Systematics of the $s \rightarrow d$ and $p \rightarrow d$ electronic transition at high pressure for the elements I through La

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Static and shock-wave compression measurements as well as theoretical calculations show that I, Xe, Cs, Ba, and La exhibit similar behavior at high pressure determined by the transfer of electrons from 6s- or 5p-like states to nearby 5d conduction bands. In shock-wave experiments these transitions occur thermally, while in static experiments, they occur by transfer to degenerate states. Such transitions profoundly influence the high-pressure thermodynamic properties of these materials, as will be reviewed in this paper.

The neighboring elements I, Xe, Cs, Ba, and La form solids with quite dissimilar properties at low temperature and ambient pressure. Iodine exists in an insulating, diatomic molecular structure, Xe forms an insulating monatomic solid, while Cs, Ba, and La are metals. In spite of their differences, each of these materials exhibits similar behavior at high pressure due to common features of their electronic structure. Specifically, we refer to the shift under pressure of electrons from occupied 6s- or 5p-like states to nearby 5d bands. Such $s \rightarrow d$ and $p \rightarrow d$ electronic transitions have a profound effect on the high-pressure equations of state of these materials, which is clearly evident in static and shock-compression data, as has been analyzed by the present authors and co-workers in a series of papers on I,[1] Xe,[2] Cs,[3] and La.[4] Ba has been investigated by others.[5] Because each of these papers has dealt only with one specific material, the very general nature of the downward moving 5d band and its consequences may not be fully appreciated. The purpose of this paper is to briefly review these calculations in order to specifically illustrate the common features shared by all of these materials in regard to $s \rightarrow d$ and $p \rightarrow d$ electronic transition. For more detailed discussion and references pertaining to the individual materials, the reader should consult Refs. 1−5.

The general electronic structure appropriate for all of the solids I through La is shown schematically in Fig. 1, as a function of volume. The figure is valid for the monatomic phase of iodine that exists above 210 kbar,[6] although the indicated zero-pressure volume per atom is for the ambient diatomic phase. The feature to note is that with compression the energy of the lowest 5d levels falls below the bottom of the 6s band and continues to drop relative to the top of the 5p band, while that band itself is broadening. At very high compression the 5p to 5d gap closes and some 5d and 5p states become degenerate. The negatives of the volume derivatives of these electron energy levels may be roughly viewed as partial pressures. Thus the 5d electrons have initially lower partial pressures than do either the 5p or 6s electrons. As a result an electron transfer into a 5d state, either by thermal excitation or compression, leads to a decrease in that electron's contribution to the total pressure, and will be observed as a softening of the pressure-volume
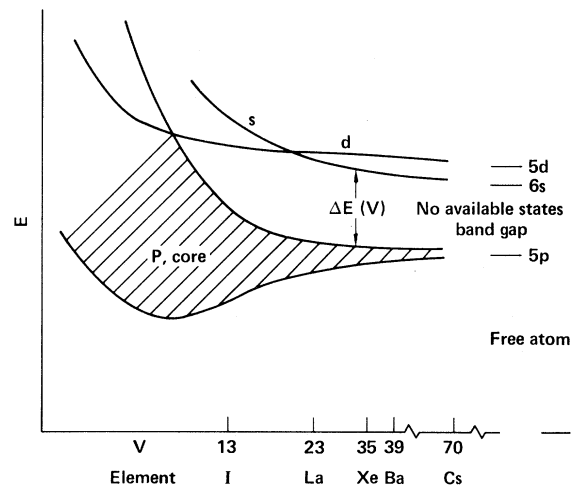

FIG. 1. Schematic energy-level diagram for the solid phase of iodine, xenon, cesium, barium, and lanthanum, arranged according to the zero-pressure volume V_0.

curve. Such an excitation-related softening is observed for all these elements. Softening is observed for I_2 (actually I) and Xe in shock-compression experiments as a result of thermal excitation of electrons across the wide band gap separating $5p$ and $5d$ bands. In static high-pressure experiments electrons in the $6s$ states of Cs, Ba, and La are transferred to the $5d$ states when the bottom of the nearby $5d$ band drops below the Fermi energy. This leads to a softening of the isotherms, which has been observed. At sufficiently high density the $6s$ band is emptied, and the isotherms are dominated by the repulsive pressure of the $5p$ and $5d$ electrons.

Xenon, with a filled $5p$ band and empty $6s$ and $5d$ conduction levels, is of particular interest. Its low-temperature and low-pressure thermodynamic properties are determined solely by the interactions of the $5s$ and $5p$ core electrons on neighboring atoms. Augmented-plane-wave (APW) band calculations predict that for an fcc lattice under compression, the energy levels of the d-like conduction band will overlap those of the $5p$ core and xenon will become metallic at a pressure in excess of 1.3 Mbar.[2] These theoretical results have been confirmed by the calculations of Ray et al.[7] and the predicted narrowing of the band gap is in very good agreement with the recent diamond-anvil-cell optical measurements up to 0.44 Mbar by Syassen[8(a)] and with those up to 0.55 Mbar by Asaumi et al.[8(b)] In 1979 Nelson and Ruoff[9] reported electrical-conductivity measurements that indicate an insulator-to-metal transition occurs at 0.33 Mbar at room temperature. Recently, Ruoff and co-workers[10] have reanalyzed this experimental configuration and now believe the transition pressure to be above a megabar and not inconsistent with Ref. 2.

CsI, which is isoelectronic with Xe, is expected to demonstrate similar electronic properties. Predictions have been made that CsI will become metallic at 0.8 Mbar as a result of the closure of the $5p$ to $5d$ gap.[11] Independently, Asaumi and Kondo[12] measured the effect of pressure up to 0.5 Mbar on the optical absorption edges of CsI with the use of a diamond anvil cell. An extrapolation of their results to higher pressures leads to an expected insulator-to-metal transition at about 0.7 Mbar, in reasonable agreement with the predicted value.

In shock-wave experiments with liquid xenon the high temperatures attained, of up to 20 000 K, are sufficient to transfer a considerable number of $5p$ electrons into the empty $6s$ and $5d$ levels at densities significantly less than that required for the conversion to the metallic state. A comparison of theoret-

ical and experimental results for the shock-compression pressure-volume curve, or Hugoniot curve, is shown in Fig. 2. Curve A is the calculated xenon Hugoniot with the use of the volume-dependent band gap and including the changes in electron partial pressures as comptued from APW theory. These results are in good agreement with experiment. Calculations that include no electronic excitation, the pure-insulator case, are shown by the uppermost curve C, and in curve B the calculations use only the normal solid xenon band gap and thus neglect the changes in electron partial pressures. Thus to compute the xenon Hugoniot it is necessary to include the decrease in electron partial pressure that occurs in transferring an electron from a $5p$ to a $5d$ state. Recently, Nellis, van Thiel, and Mitchell[13] extended the liquid-xenon shock-compression measurements to 1.3 Mbar, and their results are in good agreement with theoretical predictions.

Atomic iodine with one less electron than xenon has a nearly filled $5p^5$ shell. At equilibrium conditions the condensed phase is an insulating diatomic molecular solid. Under compression from $40-180$ kbar it undergoes a gradual transition to a conducting phase while still in a molecular state. Finally, at 210 kbar iodine transforms to a monatomic metal with a body-centered orthorhombic structure.[6] As in the case of xenon under compression, the bottom of the $5d$ band in iodine is expected to drop below
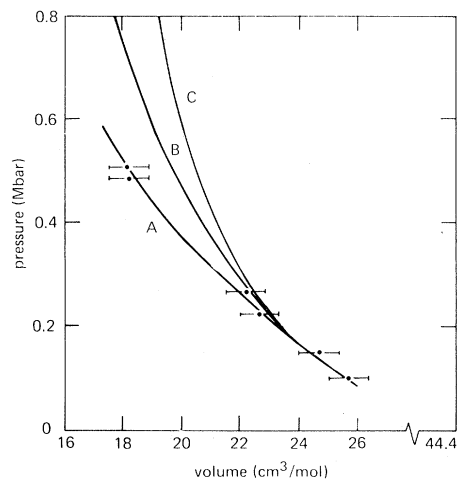

FIG. 2. Xenon Hugoniot, pressure vs volume. Bars are experimental results. See Ref. 2. Curves are theoretical results discussed in accompanying text. A includes electron band gaps obtained from APW results. B includes only band gap of normal density solid. C does not include any electron excitation (pure insulator).

the top of the 5p band. Our calculations suggest this will occur near 450 kbar for monatomic iodine. Even at this pressure, however, there is still a gap (the 5p band is only $\frac{5}{6}$ filled) from the Fermi level to the bottom of the 5d band. Nevertheless, under the high temperature (up to 30 000 K for iodine) existing in shock-wave compression, electrons are thermally excited to the 5d states, resulting in a softening of the Hugoniot curve. This can be seen in Fig. 3 where calculations including, and excluding, the 5d band are shown. Thus in iodine, as in xenon, the high-temperature, high-density properties are modified by the transfer of 5p electrons to 5d states with a decreased partial pressure.

For the metals Cs, Ba, and La, which have $1-3$ electrons, respectively, beyond the Xe core, the valence charge is already of mixed 6s and 5d character at ambient conditions. Compression causes previously unoccupied 5d levels to drop below the Fermi level, leading to a transfer of electrons from 6s to 5d states even at zero temperature. Such $s \rightarrow d$ transition can affect the equation of state in two different ways, as may be best understood from the Grüneisen-model expression for the finite-temperature pressure

$$P(V,T)=P_0(V)+3N\frac{k_BT}{V}\gamma(V) . \qquad (1)$$

Here $P_0(V)$ is the $T=0$ pressure for a static lattice of atoms, i.e., neglecting zero-point motion, the second term is the pressure contribution from thermal lattice vibrations, and electronic excitation is omitted. The lattice Grüneisen parameter $\gamma(V)$ is a measure of the volume rate of change of the lattice vibrational frequencies. The first, and most direct effect of $s \rightarrow d$ transition is simply a softening in $P_0(V)$ that arises from the difference in s and d partial pressures discussed earlier. This mechanism accounts for the unusually low bulk modulus observed for low pressure Cs as compared to expectations based on trends established by the lighter alkali metals.[14] The second type of $s \rightarrow d$ transition effect manifests itself through the lattice vibrational contribution, i.e., the $T\gamma(V)$ term in Eq. (1), and is believed[3] to be responsible for the fcc to fcc isostructural transition that occurs in room-temperature Cs at 42 kbar.[14] It is this indirect effect of the $s \rightarrow d$ transition through the lattice vibrations that leads to the most dramatic behavior in Cs, Ba, and La, and which we are primarily concerned with here.

The $T=0$ static lattice pressure $P_0(V)$ probes the forces that exist between atoms in the solid. Since the lattice vibrational frequencies are related to (length) derivatives of these forces, one might expect effects of the electronic transition that appear in $P_0(V)$ to also show up in $\gamma(V)$, and possibly to be amplified due to the additional length differentiation. This is indeed the case, and may be formalized by the Slater model[15] for the lattice Grüneisen parameter

$$\gamma(V)=-\frac{2}{3}-\frac{V}{2}\left[\left[\frac{\partial^2 P_0(V)}{\partial V^2}\right]_T \bigg/ \left[\frac{\partial P_0(V)}{\partial V}\right]_T\right] . \qquad (2)$$

As a specific illustration of this equation, we turn again to Cs. The dashed curve in Fig. 4 shows the results of linear muffin-tin orbital calculations[3] for the quantity $P_0(V)$, while the solid curve shows the total room-temperature pressure obtained from Eqs. (1) and (2). At both the lowest and highest pressures in Fig. 4, Eq. (2) yields a positive $\gamma(V)$ whose size (essentially the separation between the solid and dashed curves) reflects the degree of softness in $P_0(V)$. The Grüneisen parameter is small at low pressures where there is significant s-d transition, and it is large at high pressure where the transition is largely over, and where there is additional stiffening due to overlap of the 5p cores. The most interesting region, however, lies in the middle of the figure. The $s \rightarrow d$ transition is especially rapid in the vicinity of $V/V_0=0.43$, where a pocket of nearly pure 5d states near X_3 passes below the Fermi level. This causes sufficient softening in $P_0(V)$ so
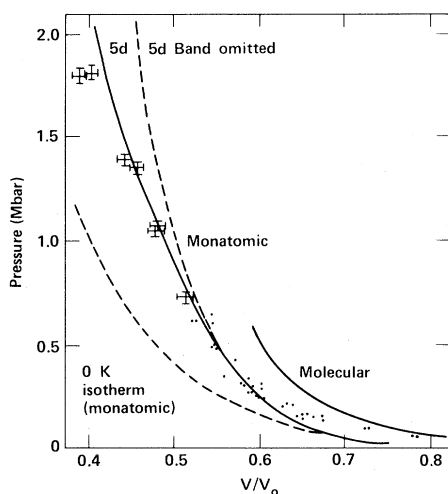

FIG. 3. Iodine Hugoniot, pressure vs relative volume. Calculations for the monatomic and molecular phases of iodine are compared to both the shock-wave data of Ref. 1 (bars) and to earlier work (dots).
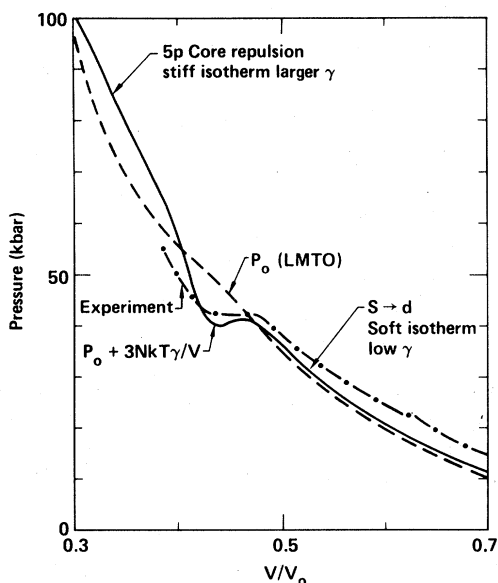
FIG. 4. Cesium 298-K pressure as a function of relative volume. In qualitative agreement with experiment, the theoretical $T=298$ K calculation (solid curve) shows an isostructural transition, i.e., the van der Waals loop. The difference between the solid curve and the $T=0$ static lattice pressure $P_0(V)$ (dashed curve) is proportional to γ.

as to create the region of negative curvature seen in the dashed curve in this region, which translates via Eq. (2) into a negative $\gamma(V)$, i.e., a region of *negative* thermal pressure. It is this effect which creates a van der Waals loop in the room-temperature isotherm (solid curve), implying a first-order isostructural phase transition in agreement with experiment. Furthermore, these simple model calculations based on Eq. (2) are also consistent with the observed dip in the Cs melting temperature[16] in the vicinity of the isostructural transition, as well as with the disappearance of the isostructural transition at low temperatures.[17] The major point to be made, however, is that the existence of the isostructural transition in Cs appears to be intimately related to the downward motion of the $5d$ band in this material, and the resulting $6s$ to $5d$ electronic transition.

The $s \rightarrow d$ transition in La is less dramatic than in Cs, but nevertheless, there are observable consequences.[4] Even at $P=0$ about two of the three valence electrons in La are already in d states, so that only a third of the valence charge is involved in the $s \rightarrow d$ transition. This is in contrast to Cs where all the conduction electrons (the single $6s$) are involved. Thus while there is softening of the pres-

sure as evidenced by the low $(P=0)$ bulk modulus, the Grüneisen parameter is small, but never negative. The important feature in La occurs at $V/V_0=0.5$ at which point the bottom of the $6s$ band rises above the Fermi level. While there is also stiffening due to overlap of the $5p$ cores, it is the stiffening in the P-V curve that arises from the *termination* of the "soft" $s \rightarrow d$ transition that leads to a particularly large peak in the lattice Grüneisen parameter. Since the Grüneisen parameter contributes to the total pressure through the second term in Eq. (1), it is clear that high temperatures are needed to detect this term against the large $P_0(V)$ "background." Shock compression offers just this feature.

Results of Hugoniot calculations[4] for La are shown in Fig. 5 (solid curve) and are compared to the experimental data. The calculations show an upward bend for $V/V_0 < 0.64$ in agreement with the data. This is due to the peak in γ. To demonstrate this more clearly, a second set of Hugoniot calculations were performed (dotted curve, Fig. 5) with the use of a γ with the peak arbitrarily removed. The difference between the solid and dotted curves thus specifically demonstrates the effect of the peak in γ. The dashed curves in the figure show the total Hugoniot pressure resolved into zero temperature $P_0(V)$, nuclear thermal $\Delta P_n = 3Nk_B T\gamma/V$, and also into an electron excitation contribution ΔP_e required at these high temperatures. The upward bend in the total (solid curve) can be seen to
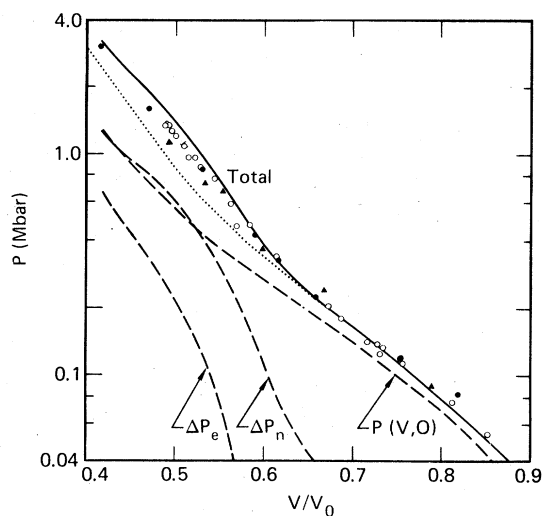

FIG. 5. Lanthanum Hugoniot, pressure vs volume. Calculations with the Slater model γ (solid curve) and a linear form of γ with the peak removed (dotted curve) are compared to the data in Ref. 22.

arise from ΔP_n, i.e., the $T\gamma$ term. Since the temperature along the Hugoniot itself depends on γ in a nonlinear manner, only a 13% reduction of the peak in γ would bring exact agreement with experiment in the region near $V/V_0=0.5$. The dotted curve was calculated with a γ smaller by a factor of more than 2 in this region. There is, therefore, unambiguous evidence in the shock data for a significant peak in γ for La which is a consequence of the $s\rightarrow d$ transition in this material.

Ba lies between Cs and La in the Periodic Table, with two electrons beyond the Xe core. While no equation-of-state calculations have been reported for Ba, Duthie and Pettifor[18] and Herbst[5] have found that there is an $s\rightarrow d$ transition in this material, as is to be expected. Furthermore, Ba appears to have an isostructural transition and a minimum in the melting temperature[19] analogous to Cs, quite likely due to this $s\rightarrow d$ transition. Additional evidence comes from shock-compression data. While we have previously shown shock-compression results for Xe, I, and La in a pressure-volume format, an equivalent representation more suited to the present discussion is to plot the actual dynamic properties measured for the shock wave. These are the velocity of the shock front (U_s) and the velocity imparted to the material after the shock front has passed, or the particle velocity (U_p). In the limit $U_p\rightarrow 0$, U_s becomes just zero-pressure sound speed in the material. The usefulness of this representation lies in the empirical fact that U_s is generally a linear function of U_p within a given phase, so that a change of slope often is indicative of a phase change or some rather abrupt change in physical properties. Figure 6 compares the shock data for Ba (Ref. 20), Cs (Ref. 21), and La (Ref. 22) in the U_s-U_p format. The solid lines represent experimental data, while the dashed lines connect the zero-pressure sound speed of Ba and Cs with the lowest experimental data point. The apparent change of slope in the La curve near $U_p=1$ km/s is
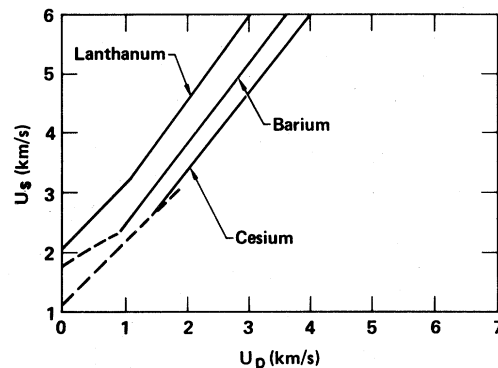

FIG. 6. Shock-wave data of Cs, Ba, and La, shock velocity (U_s) vs particle velocity (U_p). Solid lines are fits to experimental data and dashed lines are interpolations between the sound speed and the lowest data point.

due to the large peak in γ referred to earlier, which in turn comes from the termination of the $s\rightarrow d$ transition as discussed. Unfortunately, the available data for both Ba and Cs lie at pressures above their isostructural transitions. However, the slopes of the U_s-U_p curves for Ba and Cs are seen to be remarkably similar to that of La along the upper line segment, and the extrapolation of the lowest Ba and Cs data, back to the sound speed, points undeniably to the existence of a change in slope, similar to the one in La. As in the case of La, we interpret this change of slope as arising from the termination of $s\rightarrow d$ transition in these materials.

Shock compression experiments and theoretical studies on argon[23] to 0.91 Mbar and 26000 K indicate that it behaves similar to Xe. In Ar the characteristic excitation is from a $3p$ to $3d$ state. Consequently, we expect to observe a similar systematic behavior in the neighboring elements of Ar and Kr. Neon has no low-lying d states.

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