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Chemical interactions that govern the structures of metals

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Main Text

Abstract

Most metals adopt simple structures such as BCC, FCC and HCP in specific groupings across the Periodic Table, and many undergo transitions to surprisingly complex structures on compression, not expected from conventional free-electron-based theories of metals. First-principles calculations have been able to reproduce many observed structures and transitions, but a unified, predictive theory that underlies this behavior is not yet in hand. Discovered by analyzing the electronic properties of metals in various lattices over a broad range of sizes and geometries, a remarkably simple theory shows the stability of metal structures is governed by electrons occupying local interstitial orbitals and their strong chemical interactions. The theory provides a basis for predicting new structures in solids compounds and alloys over a broad range of conditions.

Significance Statement

The driving force determining the structures of simple metals has been a matter of debate for over a century, and has become more puzzling with the discovery of highly complex structures that emerge at high pressures in these materials. Conventional free-electron-based theories fail to provide a unified and predictive mechanism due to missing key components, i.e., local bonding and orbital interactions. These missing components can be represented by quasi-atoms and corresponding local orbitals, a consideration of which can explain the stability of both simple and complex different structures of elemental metals over a wide range of conditions. The results have implications for the behavior of more chemically complex materials, including alloys, intermetallics, hydrides, ionic compounds, and two-dimensional materials.

Main Text

Introduction

The modern theory of metals may be considered one of the great successes of quantum mechanics applied to solids (1, 2). This development over many decades has given rise to the modern band picture in physics, as implemented in numerous highly successful band-structure (*e.g.*, density-functional theory) methods that are now able to reproduce experimentally measured ground properties of alkali, alkaline earth, and transition metals. Despite this success, our understanding of the structural variations of elemental metals across the Periodic Table and as a function of thermodynamic conditions remains unsatisfied (2–5) within this “physics” (band) picture. In parallel with this dominant view of the field, alternative perspectives that begin with and focus on local bonding considerations were explored (6, 7), This “chemical” (bond) approach based on localized electron states has been revisited periodically in various contexts in later years (8–11) with no groundbreaking success. Here, we show that the electron occupation of the interstitial local orbitals *i.e.,* quasi-atom (11) orbitals, and their corresponding chemical interactions are the key factors that determine the structures of elemental metals and their evolutions under pressure.

The elemental metals are among the simplest solid forms of matter. However, their structures show an intricate variation across the periodic table, and many of them undergo transitions from high symmetry to complex structures on compression (2–5), A full theory of metals requires a unified framework to understand and predict all their structures, transitions, and stabilities (4, 5). Under ambient conditions, all alkali metals, Ba, and group 5 and 6 transition metals adopt a BCC structure; Be, Mg, group 3, 4, 7, and 8 transition metals (except Mn, Fe), Zn, and Cd, adopt an HCP structure; Ca, Sr, and most late transition metals (except Co) adopt an FCC structure (Fig. S1). Furthermore, on compression, alkali metals transform to an FCC structure, and Ba into an HCP structure, whereas many alkaline earth metals and group 4 transition metals, including Mg, Ca, Sr, Zr, and Hf, become BCC. While many transition metal structures remain “simple” up to very high pressures, the so-called “simple” *s*-block metals may pass through a series of complex structures with appreciable electron localization and low symmetry (5).

Modern band-structure methods can reproduce and have even predicted the existence and stability of many of the structures (12–22), but the origin of the phenomena and underlying mechanisms are not understood. Conventional band-structure approaches emphasize the delocalization aspect of the electrons in the metals (2, 23) and account for physical features such as band filling (14), Fermi surface and Brillouin zone topology (17–20), *s-d* transfer (24–26), etc. These approaches approximate various features of the electronic structure and often are limited to a group of metals or phenomena. For example, the concept of the Fermi surface nesting (19, 20, 27) has been used to explain structural changes in Li and K under pressure, but not in Na, because the Fermi surface of the latter remains spherical. (22) More recently, the existence of dynamical instabilities in which lattice becomes unstable with respect to atomic displacement has been investigated to explain structural changes in metals (20, 22, 24). However, instead of revealing the mechanism, these results actually added a new question, *i.e.,* why is the thermodynamic instability of simple metal structures often accompanied by dynamic instability? As a result, a predictive framework for structural patterns and their evolution remains to be developed. Here, we show that the structures of most metals and their pressure dependence can be explained surprisingly well by a simple theory, if we shift from a "physics" band-structure point of view to a "chemical" perspective that focuses on electron occupation of quasi-atom orbitals and their bonding interactions.

Results

Electron Localization and Close-Packed Structures

To understand and predict the full range of structures adopted by simple metals over a wide range of conditions, we first need to depart from the view of electrons occupying nearly-free delocalized states towards a picture of occupying local orbitals centered not at the atoms but at interstitials. The occupation of these interstitial orbitals, or quasi-atom orbitals, can be used to explain and predict the formation of high-pressure electrides (HPE) (11). In HPE, such as *hP*4 Na at 200 GPa (Figs. 1 Aa – Ad), the electron localization functions (ELFs) and the electron density show distinct maxima in the interstitial regions resulting from the occupation of quasi-atom orbitals and can therefore be viewed as anionic species in a solid compound (28–30).

This quasi-atom scenario can be extended to ambient or low-pressure conditions in cases where the interstitial orbitals are partially occupied, and the metals are viewed as "quasi-atom" compounds, *i.e.,* compounds consisting of quasi-atoms. For example, the ELFs of BCC Na at ambient pressure show maxima at the tetrahedral sites (E^T) (Fig. 1Ba), and FCC Na at 70 GPa show maxima at the octahedral (E^O) and E^T sites (Fig. 1Ca). Accounting for the quasi-atoms, metals in the FCC and HCP structures resemble binary compounds in NaCl and anti-NiAs structures, and BCC is isostructural to compounds such as sodalite CaH_6 (31) and SrB_2C_4 (32). Both BCC and FCC Na show very weak density maxima at interstitial sites and are not electrides (Fig. 1, Bb and Cb). On the other hand, the ELF values and patterns are consonant with the electron density differences between metal lattices and free atoms (Fig. 1, Bc and Cc), and are in accord with the crystalline wave functions (WF) showing occupation of quasi-atom orbitals (Fig. 1, Bd and Cd). Electron localization in interstitial regions has been noted in several cases of metals and metal clusters (9, 25, 33–37), but the occupation of the local quasi-atom orbitals and the significance of the corresponding chemical interactions have not been explored. We will show that the recognition of these effects lead to a general mechanism that explains the structural trends of metals.

Interstitial electron localization due to the occupation of local quasi-atom orbitals occurs in various metal lattices, despite whether or not they are the stable structures, and can also occur in metal sublattice structure (Fig. S2). The strength and location of the localization, as indicated by ELF (Figs. S3-5), show an orderly evolution across various elements, lattices, and volumes (Figs. S6-S12). With decreasing lattice constant, the electron localization tends to change from sites with fewer neighboring atoms to sites with more neighboring atoms. For example, in a simple cubic (SC) lattice, the electron occupation sites tend to change from the edge centers with 2 neighboring atoms to face centers with 4 neighboring atoms, and then to body centers with 8 neighboring atoms (Fig.

S6A). Similarly, electron localization in an FCC structure tends to change from bond centers with 2 neighboring atoms to tetrahedral sites with 4, and then to octahedral sites with 6 neighboring atoms (Fig. S6C).

The electron occupation of the localized quasi-atom orbitals and the corresponding chemical interactions between these orbitals determine the structure preference between FCC and HCP of a metal. Viewed from the standpoint of quasi-atoms, the major difference between the two structures is that the tetrahedral interstitials form pairs in HCP (Fig. S13A) but form a lattice in FCC (Fig. S13B). Electrons in close-packed Be and Mg highly localize at the E^T sites (Figs. 2, Aa and Ab), which causes very strong chemical E^T-E^T pair interactions in HCP that stabilize it (Fig. 2B). Similar chemical bonding interactions of quasi-atoms have been shown before in a Li HPE, in which the energy split of the bonding and anti-bonding states of two neighboring quasi-atoms is the origin of the small gap. (38, 39) Consequently, *c/a* ratios in Be and Mg are 1.568 and 1.626, both smaller than the ideal value of 1.633. In contrast, electrons in close-packed Ca (Fig. 2Ac) and Sr (Fig. 2Ad) localize mainly at the E^O sites (Fig. 2C) due to their weaker ion-electron interactions. Compared these elements with their related ionic compounds, and counting the localized electrons at E^O sites as partially charged anions, FCC corresponds to the NaCl structure, whereas HCP corresponds to the anti-NiAs. The electrostatic energy is lower in FCC because the Madelung constant in the NaCl structure is 1.748, which is significantly larger than the 1.693 of the anti-NiAs structure, which explains why Ca and Sr prefer FCC.

Like Be and Mg, electrons in close-packed transition metals of Groups 3 – 8 tend to localize on the E^T sites, causing their HCP structures stabilized by the strong pair interactions (Fig. 2D). Accordingly, the *c/*a ratios of their HCP structures are also below 1.633. Compared to alkaline earth metals, the octahedral site localizations are also large in the early transition metals, but the effect is not significant enough to reverse the FCC-HCP stability order. For the late transition metals, the ELF values become insignificant, indicating a weaker E^T-E^T pair interaction effect, and the FCC structure is stable for these metals (Fig. 2D).

Zn and Cd appear as a radical departure from the general trend, as they adopt the HCP structure with *c/a* ratios of 1.856 and 1.885, significantly higher (rather than lower) than the ideal value. This unusual behavior is due to the unique electron localization in these two elements. Compared with Be and Mg, electrons in HCP Zn and Cd highly localize not only on the E^T sites but also on the triangular sites in the hexagonal plane (Fig. 2E). These electrons show also strong bonding with the neighboring E^T sites. On the other hand, the chemical interactions between the localized electrons in neighboring hexagonal layers are much weaker. Thus, HCP Zn and Cd behave like layered compounds and show exceedingly large *c/a* ratios.

Sublattice Interactions and Stability of BCC

The stability of BCC is governed by a more intricate mechanism, but as we show below, is still based on the principles discussed above. To reveal that, we need to split the metal lattice into two equivalent sublattices (Fig. S13), *e.g.*, BCC to two SC lattices (Fig. S13C). While two SC lattices interpenetrate to form a BCC, the high symmetry points of one SC lattice including the lattice point (L), the edge center (E), the face center (F), and the body center (B) become the B, F, E, and the L points of another SC, respectively. Notably, the E^T point of a BCC lattice corresponds to geometrically identical quarter-center points (denoted as E^T_{BCC}) in both SC sublattices with coordinates of (0.25, 0.5, 0) (Fig. S13C).

The sublattices of a metal structure might impose strong interactions with each other due to the match or mismatch of their interstitial electron localizations (Fig. 3). These interactions can be summarized into three representative cases, including a matching, a mismatching, and a repulsing case. In a perfect matching case (Fig. 3B), the interstitial electron localization in each sublattice reproduces that of the whole; therefore, ELF patterns and WFs of all lattices (the sublattices and

the whole) match. As a result, the chemical interactions between the sublattices enhance the stability of the structure. In a mismatching case (Fig. 3C), the electron localization of each sublattice either shifts away or contributes only part (half) of the electron distribution of the whole lattice, usually corresponding to a less stable structure. In a repulsing case (Fig. 3D), the electrons in one sublattice localize on the atom sites of another sublattice (counter-atom), imposing repulsive forces due to interactions with the ion core and destabilizing the corresponding metal structure. Compared with FCC and HCP, BCC can be divided into two sublattices that do not contain nearest neighbors (Fig. S13C), in which case sublattice interaction effects are the strongest, and the metal will adopt BCC if its lattice constant is at or very close to the matching point.

The ELFs of alkali metals in BCC structures show either maxima (in the case of Li and Cs) or large values at the $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ sites (in the case of Na, K, and Rb) (Figs. 4A, 4Ca – 4Cc). In the latter case, a small compression causes a shift of ELF maxima from edge centers to $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ sites. For example, Na, K, and Rb reach perfect sublattice matching at 5.0, 1.0, and 0.7 GPa (Fig. 4Cc). In contrast, the BCC structures of most alkaline earth metals are well away from the sublattice matching point, and their ELF at $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ sites are distinctly smaller than those at the edge centers (Figs. 4B, 4Cd, 4Ce). Therefore, most alkali metals adopt the BCC structure, whereas most alkaline earth metals adopt close-packed structures at or near ambient conditions. Furthermore, Li and Ba have distinctly different electron localization features compared with other elements in the same group. In contrast to other alkaline earth metals, the sublattice ELF of BCC Ba maximizes at $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ sites (Fig. 4Cf), consistent with its stability in the BCC structure. On the other hand, although Li BCC is close to the sublattice matching point, its ELF at the body centers is very high, which gives rise to strong sublattice repulsions (Fig. 4A). Therefore, lattice matching and repulsive effects coexist in BCC Li at zero pressure, compromising its stability.

For transition metals, the electron localization in interstitial regions, as quantified by the ELF, decreases with an increasing number of *d* electrons because of the increase in the nuclear attraction potential (Figs. 4D – 4F, Fig. S14). For early transition metals such as Y and Zr, ELF values are high at all high symmetry points, including the body centers, indicating strong sublattice repulsions that destabilize the BCC structure (Figs. 4D, 4F, S11B, S14D). On the other hand, the sublattice of their HCP structures exhibits ELF maxima located close to the octahedral sites of the original HCP structure, indicating strong sublattice matching that stabilizes HCP (Figs. 4E, 4G, S14F). For elements in Groups 5 and 6 (*e.g.,* Nb and Mo), the BCC sublattice ELF at the body centers decreases more significantly than at other points, greatly reducing sublattice repulsions (Figs. S14B, S14E). Furthermore, their BCC lattices are close to the sublattice matching point, gaining notable stability against other structures. Later transition metals exhibit lower interstitial localization and, therefore, weaker sublattice interactions and tend to adopt close-packed structures. On compression, some transition metals, such as Zr and Hf, transform to BCC (5) because the increasing localizations at sublattice face centers move it closer to the sublattice matching point (Figs. S15A, S15B). Group 5 and 6 transition metals remain in the BCC structure up to a very high-pressure (40) as a result of very low compressibility and weak dependence of the ELF on the lattice constant (Figs. S15C, S15D).

Structures of Metals under Pressure

Any theory of metals must also explain their structure changes under pressure. It has long been known, for example, that alkali metals transform from BCC to FCC, whereas alkaline metals change from HCP or FCC to BCC. Sodium crystallizes in the BCC structure at ambient pressure and transforms to FCC at 65 GPa, and to *cI*16 at 104 GPa (5, 28, 41). The perfect matching point of BCC Na occurs at 5 GPa, at which point the ELF maximizes at the $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ of both SC sublattices (Figs. 5, A and C). With increasing pressure, the electron localization in the SC lattice shifts from $\mathrm{E}_{\mathrm{BCC}}^{\mathrm{T}}$ to F and then to C sites, lowering the matching effect and enhancing the sublattice repulsions. At higher pressure of 65 GPa, the sublattice repulsion is strong enough to destabilize BCC. On the other hand, the electrons in one sublattice of FCC Na localize mainly between two Na atoms of the

other sublattice, consistent with the stability of FCC Na at this pressure (Figs. 5, B and C). At a higher pressure of 110 GPa, FCC Na develops strong enough sublattice repulsions to destabilize it (Fig. 5C). Similar trends are also found for other alkali metals (*e.g.,* K; Fig. S16).

Sublattice interactions also explain the fact that most alkaline earth metals transform from FCC or HCP to BCC under pressure, a trend that is opposite to that of alkali metals. Alkaline earth metals, except Ba (Fig. S17), exhibit large ELF values at the edge centers of SC lattice (BCC sublattice) at ambient and low pressures (*e.g.,* Ca; Fig. S18) (5, 42). The BCC structure has no advantage over FCC in sublattice matching. On compression, however, the ELF maxima change from edge centers to the face centers in a specific pressure range (*e.g.,* Ca at 10 GPa; Fig. S18), the ELF maximum locates at $\mathrm{E}^{\mathrm{T}}_{\mathrm{BCC}}$, showing perfect sublattice matching, which drives the phase transition from FCC to BCC. At around 30 GPa, BCC loses its stability due to the sublattice repulsion (Fig. S18). In contrast to other alkaline earth metals, Ba shows a reverse structure transformation under pressure from BCC to HCP. This can be understood by the observation of a matching point for its BCC structure at zero pressure which is removed with increasing sublattice repulsion on compression (Fig. S17).

Sublattice repulsions also cause dynamic instabilities in high symmetry structures and the formation of the "open" structures of alkali and alkaline earth metals at high pressure because by moving the atoms away from the high symmetry points these structures can avoid sublattice repulsion and lower their energy. For example, the *cI*16 structure of Na that is stable from 104 GPa to 117 GPa can be viewed as distorted BCC. Splitting *cI*16 into sublattices analogues to the corresponding BCC, the ELF maxima of one sublattice are no longer located on the lattice points of the second sublattice. The distance between ELF maxima and the lattice point changes with pressure (Fig. 5D). For Na, at 110 GPa, this distance is about 0.5 Å, large enough to effectively avoid sublattice repulsion.

Electron occupation at the interstitial orbitals is a key feature of these 'open' structures under pressure. Moreover, when the quasi-atoms orbitals are partially occupied, the complex structures that emerge are also analogous to solid compounds. For example, *cI*16 Na can be viewed as a binary compound of A_4B_3 composition with the $I\bar{4}3d$ structure such as Ba_4As_3, in which As atoms occupy the positions of the quasi-atoms (Fig. 5E, S16A, S19B). Similarly, the *tI*19 Na host-guest structure is isostructural to the ternary compound Ti_5CuSb_2, in which Cu and Sb play the roles of two types of quasi-atoms inside *tI*19 structure (Fig. 5F, S19C, S19D). The actual charge transfer from metals to quasi-atoms in all phases is comparable, as calculated by integrated charge difference (ICD), especially at lower pressures (Fig. 5G, S19G). Charge transfer increases in high-pressure structures above 120 GPa because of the relative energy change of the atomic and quasi-atomic orbitals. Heavier alkali and alkaline earth metals (as well as transition metals) show different pressure dependencies of their charge transfer into interstitial sites because of the increasing electron transfer into their *d* orbitals. This strong degree of charge transfer into interstitial sites and *d* orbitals also reduces the sublattice repulsions. The theory thus also explains the re-emergence of higher symmetry structures such as HCP and *hP*4 at very high compressions predicted in structure-search calculations and documented experimentally (28).

Similar structure evolution under pressure could happen to metals showing very weak electron localizations at the interstitial sites, because the reduced volume under pressure might largely enhance the quasi-atom orbital occupation, causing stronger sub-lattice interactions. A good example is Al. Being a *p*-block metal, Al exhibits high electron density due to its large number of valence electrons but shows very weak electron localization at the interstitial sites at ambient conditions (Fig. S20) and is stable in FCC structure as many late transition metals. Under increasing pressure Al undergoes structural transformations similar to *s*-block metals but over a much broader scale due to its weaker pressure-dependent change in electron localization (Fig. S20).

Discussion

A remarkably general theory is presented that demonstrates the important role of chemical interactions in governing the structures and properties of metals. Using as a starting point the local electronic states of metals and their sublattices instead of the traditional free electron perspective of metals, the work extends previous approaches that recognize the potential role of off-atom electron densities and molecular interactions in crystalline solids (9–11, 15, 16, 43). Our theory provides a quantitative explanation for both the structural diversity of metals across the periodic table under ambient conditions and their complex changes under compression. As such, the approach resolves long-standing questions about elemental structures (2, 3) and recently observed remarkable phenomena associated with structures of metals (4, 5) By showing that it is not the density but the occupation of local orbitals that govern structural preference and evolution under pressure, the approach also provides a basis for predicting of a potentially wide range of phenomena in materials beyond simple metals, including superhydrides, ionic compounds, intermetallics, and novel low-dimensional materials. By considering local quantum orbitals at interstitial sites (quasi-atoms) in such compounds, empirical approaches can be replaced by this quantitative and predicted chemical theory. The theory can also be extended beyond perfect crystals and can be applied to defects, dislocations, grain boundaries, phase transitions, and other dynamic processes, as far as these structural and kinetic phenomena change the quasi-atom orbitals and their occupation. The full potential of the approach is yet to be thoroughly explored.

Our concept of sublattice interactions in metals proposed here may be compared to earlier efforts to understand the structure and stability of ionic compounds in terms of anions inserted into pre-existing metal lattices (43–46). The approaches were inspired by the observations that metal sublattices in many compounds, notably CaO and AlX_3 (X=F, Cl, Br), often resemble the stable structure of metals under ambient or even high pressure conditions (44–46, 33). The later Anions-in-Metallic-Matrices (AMM) approach (43, 47–50) correlated ELF maxima and high electron densities at interstitial sites of metal lattices with nonmetal atoms insertion to form these compound structures. Extending the present interstitial electron localization and local quasi-atom orbital theory, we developed an empirical bond theory approach that explains the formation of superhydrides (51). Notably, the theory explains the general trend that metals close to the s-d border tend to form stable superhydrides (52–57) (Fig. S21).

Materials and Methods

Density functional calculations. The underlying first-principles density functional theory (DFT) calculations were carried out by using the plane-wave pseudopotential method as implemented in Vienna *ab initio* Simulation Package (VASP) (58, 59). The electron-ion interactions were described by the projector augmented wave pseudopotentials(60, 61) and the used valence electrons are listed in Table 1. We used the generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof(62) as exchange-correlation functional. A kinetic energy cutoff of 520 eV was adopted for wave-function expansion. The *k*-point meshes with interval smaller than $2\pi \times 0.03$ Å^{-1} for electronic Brillouin zone to ensure that all enthalpy calculations converged within 0.02 eV/atom. The high-throughput first-principles calculations were performed by using the Jilin Artificial-intelligence aided Materials-design Integrated Package (JAMIP), which is an open-source artificial-intelligence-aided data-driven infrastructure designed purposely for computational materials informatics(63).

Electronic structure analyses. The electronic structures of metal superhydrides were calculated and analyzed by use of several methods, including the Bader's Quantum Theory of Atoms in Molecules (QTAIM)(64), the Electron Localization Function (ELF)(65), the Crystalline Orbital Hamiltonian Population (COHP) and integrated COHP (ICOHP)(66), etc. A systematic study of the Electron Localization Functions at the high symmetry points of metals and their sublattices as functions of lattice lengths are shown in Fig. S6 to S13.

Integrated charge differences. For a given metal, two electron charge densities are calculated, including a self-consistent charge density (M_{scf}) and a superposition of atomic charge density (M_{atom}). The charge difference is then calculated as $\Delta\rho = \rho(M_{scf}) - \rho(M_{atom})$. The $\Delta\rho=0$ surface divides the crystal space into different regions surrounding the atomic sites and the interstitials. $\Delta\rho$ has positive maxima or negative minima in these regions. The integrated Charge Differences (ICD) are defined for each region by integrating $\Delta\rho$ inside the region. The structures under study may contain one or more types of interstitial quasi-atoms. Their ICDs are calculated separately.

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Figures and Tables

FIG. 1. Electron localization and sublattice interactions in metals. (Aa – Ad) ELF, charge density, the charge density difference between metal lattice and metal atoms, and a crystal orbital at the G point of Na in *hP*4 structure at 200 GPa. (Ba – Bd) The same as (Aa – Ad) for Na in BCC structure at ambient pressure. (Ca – Cd) The same as (Aa – Ad) for Na in FCC structure at 70 GPa. The color code in (Ab, Bb, Cb) is adjusted to signify the maxima.

FIG. 2. ELF distributions in metals. (Aa – Ad) ELF graphs showing ELF values at the high symmetry points in FCC Be, Mg, Ca, and Sr. The vertical lines show the pressures of the FCC lattices. (Ba – Bb) ELFs of Be in FCC and HCP structures. They show large electron localization at E^T sites that form an SC lattice in FCC and pairs in HCP structures. (Ca – Cb) ELFs of Ca and Sr in FCC and HCP structures. They show large electron localization at E^O sites. (D) The ELF values at the E^T sites of various metals in FCC structure. (Ea – Eb) The top and the side views of ELF of Zn in HCP structure.

FIG. 3. Sublattice interactions in metals. (Aa) Schematic diagram of electron localization in metal lattices. (Ab) ELF shows the electron localization in BCC Na at 5 GPa. (B) Schematic of sublattice matching in a metal lattice. (Ba – Bb) Two sublattices that perfectly match that of the central metal lattice as shown in (Aa). (Bc) SC Na as a sublattice of BCC Na at 5 GPa. (C) Schematic of partial sublattice matching. (Ca – Cb) The electron localization in two sublattices that partially match that of the metal lattice. (Cc) SC Na as a sublattice of BCC Na at zero pressure. (D) Schematic of sublattice repulsion. (Da – Db) Two sublattices that repulse each other. (Dc) SC Na as a sublattice of BCC Na at 70 GPa.

Fig. 4. Stability of BCC structure at zero pressure unless otherwise specified. (A) ELF/ELF(edge center) ratios in the sublattices of alkali metals having BCC structures. (B) ELF/ELF(edge center) ratios in the sublattices of alkaline earth metals in BCC structure. (C) Sublattice ELF of selected alkali and alkaline metals having BCC structures, including Li, Cs, K at 1 GPa, Be, Ca, and Ba. (D) Sublattice ELF values at high symmetry points of 5^{th}-row transition metals in the BCC structure. (E) Sublattice ELF values at high symmetry points of 5^{th}-row transition metals in FCC. (F) ELF of 4*d* transition metals BCC sublattice (SC). From left to right are Y, Nb, Tc, Rh, and Ag. (G) ELF of Y HCP sublattice. The green and the grey balls show the atoms in two sublattices. The ELF of the sublattice has maxima at the E^O sites of the HCP, showing sublattice matching.

FIG. 5. Metals under pressure. (A) The ELF values at the high symmetry points of SC Na with lattice parameters of 2.5 to 4.5 Å. The vertical lines show the pressures of BCC with the same lattice parameters. SC is the sublattice of BCC. (B) The ELF values at the high symmetry points of a Na lattice that is the sublattice of FCC, with lattice parameters from 3.0 to 6.0 Å. The vertical lines show the pressures of the corresponding FCC lattice. (C) Schematic evolution of ELF of BCC and FCC Na sublattice with increasing pressure. (D) Reduction of the sublattice repulsion in *cI*19 Na due to its deviation from an ideal BCC structure. The inset shows the sublattice lattice and its ELF maximum at the body center. The plot shows the distances between the ELF maximum (green spot) generated by one sublattice (yellow balls) and the closest Na atom from the other sublattice (grey ball). At about 60 GPa, *cI*19 reduces to a perfect BCC structure, and the ELF maximum starts to shift away from body centers to face centers and then to edge centers with decreasing pressure. (E) Ba_4As_3 in $I\bar{4}3d$ structure, in their yellow and red balls represent the Ba and the As atoms. (F) Structure of Ti_5CuSb_2, where the light blue balls represent Ti atoms, and the dark blue and brown balls represent Cu and Sb atoms, respectively. (G) The calculated integrated charge differences (see Methodology Section) of Na atoms in various structures as functions of pressure.

Table 1. The valence configurations of the pseudopotentials used in our solid-state DFT calculations.

Li	Be										
$1s^2 2s^1$	$1s^2 2s^2$										
Na	Mg										
$2p^6 3s^1$	$2p^6 3s^2$										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3s^2 3p^6 4s^1$	$3p^6 4s^2$	$3s^2 3p^6 3d^1 4s^2$	$3p^6 3d^2 4s^2$	$3p^6 3d^3 4s^2$	$3p^6 3d^5 4s^1$	$3p^6 3d^5 4s^2$	$3p^6 3d^6 4s^2$	$3p^6 3d^7 4s^2$	$3p^6 3d^8 4s^2$	$3p^6 3d^{10} 4s^1$	$3p^6 3d^{10} 4s^2$
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4s^2 4p^6 5s^1$	$4s^2 4p^6 5s^2$	$4s^2 4p^6 4d^1 5s^2$	$4s^2 4p^6 4d^2 5s^2$	$4s^2 4p^6 4d^3 5s^2$	$4p^6 4d^5 5s^1$	$4p^6 4d^5 5s^2$	$4p^6 4d^6 5s^2$	$4p^6 4d^7 5s^2$	$4p^6 4d^8 5s^2$	$4p^6 4d^{10} 5s^1$	$4d^{10} 5s^2$
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$5s^2 5p^6 6s^1$	$5s^2 5p^6 6s^2$	$5s^2 5p^6 5d^1 6s^2$	$5p^6 5d^2 6s^2$	$5p^6 5d^3 6s^2$	$5p^6 5d^5 6s^1$	$5p^6 5d^5 6s^2$	$5p^6 5d^6 6s^2$	$5d^7 6s^2$	$5p^6 5d^8 6s^2$	$5d^{10} 6s^1$	$5d^{10} 6s^2$