, the choice of $\alpha = 2/3$ taken in this work is appropriate for carrying out detailed quantitative comparisons with predictions of the statistical models.

RESULTS

In Fig. 1, the radial electron density obtained from the APW calculations is shown for an atom in the solid under various degrees of compression. The curves are labelled by the reduced lattice constant a/a_N and terminate at half the near neighbor distance appropriate to each density. For comparison, the free atom case is also given, clearly showing the three shells (K,L,M) in the aluminum atom. It is apparent that at normal density ($a/a_N = 1$) the M shells are already ionized and free-electron like, while the inner K and L shells are intact and essentially the same as in the isolated atom. As the solid is compressed, one may conclude from Fig. 1 that the L-shells are pressure ionized for a/a_N between about 0.6 - 0.3; the K-shells, between about 0.2 - 0.1. The behavior of the band structure is consistent with this

interpretation. In the first range (see Figs. 2a and 2b) the narrow 2s and 2p bands broaden dramatically and the 3s band inverts (the X state becomes lower than the Γ state). In the second range (See Figs. 2c and 2d) the 1s band broadens and the 2s band inverts. As the free-electron limit is approached, $n(r) \sim \text{constant}$, and so $4\pi r^2 n(r)$ should become a straight line on a log-log plot, as seen in Fig. 1.

In Fig. 3, the APW pressure-volume isotherm is compared with predictions of the two statistical models in most frequent use for high pressure equation of state. They are the Thomas-Fermi-Dirac (TFD) model,⁵ which includes exchange in a self-consistent manner, and the Thomas-Fermi-Corrected (TFC) model⁴ which treats both quantum and exchange corrections, but only in leading order. All results are presented relative to the larger Thomas-Fermi pressures according to the reduced pressure ratio $(P_{TF}-P)/P_{TF}$. In the high density limit, the reduced pressure ratio for the TFD model is proportional to the exchange contribution to the pressure, while the TFC ratio is larger by 2/9-ths due to Kirzhnits' quantum correction. All of the statistical model pressures and their ratios are smooth, monotonic functions of the lattice constant. In contrast, the APW results show two clear modulations, the first for a/a_N between 0.55 - 0.35, and the second, between about 0.2 - 0.1. Given the behavior seen in Fig. 1, these effects are clearly due to pressure ionization of the L and K shells respectively. The first modulation corresponds to an oscillation of the APW pressure about the statistical model predictions with an amplitude of about 13%. This occurs throughout a region in which the absolute size of the APW pressure increases from 5 to 75 TPa, and so it should be realized that a direct plot of pressure vs. volume will not show dramatic behavior. Neither the TFC nor

TFD results exactly average the APW pressures in the vicinity of the first modulation, and are in worse agreement with the APW calculations on the low pressure side of this phenomenon. For example at $a/a_N = 0.6$, the TFC and TFD pressures are lower than the APW predictions by 32% and 16% respectively. The bulk modulus for both statistical models is also smaller than the APW value by about 20% for a/a_N in the range 0.8 - 0.6. It seems likely for aluminum that any statistical model which is not explicitly corrected for shell structure effects will contain inaccuracies in the pressure and bulk modulus of at least 13% and 20% respectively for pressures below 100 TPa.

Statistical models ignore shell structure, and are approximately correct for all densities. In contrast, pseudopotential theories treat the filled inner electron shells along with the nucleus as a fixed unit. They are potentially very accurate over limited density regions, but must break down at compressions where these ion cores come into contact. This is seen in Fig. 4 where the APW pressures are compared to predictions of second-order free-electron perturbation theory, using the Ashcroft empty-core pseudopotential,¹²

$$V(k) = - (8\pi Z_c/k^2) \cos(kr_c) .$$

The parameters chosen are shown in the figure, and correspond to the bare nucleus (true coulomb potential), nucleus shielded by the K shell, and shielded by both K and L shells. The latter (right hand dashed curve) is essentially an extension of the published calculations of Friedli and Ashcroft,¹³ which go up to only 0.3 TPa. Below 0.1 TPa, their results were found to be in excellent agreement with APW calculations using the Hedin-Lundqvist exchange-correlation

potential, and with shock-wave data reduced to zero temperature.¹⁰ By 0.3 TPa however, their pressures are about 9% larger than the Hedin-Lundqvist results, indicating the beginning of the deviation apparent in Fig. 4. While this initial effect may reflect inadequate treatment of the $k = 0$ terms in the perturbation expansion,¹⁴ the dramatic deviation from the APW results for $a/a_N < 0.6$ seems clearly to be the local breakdown of the pseudopotential approach itself occasioned by the overlap of the L shells. At somewhat higher compressions where the L shells have been fully ionized, it would seem that a pseudopotential treatment based on the nucleus plus screening by the K shell electrons should apply. At much higher pressures still, the ion core must be taken as the bare nucleus. These pseudopotential calculations are seen in Fig. 4 to be in modest agreement with the APW results over appropriate density regions, and of course, to break down outside of these regions. It should be noted that the pseudopotential calculations in Fig. 4 represent very simple treatments which have not been optimized in any way. More sophisticated efforts are likely to yield improved agreement with the APW results over larger density regions. Nevertheless, the qualitative point illustrated in Fig. 4 is the dramatic manner in which even such improved pseudopotential calculations can be expected to break down as the ion cores come into contact.

SUMMARY

This work provides quantitative results for shell structure effects in aluminum, which are quite consistent with conventional ideas. Electrons are not continuously ionized when matter is compressed, as the statistical models presume. Such ionization occurs only periodically as successively deeper electron

shells in neighboring atoms come into contact. In between these regions, the concept of a fixed ion core seems valid. This overall periodic behavior should be manifest to some degree in the equation of state. It is seen here for aluminum that the $T = 0$ pressure-volume isotherm shows modulations in the pressure which are as large as 13% due to these effects.

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NOTATION

a	=	lattice constant
a_N	=	7.65288 bohr (normal density, room temperature)
$n(r)$	=	electron density
$4\pi r^2 n(r)$	=	radial electron density
P_{APW}	=	self-consistent, augmented-plane-wave pressure
P_{TF}	=	Thomas-Fermi pressure
P_{TFC}	=	Thomas-Fermi-Corrected pressure
P_{TFD}	=	Thomas-Fermi-Dirac pressure
r_c	=	ion core radius in $V(k)$, given in bohr units
$V(k)$	=	Ashcroft empty-core pseudopotential
Z_c	=	ion core charge in $V(k)$

- α = exchange-correlation potential factor
 α_c = $4\pi r_c^2$ or as specified, given in bohr² units
 E_F = Fermi energy

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FIGURE CAPTIONS

- Fig. 1 Radial electron density as a function of radius for an aluminum atom in the solid under various degrees of compression. The free atom result is shown for comparison.
- Fig. 2 Aluminum band structure in the (100) direction at four densities: (a) $a/a_N = 0.6$, (b) $a/a_N = 0.3$, (c) $a/a_N = 0.2$, and (d) $a/a_N = 0.1$. Energies are given relative to the muffin-tin zero. The Fermi energy is given by the dashed lines.
- Fig. 3 Comparison of APW, TFC and TFD pressures for $T = 0$ aluminum. Pressures are given relative to P_{TF} as shown, and are plotted against reduced lattice constant. The data points indicate the actual APW calculations.
- Fig. 4 Comparison of APW and pseudopotential pressures. From left to right, the three pseudopotential calculations take the ion core to be the bare nucleus, nucleus shielded by K shell electrons, and nucleus shielded by both K and L shell electrons.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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