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PRESSURE-INDUCED CHANGES IN THE
ELECTRONIC STRUCTURE OF SOLIDS

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PRESSURE-INDUCED CHANGES IN THE ELECTRONIC STRUCTURE OF SOLIDS

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ABSTRACT

A variety of high-pressure metalization and metal-semimetal transitions, crystallographic phase transitions, and equation of state and lattice vibrational anomalies are reviewed in terms of the concepts of electronic transition and pressure-induced loss of covalency.

1. Introduction

There has been considerable experimental activity recently in the study of high-pressure insulator-metal and crystallographic phase transitions [1-6]. Many of these transitions have been associated either with electronic s-d transition or with loss of covalency. Theoretical work in the first category has focused on metalization of closed-shell systems such as Xe [7]; structural transitions in the alkali [8,9], alkaline earth [9], rare earth [9-11], and simple [12,13] metals; and lattice vibrational anomalies in Cs [14] and La [15]. Work in the second category has focused on structural transitions and metalization of group-IV semiconductors [16-20], and some diatomic

molecular solids [21]. The present paper reviews these phenomena in terms of the underlying changes in electronic structure associated with the concepts of electronic transition and pressure-induced loss of covalency.

In the remainder of the paper, theoretical techniques are reviewed in Section 2, and some background material is introduced in Section 3. Sections 4 and 5 present specific examples of effects associated with electronic s-d transition and the loss of covalency, respectively. Summary comments are given in Section 6.

2. Theoretical Techniques

Calculated quantities which will be involved in subsequent discussion are the total energy, pressure, and the electron energy bands for the materials under consideration. Invoking the Born-Oppenheimer approximation, the total energy of a solid at volume V and temperature T may be separated into a static-lattice contribution E_{SL} and a nuclear vibrational correction ΔE_n ,

$$E(V,T) = E_{SL}(V,T) + \Delta E_n(V,T), \quad (1)$$

and similarly for the pressure.

The static-lattice contributions and electron energy bands are routinely obtained at $T=0$ from local-density functional theory, as

described in detail elsewhere [22]. Generalization to finite temperature is straightforward [23], although required for the applications below only at temperatures achieved in shock compression.

The local-density total energy is often subdivided into two parts for the purposes of discussion. One is the electrostatic Madelung or Ewald energy. The second is variously called the electronic contribution in some ab initio pseudopotential calculations [16], the band structure energy in free-electron perturbation theory [24], or just the one-electron eigenvalue sum within the context of the force theorem [25] as applied to linear muffin-tin orbital [26] calculations. This second part is observed generally to favor structures with dips or gaps in their density of states at the Fermi level ϵ_F , a presumption which will be made in discussion below.

At temperatures where $\Delta E_n(V,T)$ and $\Delta P_n(V,T)$ are important, these quantities will be approximated by a high temperature Debye model so that $\Delta E_n(V,T) = 3k_B T$ and $\Delta P_n(V,T) = 3k_B T \gamma(V)/V$. Approximations to the lattice Grüneisen parameter $\gamma(V)$ may be obtained from the bulk modulus $B_{SL} = -V(\partial P_{SL}/\partial V)_T$ according to various prescriptions such as that of Slater (see, e.g. [22]).

$$\gamma(V) = -\frac{1}{6} - \frac{1}{2} \frac{\partial \ln B_{SL}}{\partial \ln V} \Big|_T \quad (2)$$

3. Background

The concepts of electronic transition, band broadening, and core orthogonality underlie many trends to be discussed in this paper, and are introduced here. The perspective taken will be to first view such phenomena in terms of unhybridized bands of well characterized angular momentum l , and then where necessary to introduce hybridization.

Figure 1 shows the unhybridized band edges for Al as a function of reduced volume V/V_0 (V_0 being the 1-atm volume), obtained from potentials generated in fully hybridized, self-consistent, augmented-plane-wave calculations [27]. Energies ϵ are measured from the muffin-tin zero, which decreases with compression. This and division by the Fermi energy ϵ_F to suppress the large band widths at small volumes, make the narrow core levels seem to diverge at the figure bottom.

3.1 Electronic transition

It is evident in fig. 1 that energy bands of low angular momentum character tend to move upwards relative to those of higher angular momentum character, as volume is reduced. Thus as 1-atm Al is compressed the 3s and 3p bands are seen to rise in energy, passing entirely above ϵ_F by $V/V_0 \sim 0.06$ at which point all three valence electrons have been transferred to the 3d band. Such electronic transition arises from the different scaling with volume of the kinetic

and potential energy contributions to the one-electron eigenvalues, $V^{-2/3}$ and $V^{-1/3}$, respectively. As the kinetic contributions win out at small volume, those states with fewer nodes in their radial wavefunctions, such as the 3d with none, are increasingly favored over those such as the 3s with two.

Electronic transition occurs not only by the transfer of electrons between states crossing at ϵ_F , but also via hybridization in the gradual alteration of the l composition of individual states lying below ϵ_F . These mechanisms usually result in increased d and f (mostly d) character at the expense of s and p (mostly s) character, thus the reference to s-d electronic transition.

3.2 Band broadening

As suggested by the sketch of the radial wavefunction $R_{nl}(r)$ shown in fig. 2, band broadening results from the growing differences between bonding (dotted curves, bottom of band) and antibonding (dashed curves, top of band) states as compression shrinks the Wigner-Seitz radius from S_1 to S_2 . The former state, for example, is energetically favored due to its increased buildup of electron density midway between the atoms, i.e. at S . The latter is penalized for the opposite reason.

Pressure ionization involves the broadening of core levels into bands, as compression brings a given set of R_{nl} orbitals on different

atoms into significant overlap. Subsequent compression will eventually initiate pressure ionization of the $R_{n-1,l}$ orbitals in similar manner. Due to the orthogonality of the two orbitals sketched in fig. 2, however, this will generally occur at S_3 inside the outer maximum of $R_{n,l}$. This is a region where the kinetic energy penalty incurred by $R_{n,l}$ in satisfying the boundary conditions dominates the behavior of all states in the band, and thus contributes to the upward motion of the n band as a whole. It is no accident in fig. 1 that both pressure ionization of the L shell and pronounced electronic s-d transition occur in the same region, $V/V_0 \sim 0.1$. The two phenomena are intimately related.

3.3 Orthogonality to the core

The far left of fig. 1 shows l -decomposed free-electron bands, due to the ultimate domination of the kinetic energy as $V \rightarrow 0$. Between regions of pressure ionization, different sets of l bands may also be positioned so as to approximate free-electron valence states, e.g. $V/V_0 = 1$ in fig. 1. While 1-atm Al is an excellent free-electron metal, however, other materials in equivalent regions are far less successful.

It is the requirement of orthogonality to the core reflected in the principal quantum number n which creates these differences. Thus, for example, the distance between s and p-band centers for such second period elements as Be is $\sim \frac{1}{2}$ that of free electrons [28]. The close

2s-2p separation is also well known to be responsible for the much stronger covalent bond in diamond-phase C than in diamond-phase Si. Similarly, for the 1-atm alkali and alkaline earth metals, the distance from the ns-band center to the bottom of the n-1,d band decreases steadily as n increases from 4 to 6 [28]. It is for this reason that, e.g., 1-atm Cs acts like a high pressure version of Rb, given that pressure also decreases this separation.

4. Electronic s-d transition

This Section describes changes in conductivity, structural phase transitions, and phonon anomalies which are attributed to electronic s-d transition.

4.1 Metals, semimetals, and insulators

The qualitative manner in which all of the rare gas solids will eventually metalize is correctly indicated by the behavior of the rare gas cores in fig. 1 for Al. Thus in the case of fcc Xe, predicted to become metallic in the range 130 to 200 GPa [7], the insulating gap at 1 atm is between the top of the filled 5p band, and the bottom of the empty 6s conduction band, analogous to the 2p-3s gap in fig. 1 near about $V/V_0 \sim 0.2$. In continuing analogy with the figure, however, it is the bottom of the empty 5d band in Xe which quickly drops below that of the 6s and becomes the eventual cause of metalization. Optical

absorption experiments in diamond anvil cells yield results consistent with theoretical calculations [7] of the decreasing gap, and extrapolate to metalization in the vicinity of 200 GPa [1]. Metalization has in fact been achieved for Xe, however, by the diamond indenter technique for which determination of pressure achieved is difficult [29].

The lighter rare gas solids with larger 1-atm insulating gaps will require considerably larger pressures to achieve metalization, e.g., 580 GPa (5.8 Mbar) for Ar [30]. He at 11.2 TPa (112 Mbar) [30] is qualitatively different, as it is the 2p levels which eventually overlap with the 1s band (see, fig. 1). Recent work of Hama [31] points out that the last holdout will certainly not be He, but rather Ne at 158 TPa! Metalization of closed-shell systems requires an empty conduction band of the next highest l , thus d for Ne, yet there is no nearby d band for Ne, as for Ar (3d), Kr (4d), and Xe (5d). Consequently, considerably larger compression is needed to bring the nearest available d band, the 3d, into overlap with the 3p.

The fact that for Ne the 3d band is simply the first d-like constituent of its l -decomposed continuum states makes it no less of a band than the 3d band lying above the Ar Fermi level, which becomes occupied at 1 atm in elements of only slightly greater atomic number. The difference is purely quantitative, in band mass (inverse width) and position. In fact for Ne and Ar it is largely position, as the 3d-band mass in 1-atm solid Ar is also nearly that of free electrons.

This point is also illustrated by the metal-semimetal-metal transitions which occur in compressed, divalent, fcc, nearly free-electron metals. Such behavior has been observed in Ca, Sr, and Yb, and would also have occurred in Ba and Eu had not these solids already transformed to the bcc structure by 1 atm [32]. There has been considerable theoretical discussion of these semimetal transitions, most recently by Skriver [9]. To emphasize the generality of the principles involved, however, this behavior will be introduced here for the case of Mg which, like Ne, has only a distant 3d band to drive the s-d transition.

Figure 3a gives a representative, fcc, nearly-free-electron (actually 1-atm Al) band structure, with the Fermi level placed for divalency. Only the slight splittings as for example between the X_4' and X_1 levels distinguish fig. 3a from a free-electron gas. The bottom of the 3d band is in the vicinity of the purely d-like X_3 level, however, through hybridization, the sd-hybrid X_1 level is also carried downward in the course of the s-d transition. As the mostly p-like dashed segment and the lower dotted segment approach, and pass by one another in the course of compression, they exchange connections with the rest of the band structure. This symmetry allowed exchange leaves ϵ_F cutting the bands at single point in fig. 3b, resulting in zero density of states (hybridization gap) at ϵ_F and semimetallic behavior. Further compression brings the X_3 level below ϵ_F , and metallic behavior returns.

In each of Ca, Sr, and Yb the s-d transition is already well underway at 1 atm, given the close separation of their relatively massive d bands to the Fermi level. Predicted and observed metal-semimetal-metal transitions occur at pressures under 30 GPa or so for these materials [9]. In sharp contrast, fcc Mg is not predicted [12] to become semimetallic until 2.4 TPa ($V/V_0=0.15$), returning to metallic conductivity around 6.2 TPa ($V/V_0=0.1$). As with the Ne metalization, this difference follows from the greater separation between Fermi level and d band that exists for the second and early third period elements.

A final example of the effects of s-d transition on conductivity is the prediction of an insulating region in highly compressed Ni [33]. At 34 TPa, the bottom of the 4s band should move above ϵ_F , thus completing the 4s to 3d electronic transition in this material. Left with a full 3d valence band below the resultant 3d to 4s gap, Ni is then an insulator. It is predicted to remain so until 51 TPa at which point the relative downward motion of the 4f band (next highest ϵ_F , as usual) restores metallic conductivity.

The s-d transition terminates at much lower pressures for elements on the left side of the periodic table, as for example in Cs (15 GPa), La (60 GPa), K (60 GPa), and Ca (135 GPa) [8,15]. These numbers suggest about a factor of two increase in completion pressure for each successive element to the right in a given period. Carrying out such

multiplication from K all the way to Ni yields a result consistent with the above 34 TPa.

4.2 Structural phase transitions

The heavier alkali and alkaline earth metals evolve from s-band metals at 1 atm to d-band transition metals by the conclusion of their s-d transitions. Such dramatic changes in bonding cause a host of structural phase transitions, which have been summarized as bcc $\rightarrow$ fcc $\rightarrow$ complex $\rightarrow$ Cs-IV and fcc $\rightarrow$ bcc $\rightarrow$ complex $\rightarrow$ Ba-IV for these monovalent [2,3] and divalent [4] groups, respectively. The latter sequence also applies in part to the two divalent rare earths (see, e.g. [34]), Eu and Yb, since the 4f electrons play no discernable role in structural stability of the rare earths in their low-pressure localized regime [35]. Indeed, the original trivalent rare earth series [36] of hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ fcc was the first structural sequence clearly demonstrated to be driven by s-d transition [11].

Both for different elements at 1 atm, and individual elements under pressure, these transitions correlate with the number of d-like valence electrons [9], and with the ratio R_i/S of the ion-core radius R_i to the Wigner-Seitz radius S [2-4,10]. Both parameters quantify the important feature, progress of the s-d transition; the first, in an obvious manner. The second measures the compression of the valence electrons, since they may be considered to be confined between the two radii [10].

Thus compression can arise either from pressure reduction of S , or from the increase in R_1/S at 1 atm on moving to heavier (lighter, for the rare earths) members of the sequence.

While the s - d transition is the ultimate cause, the details of the transitions vary from case to case. Skriver's explanation of the bcc to fcc transition in the alkali metals offers one example [9]. He argues that the Madelung energy stabilizes the bcc structure until the s - d transition has driven the empty, d -like, doubly-degenerate H_{12} level close to ϵ_F . By transforming to the fcc phase at this point, this level is in effect split into the fcc X_1 and X_3 levels, with the X_1 and neighboring levels carried far enough below ϵ_F to provide the energy gain required for the transition.

Even third period metals undergo structural phase transitions driven by s - d transition, including some at obtainable pressures, as the hcp to bcc transition in Mg first predicted theoretically [12] and recently observed in the vicinity of 50 GPa [37]. This transition results from a small distortion in Mg's nearly free-electron density of states, a distortion easily reproduced by the simplest forms of free-electron perturbation theory. Nonetheless, the cause of this distortion is the downward motion of the 3d band far above the Mg Fermi level which acts at a distance via hybridization to alter occupied states.

Figure 4 shows a plot of l -band centers [28] for Mg (solid lines) among other materials as a function of reduced volume V/V_0 . The centers are measured from the bottom of the valence s band, and scaled by the square of the Wigner-Seitz radius, so that the free-electron positions (dotted lines) are constant. While the l s and p bands are quite free-electron like as to be expected, the relative downward motion of the Mg 3d band is just as evident. Even though the divalent Fermi level is ~ 5.8 on the scale in fig. 4, far below the d-band center, the latter is sufficient to depress the sd-hybrid X_1 level (see fig. 3a) near ϵ_F by 5.8% at the volume $V/V_0=0.56$ calculated for the hcp $\rightarrow$ bcc transition. In contrast, the pure p-like X_4' level has changed by only 2.3% at this volume. Such differences are important, as the transition does not occur in calculations where d components have been removed from the basis [12].

4.3 Equation of state and phonon anomalies

Electronic transition may dramatically soften the pressure volume curve. This possibility is evident at $T=0$ by noting that $P_{SL} = -dE_{SL}/dV$ contains a sum over occupied states of $-d\epsilon_i(V)/dV$, where ϵ_i are the one-electron eigenvalues. The softening is caused by reduction of $-d\epsilon_i(V)/dV$ both by electron transfer at ϵ_F , which must occur into states of smaller negative slope, as well as by the growing depression of

levels below ϵ_F due to hybridization with the d band approaching from above.

Figure 5 shows calculated results for the bulk modulus B_{SL} of four metals, with progress of their s-d transitions indicated by volumes at which various levels (X_3 , Δ_1 , Γ_1) cross ϵ_F , and the growing core contributions to the total pressure indicated by percentages. Cesium already has an unusually low bulk modulus at 1 atm, even for an alkali metal, due to the hybridization mechanism just mentioned [38]. Far more dramatic, however, is the softening which occurs when the states near X_3 reach ϵ_F . These pure-d states are unable to hybridize with the 6s band, and lead to such abrupt electron transfer so as to drive dB_{SL}/dV temporarily negative. According to eq. (2) this implies a negative $\gamma(V)$, or phonon frequencies which temporarily decrease with compression.

It is this anomalous phonon behavior which drives the well known 4.2 GPa isostructural (fcc to fcc) transition in Cs [14]. As evident in fig. 6, the required van der Waals loop is introduced into the calculated 298-K pressure (solid curve) by the anomalous $3k_B T \gamma(V)/V$ phonon correction, and not by the $T=0$ static lattice pressure (dashed curve). Although crude, this model also accounts for the dip in the Cs melting curve, as well as the low temperature absence of the isostructural transition [14]. Moreover, recent measurements for Cs find a dramatic decrease $\gamma(V)$ just prior to the transition [39].

Barium has a similar dip in its melting curve, and was once thought to also have an isostructural transition [40]. More recent experiments suggest a symmetry for Ba-III lower than hcp, possibly due to a superlattice structure [4]. Precisely such features would be expected if the phonon softening causing the negative or small γ were to come from a soft mode in one part of the Brillouin zone. Thus the "complex" regions of the alkali and alkaline earth structural sequences are likely due to phonon anomalies brought on by extremely rapid s-d transition.

The strength of the pressure anomalies is governed by the fraction of valence electrons participating in the s-d transition. Thus for La with roughly two of its three valence electrons already in d states, the softening is far less dramatic than for Cs (see fig. 5), although values of the bulk modulus and Grüneisen parameter are low. More interesting for all of the rare earths is the end of the s-d transition, which begins to run out and then ends when the Δ_1 maximum and then Γ_1 pass above ϵ_F . The loss of this softening mechanism causes a rapid increase in B_{SL} for decreasing volume, as seen in fig. 5 for La between the Δ_1 and Γ_1 labels. The resultant phonon anomaly is a pronounced peak in γ which leads to a marked anomaly in the shock data for the rare earths [15].

Figure 5 also presents two normal materials, Al and Cu, for contrast. In the first case the s-d transition comes at such high pressures that percentage differences in $d\epsilon_1(V)/dV$ between s and d

states are small. In the second case, only a small fraction of the valence electrons are involved in the s-d transition.

5. Loss of covalency

Covalency is associated with structures of low-coordination number, the localization of bond charge between neighboring atoms, and gaps or significant depressions in the density of states separating bonding and antibonding levels. These characteristics are vulnerable to compression due to the buildup of large repulsive forces between the overly-close near neighbors in low-coordinated structures, the dominance of kinetic energy terms which favor delocalized charge, and to the broadening and shifts in relative position of the different l bands.

5.1 Group IV semiconductors

The semiconducting properties of the diamond-phase, group-IV elements are due to the well known hybridization gaps which occur at the Fermi levels of these materials. The origin of the gap is sketched in fig. 7 for Si, where fig. 7a denotes the isolated atomic-like 3s and 3p bands at expanded volumes. As the atoms are brought closer together these bands broaden to the point that the antibonding-3s Γ_2' and the bonding-3p Γ_{25}' levels pass by one another, causing the two dashed curves to cross. Given the common Δ_2' symmetries of the dashed curves,

such crossing must be avoided as in fig. 7b, thus introducing the shaded hybridization gap between the bonding and antibonding sp^3 levels.

The hybridization gap in diamond phase Si (from [20]) is shown as the shaded region in fig. 8, bounded below by the mostly p-like Γ_{25}' level, above by Γ_2' at expanded volumes. For $V/V_0 \leq 1.2$ it is bounded above by a Δ_1 level (omitted for visual clarity) lying slightly below the dashed X_1 curve, and briefly near $V/V_0 \sim 1.2$ by an L_1 level also not shown. Whereas at 1-atm the (local density functional) gap in diamond phase Si is about 4% of the valence band width, that in diamond phase C is about 20% of the valence band width. Moreover, the gap in C persists under compression, and is still about the same relative width by $V/V_0 = 0.26$ at $P = 5.7$ TPa.

It is well known that the strong covalent bond in C comes from the small separation of the carbon s and p levels, and the large separation between these and the nearest d levels. Both features are evident in fig. 4 by comparison of the band centers (obtained from fcc potentials) for C (short dashed lines) and Si (long dashed lines). In regard to the latter, the spd-hybrid Δ_1 level which bounds the hybridization gap from above should be depressed less in C than in Si. However, even removal of the d components from the Si calculations delays the Γ_{25}' - X_1 crossing only from $V/V_0 = 0.78$ to 0.58. The more significant cause of the Γ_{25}' - X_1 crossing in Si may be that Γ_{25}' is far more localized (almost no charge

in the tetrahedral interstitial sites) than X_1 (about half), and therefore pays a growing kinetic energy penalty with compression.

More important for C is the close separation of the s and p levels, leading to stronger hybridization and the larger gap in C as compared to Si. It is presumably this same reason which leads to a pronounced dip in the hcp Be density of states at ϵ_F in comparison to the nearly free-electron state density in Mg [41,12]. Not only are the s and p bands closer in second period elements, but they move even closer under compression. As evident from fig. 1, all p bands shift downwards under compression relative to s bands of the same principle quantum number. Figure 4 shows this process to be much more rapid for second period C than for third period Si. Given the predominantly p-like $\Gamma_{25'}$ level which bounds the diamond phase hybridization gap from below, this fact may contribute to the longevity of the C gap.

The total energy of group IV solids has been discussed in terms of the competition between an electronic contribution which favors low-coordination number structures and an Ewald contribution which favors higher coordination [16]. The former dominates in covalent bonded materials, one attribute of which is the gap or low state density at ϵ_F between bonding and antibonding levels. Given the loss of the gap for Si seen in fig. 8 for $V/V_0 < 0.8$, one might expect a diminished role for this electronic contribution in compressed Si, which is consistent with the observed structural transitions to phases of higher coordination.

Recent experiments [5,6] on Si up to 50 GPa have found the sequence diamond $\rightarrow$ β -tin $\rightarrow$ simple hexagonal $\rightarrow$ Si-VI $\rightarrow$ hcp, which is now theoretically calculated [16-20] except for the unknown Si-VI structure. Figure 9 illustrates the grouping of total energies (first calculated in [16], shown here from [20]) according to coordination number, with the simple cubic (6) intermediate between diamond (4) and the relatively close packed bcc (8), fcc(12), and hcp (12). The correlation is only approximate, as the very close β -tin (6) and simple hexagonal (8) structures would lie somewhat below that of simple cubic (sc) in this figure [16,19]. While β -tin is already metallic, the steady increase in coordination number throughout the above sequence suggests that the evolution from covalent to simple metallic binding is not completed until the final hcp phase, consistent with theoretical expectations for a simple metallic form of Si [12].

The situation for C is quite different, as might be expected given the persistence under compression of the larger gap in this material. Indeed the separations between diamond and sc, and between sc and the three structures above, are nearly an order of magnitude larger than seen in fig. 9. The best theoretical estimates at present suggest continued stability of the diamond phase until 1.2 TPa, at which point the so called B-8 structure should become more stable [17,18].

5.2 Diatomic molecular solids

The weak forces which perturb the intramolecular covalent bond at 1 atm in diatomic molecular solids, will evolve into stronger interactions under compression. In the absence of structural transition, these must eventually cause metalization via overlap of the broadening molecular energy bands. Dissociation may occur first, however, by transition to a structure (not necessarily monatomic) of greater coordination number. The triply-bonded N_2 and singly-bonded I_2 molecules will be contrasted in regard to the order expected for these two changes.

Recently it has been predicted that solid diatomic molecular nitrogen will dissociate at a pressure under 100 GPa [21]. While the calculations were carried out for an assumed sc form of the dissociated phase, slightly distorted sc phases are common to group-V elements, and the arsenic-like A7 distortion of sc has now been shown more stable in N than sc [42].

The relative stability of these structures can be understood from fig. 10, where the density of states for bcc, sc, and diamond phase N are plotted at a volume of $33.5 \text{ bohr}^3/\text{atom}$. These curves are quite similar to those for C, including a large hybridization gap for the diamond structure (dashed curve), which is now a disadvantage given the fifth electron in N which must go into the antibonding levels above the gap. The sc structure (solid curve) has a broad minimum in the vicinity of its ϵ_F (vertical solid line) which contributes to its lower total energy than bcc (dotted curve). This stability can be enhanced [42], by

introducing an A7 distortion of sc, which deepends the minimum at ε_F to the point of semimetallic behavior in P and As [43].

The situation is analogous to the group-IV elements where the electronic contribution to the total energy favors structures with low state density at ε_F and low-coordination number, while the Ewald energy favors high symmetry structures. This same competition drives the observed A7 phases of P, As, and Sb towards sc under compression, although As and Sb may transform to other structures before actually becoming sc [43]. With this qualification in mind, the group-V elements might be considered to follow the sequence diatomic (1) $\rightarrow$ orthorhombic (3) $\rightarrow$ A7 (3) $\rightarrow$ sc (6), generalized from [44]. The numbers in parentheses are coordination numbers, noting that an atom in a diatomic phase has only one near neighbor.

This group-V sequence is taken to begin with the N_2 dissociation, to possibly the semiconducting, orthorhombic, black phosphorous (also distorted sc [45]) phase. Solid iodine, on the other hand, achieves full metallic conductivity by 18 GPa while still in a diatomic phase [46]. Compression gradually moves the molecules very close to a monatomic arrangement, when dissociation to a Bravais body centered orthorhombic structure occurs at 21 GPa with a 4% volume change [46].

The difference between I_2 and N_2 is consistent with the fact that the singly-bonded halogen molecules had no other bonding alternatives,

whereas the triply-bonded N_2 molecules can polymerize to the singly-bonded, 3-fold coordinated networks of the distorted sc structures. Thus, the I_2 molecules are pushed close enough together to bring about metalization through molecular band overlap, and eventual destabilization of the diatomic bond. Long before this point, in the case of nitrogen, the polymerized state becomes thermodynamically more stable than the diatomic state. The diatomic state, however, should still be metastable beyond this point. Thus, given the 4 eV/atom difference in energy between the N_2 single and triple bond [45], there may be a considerable barrier to dissociation in the case of nitrogen.

6. Conclusions

Metalization of closed-shell systems and the conversion of alkali and alkaline earth metals into new high-pressure d-band metals are seen to follow from the shifts in relative positions of bands of different angular momentum character, reflecting the growing dominance of kinetic energy contributions with compression. Consideration of core orthogonality refines this perspective to explain differences between group members such as the immense pressures expected to achieve semimetallic Mg and to metalize C and Ne in comparison to heavier counterparts. While more complex, the pressure-induced loss of covalency also reflects the growing kinetic energy dominance in a

tendency for antibonding but delocalized states to be energetically favored over bonding but localized states.

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Figure Captions

Figure 1 Unhybridized band edges versus relative volume V/V_0 for Al.

Energies ϵ are divided by the Fermi energy ϵ_F .

Figure 2 Sketch of radial wavefunction $R_{nl}(r)$ versus r . Bonding (dotted curves) and antibonding (dashed curves) are shown at three Wigner-Seitz radii S . Tail of $R_{n-1,l}(r)$ occurs near maximum of $R_{nl}(r)$ due to orthogonality.

Figure 3 Metal-semimetal-metal transition in fcc divalent metals. (a) Dotted d and sd-hybrid curves move downward under compression relative to predominantly p-like dashed region. (b) Symmetry permitted interchange of dashed and lower dotted portions leaves Fermi level ϵ_F cutting bands at only a single point resulting in zero density of states at ϵ_F .

Figure 4 Valence band centers versus reduced volume V/V_0 for Mg (solid curves), Si (long-dash curves), and C (short-dash curves), and free electron case (dotted). Centers C_l are measured from bottom of s band B_s and multiplied by Wigner Seitz radius squared, following definitions in [28].

Figure 5 Bulk modulus versus relative volume V/V_0 for fcc Cs, La, Al, and Cu. Arrows labeled Γ_1 , Δ_1 , and X_3 show where these states cross the Fermi level. Percentages show core contribution to total pressure.

Figure 6 Pressure versus relative volume V/V_0 for Cs showing fcc $\rightarrow$ fcc

transition. Anomalous phonon contribution (bold arrow) creates van der Waals loop in 298-K pressure (solid curve). Maxwell construction (dotted line) for isostructural transition may be compared to experiment (dash-dot curve).

Figure 7 Sketch of hybridization gap in diamond-phase Si. (a) Separate 3s and 3p bands at expanded volumes broaden with compression. (b) After Γ_2' and Γ_{25}' levels cross, the two Δ_2' branches (dashed lines) mix to avoid crossing, creating shaded gap.

Figure 8 Symmetry levels in diamond-phase Si showing behavior of gap (shaded area) as a function of relative volume V/V_0 . Actual gap is slightly smaller as noted in text.

Figure 9 Total energy relative to isolated atoms of five structures of Si versus relative volume V/V_0 .

Figure 10 Density of states of bcc (dotted curve), sc (solid curve), and diamond (dashed curve) structures of N at 33.5 bohr³/atom. Vertical lines bordering right side of shaded areas show five-electron Fermi levels.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10