The electron localizations and the corresponding chemical interactions that govern the structures of elemental metals

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Abstract

Elemental metals adopt and transform between very simple structures in an intriguing pattern under zero and high compressions. While most transition metals are only found in simple structures so far, the “simple” alkali and alkaline earth metals may transform into complicated structures under high pressure. Here, by employing large scale high-throughput calculations, we demonstrate a surprisingly simple and all-embracing theory that emerges after replacing the orthodox metallic bond concept with a new perspective emphasizing the electron localizations at the interstitials. The success of this exceedingly simple and universal mechanism demonstrates that intricate chemistry resides in metals and governs their fundamental properties, and the chemical interactions of localized electrons inside metals are necessary additions to the current chemical bond theory of metals and solid states.
**Introduction**

Elemental metals are the simplest solid form of matter, and yet their structure variations across the periodic table and under pressure remain puzzling for many decades. [1–4] They adopt and transform between very simple structures in an intriguing pattern under zero and high compressions. Despite that quantum mechanics calculations can reproduce and/or predict most of the metal structures [5,6] and many aspects of the electronic structures have been applied to explain the results, [7–14] we do not know a simple, real-space and universal mechanism that directly elucidates all the structure patterns and evolutions.

A unified and complete theory of metals needs to explain following structural patterns and changes. [4,3] Under ambient condition, all alkali metals, Ba, and group 5 and 6 transition metals (TM) adopt body-centered cubic (BCC) structure; Be, Mg, group 3, 4, 7 and 8 TMs (except Mn, Fe), Zn, and Cd, adopt hexagonal close packed (HCP) structure; Ca, Sr and most late TMs (except Co) adopt face centered cubic (FCC) structure (Fig. S1). When being compressed, alkali metals transform into FCC, Ba into HCP, whereas many alkaline earth metals and group 4 TMs including Mg, Ca, Sr, Zr and Hf become BCC. While most TM structures remain “simple” up to very high pressure, the “simple” s-block metals may pass through a series of complex structures with large interstitials and low symmetry.

Most existing theories emphasize electron delocalization in metals [2,15] and consider corresponding physical features such as band filling, [7] Fermi surface and Brillouin zone topology, [9–12] s-d transfer, [16–18] etc. These theories are intricate and entangle various features of the electronic structures, and often are limited for a group of metals or phenomena. For example, the Fermi surface nesting [11,12,19] may explain the structural change of Li and K under pressure but not Na, because the Fermi surface of the latter remains spherical. [14] More recently, dynamic instability, i.e. metal lattice becomes unstable against lattice deformation and shift of atomic positions, has been investigated to explain the change of simple structures of metals. [12,14,16] However, instead of revealing the mechanism, these studies actually added a new question to the conundrum, i.e. why is the thermodynamic instability of simple metal structures often accompanied by a dynamic instability?

**Electron localizations and subset interactions**

The first step toward understanding metal structures is investigating the localization of electrons inside metals. This electron localizations in interstitial regions have been well recognized (Fig. 1Aa), [20–25,17] especially for extreme cases in which the electron density shows distinct maxima in the interstitials, such as hP4 Na at 200 GPa (Fig. 1Ab and 1Ac) and can therefore be viewed as anionic species in a solid compound. [26–28] The formation of these high pressure electrides (HPE) can be explained by the occupation of the quantum orbitals locating at the interstitial sites (Fig. 1Ad), i.e. quasiatoms, which promotes the distribution of electrons into the interstitial regions. [29] This scenario of quasi-atoms can be extrapolated to lower and ambient pressures, at which the interstitial orbitals might be partially occupied and the metals can be viewed as “electron” compounds. For example, the Electron Localization Functions (ELF) of BCC and FCC Na at 0 and 70
GPa show maxima at the tetrahedral sites (E$^T$) and the octahedral (E$^O$) and E$^T$ sites (Fig. 1Ba and 1Ca), respectively. However, both BCC and FCC Na show very weak density maxima at interstitial sites and are not electrides (Fig. 1Bb and 1Cb). On the other hand, the ELF values and patterns are consonant with the electron density differences between metal lattices and free atoms (Fig. 1Bc and 1Cc) and accord with the occupation of quasi-atom orbitals (Fig. 1Bd and 1Cd).

Figure 1. Electron localizations and subset interactions in metals. Aa – Ad. ELF, charge density, charge density difference, and a crystal orbital at the $\Gamma$ point of Na in $hP4$ structure at 200 GPa. The color code in Ab is adjusted to signify the maxima. 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. Da. The schematic of electron localization in a metal lattice. Db. The ELF that shows the electron localization in BCC Na at 5 GPa. Ea – Eb. The schematics of electron localization in two subsets that perfectly match that of the whole metal lattice as shown in Da. Ec. The ELF of SC Na as a subset of BCC Na at 5 GPa. F | Schematic of partial subset matching. Fa – Fb. The schematics of electron localization in two subsets that partially match that of the whole metal lattice.Fc. The ELF of SC Na as a subset of BCC Na at 0 GPa. G | Schematic of subset repulsion. Ga – Gb. The schematics of electron localization in two subsets that repulse each other. Gc. The ELF of SC Na as a subset of BCC Na at 70 GPa.

Similar electron localizations could occur to various metal lattices, stable or unstable, and their locations and strengths show orderly evolutions upon volume changes (Fig. S2). While lattice constants decrease, the electron localizations tend to change from sites with less neighboring atoms to sites with more neighboring atoms. For example, in a simple cubic (SC) lattice, the electron localization sites tend to change from the edge centers with 2 neighboring atoms to face centers with 4, and then to body centers with 8 neighboring atoms (Fig. S2A). Similarly, the electron localizations in an FCC lattice tend to change from bond centers with 2 neighboring atoms, to tetrahedral sites with 4 and then to octahedral sites with 6 neighboring atoms (Fig. S2C).
The next step to understand the structures of metals is to split the lattice to two equivalent subsets (Fig. S3), e.g., BCC to two simple cubic (SC) lattices (Fig. S3a). While interposing two SC lattices to form a BCC lattice, the four high symmetry points including the lattice point (L), the edge center (E), the face center (F) and the body center (C) of one SC match the C, F, E, and the L points of another SC, respectively. Especially, the $E^T$ point of the BCC corresponds to geometrically identical quarter-center points (denoted as $E^T_{BCC}$) in SC with coordinates of $(0.25,0.5, 0)$. These subsets might impose strong interactions to each other due to the match or mismatch of their electron localizations (Figs. 1D – 1G). In a perfect matching case (Fig. 1E), the electron localizations in two subsets coincide and match that of the whole metal lattice, and the interactions between the subsets enhances the stability of the whole lattice. In many cases, the electron localizations of each subset contribute only to part (half) of the electron distributions of the whole lattice (Fig. 1F). In another important case, the electrons in one subset localize right on the atom sites of another subset (counter-atom), it will impose strong repulsive forces due to their large interactions with the ion core, destabilizing the corresponding metal structure (Fig. 1G).

**Structure trends determined by subset interactions**

Subset interactions can explain many structure trends of metals, e.g., Na adopts BCC at 0 GPa and transforms into FCC and then to c/16 at 65 and 104 GPa. BCC Na is stable in low pressure range because of subset matching. [4,26] The perfect matching point happens at 5 GPa, at which the ELF maximizes at the $E^T_{BCC}$ points of both SC lattices (Figs. 2a and 2b). Under increasing pressure, the electron localization in SC lattice shifts from $E^T_{BCC}$ to F and then to C points, lowering the matching effect and enhancing the subset repulsions. At 70 GPa, the subset repulsion is strong enough to destabilize the Na BCC structure. On the other hand, the electrons in one subset of FCC Na localize mainly in the region between two Na atoms in another subset, agreeing with the fact that FCC Na is stable at this pressure (Figs. 2b and 2c). While pressure further increases to 110 GPa, FCC Na develops strong enough subset repulsions that destabilize it (Fig. 2b). Similar trends are also found for other alkali metals such as K (Fig. S4).

Subset repulsions also cause the dynamic instabilities of BCC and FCC Na under pressures beyond 70 and 110 GPa, because moving the atoms away from the high symmetry points in these structures can avoid the subset repulsion and lower the energy. Indeed, driven by the subset repulsions, many high-pressure structures that are distortions of high symmetry structures, may form. For example, the c/16 structure of Na that is stable from 104 GPa to 117 GPa is a distorted BCC. While splitting c/16 into subsets in parallel to the corresponding BCC, the ELF maxima of one subset no longer locate on the lattice points of another subset. The distance between ELF maxima and the lattice point changes with pressure (Fig. 2d). For Na, at 110 GPa, this distance is about 0.5 Å, large enough to effectively avoid the subset repulsion.
Alkaline metals, except Ba, show large ELF values at the edge centers of BCC subsets at ambient and low pressures (Fig. S5 for Ca). [4] It has no advantage over FCC structure in subset matching. However, under compression, the ELF maxima changes from edge centers to the face centers and in certain pressure range, around 10 GPa for Ca (Fig. S5), the ELF maximum locates at $E^{1}_{\text{BCC}}$, showing a perfect subset matching, which drives the phase transition from FCC to BCC. While the pressure goes up to about 30 GPa, BCC also loses its stability due to the subset repulsion (Fig. S5). The early experiments on high pressure Ca observed a transition from BCC to SC structure at 27 GPa, but was later replaced by the $\beta$–tin structure that is a distorted SC. [30] A SC lattice can be split perfectly into two interposing FCC subsets. At 30 GPa, these two FCC subsets exhibit strong repulsive interactions because their ELF maxima locate right on the lattice points of each other. The distortion of the $\beta$–tin structures shift the ELF maxima away from the lattice points, significantly reducing the subset repulsion. In contrast to all other alkaline metals, BCC Ba show perfect subset matching at 0 GPa and therefore is stable (Fig. S6a and S6b). [4,31] At 5.5 GPa, it transforms into HCP structure due to the increasing subset repulsion in BCC. Its FCC structure is not as stable as HCP also because of the subset repulsion that can be avoided in HCP structure due to lower symmetry (Fig. S6).

Figure 2. Subset interactions and the structures of metals. a. The ELF values at the high symmetry points of SC Na with unit lengths from 2.5 to 4.5 Å. The vertical lines show the pressures
of the BCC lattice that has the same unit lengths. SC is the subset of BCC. b. Schematics that shows the evolution of ELF of BCC and FCC Na subsets under increasing pressure. c. The ELF values at the high symmetry points of a Na lattice that is the subset of an FCC lattice, with unit lengths from 3.0 to 6.0 Å. The vertical lines show the pressures of the corresponding FCC lattice that has the same unit lengths. d. Reduction of the subset repulsion in cI19 Na due to its deviation from an ideal BCC structure. The inset shows the subset lattice and its ELF maximum at the body center. The plot shows the distances between the ELF maximum (green spot) generated by one subset (yellow balls) and the closest Na atom from the other subset (grey ball). At about 60 GPa, cI19 reduces to a perfect BCC structure, and the ELF maximum start to shift away from body centers to face centers and then to edge centers while pressure further decreases. e. ELF of 4d transition metals BCC subset (SC). From left to right are Y, Nb, Tc, Rh, and Ag. f. ELF of Y HCP subset. The green and the grey balls show the atoms in two subsets. The ELF of the subset has maxima at the E\textsuperscript{O} sites of the HCP, showing subset matching.

For transition metals, the electron localizations in interstitial regions as quantized by ELF decrease with increasing number of d electrons because of the increasing nuclear attraction potential (Fig. 2e and S7). For early transition metals such as Y and Zr, ELF values are high at all high symmetry points including the body centers, indicating strong subset repulsions that destabilize the BCC structure (S7b,S7d). On the other hand, the subsets of their HCP lattice exhibit ELF maxima locating close to the octahedral sites of the original HCP lattice, indicating a strong subset matching that stabilizes HCP (Fig. 2f, S7f). For group 5 and 6 elements, such as Nb and Mo, the BCC subset ELF at body centers decreases more significantly than other points, greatly reducing the subset repulsions (Fig. S7b, S7e). Furthermore, their BCC lattices are close to the subset matching point, gaining notable stability against other structures. Later TMs show lower interstitial localization and therefore weaker subset interactions and tend to adopt close packed structures. While being compressed, some TMs such as Zr and Hf, transform into BCC structure [4] because the increasing localizations at subset face centers move it closer to subset matching point (Figs. S8a, S8b). Group 5 and 6 TMs remains in BCC structures up to very high pressure, [32] which is the result of very low compressibility and the slow change of ELF under the change of lattice constant (Figs. S8c, S8d).

**Localized electrons in FCC and HCP structures**

The preference between FCC and HCP structures in various metals is also a long-time puzzle. We show here it is determined by the electron localizations at the E\textsuperscript{T} sites and especially the fact that they can chemically interact. E\textsuperscript{T} interstitials form pairs in HCP (Fig. S3e) in contrast to forming SC lattice in FCC (Fig. S3f). Electrons in close packed Be and Mg highly localize at the tetrahedral sites (Fig. 3Aa, 3Ab), which causes very strong chemical E\textsuperscript{T}-E\textsuperscript{T} pair interactions in HCP and stabilize it (Fig. 3B). Similar pair interactions of quasi-atoms have been shown before. [33,34] Consequently, c/a ratios in Be and Mg are 1.568 and 1.626 that are considerably smaller than the ideal value of 1.633. In contrast, electrons in close packed Ca (Fig. 3Ac) and Sr (Fig. 3Ad) localize mainly at E\textsuperscript{O} sites (Fig. 3C) due to their weaker ion-electron forces. By analogy with ionic compounds, FCC corresponds to NaCl structure whereas HCP corresponds to anti-NiAs structure, while counting the localized electrons at E\textsuperscript{O} sites as partially charged anions. The electrostatic energy is lower in FCC, because the Madelung constant in NaCl structure is 1.748 that is significantly larger than that of 1.693 in anti-NiAs structure, which explains why Ca and
Sr prefer FCC.

Similar to Be and Mg, electrons in close packed TM of group 3 – 8 tend to localize on $E^T$ sites, and their HCP structures could be stabilized by the strong pair interactions (Fig. 3D). Due to the same reason, the $c/a$ ratios of their HCP structure are smaller than 1.633. Comparing with alkaline metals, the octahedral site localizations are also large in early transition metals, but its effect is not significant enough to flip the FCC-HCP stability order. For late transition metals, the ELF values become insignificant, indicating a weaker $E^T$-$E^T$ pair interaction effect, and FCC structure is stable for these metals (Fig. 3D).

Figure 3. **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 lattice that has the same unit lengths. **Ba and Bb.** ELFs of Be in FCC and HCP structures. They show large electron localizations at $E^T$ sites that forms a SC lattice in FCC and pairs in HCP structures. **Ca andCb.** ELFs of Ca and Sr in FCC and HCP structures. They show large electron localizations at $E^O$ sites. **D.** The ELF values at the $E^T$ sites of various metals in FCC structure. **Ea and Eb.** The top and the side views of ELF of Zn in HCP structure.

Zn and Cd appear as a radical departure from the general trend, as they adopt HCP structure with $c/a$ ratios of 1.856 and 1.885 that significantly higher instead of lower than the ideal value. This unusual behavior is due to the unique electron localizations in Zn and Cd. Comparing with Be and Mg, electrons in HCP Zn and Cd highly localize not only on $E^T$ sites but also on the triangle sites in the hexagonal plane (Fig. 3E). 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.

**Chemistry inside metal structures**

Our results show that electron localization is a ubiquitous and essential feature of metals in all phases. Like HPE, these phases are also analogous to compounds if the electrons localized, partially or fully, at the interstitial sites are viewed as anionic species. For
example, metals in FCC and HCP structures resemble compounds in NaCl and anti-NiAs structures, whereas BCC metal is isostructural to sodalite CaH₆ [35] and SrB₂C₄. [36] Under high enough pressure, all alkali and alkaline earth metals abandon the simple highly symmetric structures, which is the results of interplay between the increasing electron localizations, strong subset repulsions, and the s-p-d electron transitions. Like simple structures with localized electrons, the complex high-pressure structures can also find analogous compounds. For example, cl16 Na can be viewed as a binary compound with A₄B₃ composition and I⁴3d structure, such as Ba₄As₃, in which As atoms occupy the positions of the quasi-atoms (Fig. 4a, S9a-b). Similarly, Na t19 host-guest structure is isostructural to ternary compound Ti₅CuSb₂, in which Cu and Sb play the roles of two types of quasi-atoms inside t19 (Fig. 4b,S9c-d). The actual charge transfer from metals to quasi-atoms in all phases are comparable, as calculated by Integrated Charge Difference (ICD), especially at lower pressures (Fig. 4c, S9g). At pressures higher than 120 GPa, the charge transfers become higher for high pressure structures because of the relative energy change of the atomic and quasi-atomic orbitals. Heavier alkali and alkaline earth metals and especially transition metals show different pressure dependence to their charge transfer into interstitial sites, because of the increasing electron transition into their d orbitals. The large charge transfer into interstitial sites as well as to d orbitals also reduces the subset repulsions, which causes the presence or reappearance of high symmetry structures such as HCP, hP4 under very high pressure.

**Figure 4. Chemistry inside metals.** a. Ba₄As₃ in I⁴3d structure. The yellow and the red balls represent the Ba and the As atoms. b. Structure of Ti₅CuSb₂. The light blue balls represent Ti atoms, the dark blue and the brown balls represent Cu and Sb atoms. c. The calculated Integrated Charge Differences (see methodology section for definition) of Na atoms in various structures as functions of pressure.

**Discussions and conclusions**

The surprising and ubiquitous validity of our theory demonstrates the electron localizations in metal interstitials and the importance of their chemical interactions at determining the structural stabilities. The extension of this theory to p-block metals such as Al distinctly shows that it is not the density but the electron localization that governs the structural evolution under pressure. FCC Al is a good metal with high electron density at ambient
pressure but shows very weak electron localizations at the interstitial sites. It undergoes similar structural transformations as $s$-block metals but with much larger pressure scale due to its sluggish change of electron localizations (Fig. S10). Our results also show that while studying solid-state materials, one needs to compare the solid electron states with those of the sub-lattices, instead of directly with those of the free atoms as in traditional chemical bond theory.
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METHODOLOGY

Solid-state 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). [37,38] The electron-ion interactions were described by the projector augmented wave pseudopotentials [39,40] and the used valence electrons are listed in the table. We used the generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof [41] 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. [42]

| Li  | Be  | Na  | Mg  |
|-----|-----|-----|-----|
| 1s 2s | 1s 2s | 2p 3s | 2p 3s |

| K  | Ca  | Sc  | Ti  | V  | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|----|-----|-----|-----|----|-----|------|------|------|------|------|------|
| 3s 3p | 3p 4s | 3s 3p 3d | 3p 3d | 3p 3d 3s | 3p 3d | 3p 3d | 3p 3d | 3p 3d | 3p 3d | 3p 3d | 3p 3d |

| Rb | Sr  | Y  | Zr  | Nb  | Mo  | Tc  | Ru  | Rh  | Pd  | Ag  | Cd  |
|----|-----|----|-----|-----|------|------|------|------|------|------|------|
| 4s 4p | 4s 4p | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d | 4d 4p 3d |

| Cs  | Ba  | La  | Hf  | Ta  | W  | Re  | Os  | Ir  | Pt  | Au  | Hg  |
|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|-----|-----|
| 5s 5p | 5s 5p 5d | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s | 5p 5d 6s |

Table M1. The valence configurations of the pseudopotentials used in our solid-state DFT calculations.

Electronic structure Analyses of solid compounds. The electronic structures of metal superhydrides are calculated and analyzed by use of several methods, including the Bader’s Quantum Theory of Atoms in Molecules (QTAIM), [43] the Electron Localization Function (ELF), [44] the Crystalline Orbital Hamiltonian Population (COHP) and integrated COHP (ICOHP), [45] etc.

Integrated Charge Difference. For a given metal, two electron charge densities are calculated, including a self-consistent charge density ($M_{\text{scf}}$) and a superposition of atomic charge density ($M_{\text{atom}}$). The charge difference is then calculated as $\Delta \rho = \rho(M_{\text{scf}}) - \rho(M_{\text{atom}})$. 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 Difference (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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Author contributions M.M. proposed the mechanism and designed the research. Y.S. and L.Z. made equal contributions and conducted all the calculations. All authors analyzed the results together. M.M. wrote the manuscript. M.M. and Y.S. plotted the figures together.

Competing financial interests The authors declare no competing financial interest.

Supplementary Information is available for this paper.

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Supplementary Information

The electron localizations and the corresponding chemical interactions that govern the structures of elemental metals

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Figure S1. Crystal structures of metals at ambient pressure.
Figure S2. Evolution of electron localization in various structures upon the change of volume. A | Evolution of electron localization in simple cubic (SC) Na. **Aa.** ELF values at centers as functions of unit lengths. **Ab – Af.** ELF of SC Na with the unit lengths of body centered cubic (BCC) Na at 70, 20, 5, 0 and -1.5 (unit length of 5.0 Å) GPa, corresponding to the vertical lines in **Aa.** B | Evolution of electron localization in BCC Na. **Ba.** ELF values at centers as functions of unit lengths. **Bb – Be.** ELF of BCC Na at 80, 0, -1.5 (unit length of 5.0 Å) and -1.1 (unit length of 6.0 Å) GPa, corresponding to the vertical lines in **Ba.** C | Evolution of electron localization in face centered cubic (FCC) Na. **Ca.** ELF values at centers as functions of unit lengths. **Cb – Ce.** ELF of FCC Na at 80, 0, -1.5 (unit length of 6.0 Å) and -1.4 (unit length of 7.0 Å) GPa, corresponding to the vertical lines in **Ca.** D | Evolution of electron localization in hexagonal close packed (HCP) Na. **Da.** ELF values at centers as functions of unit lengths. **Db – De.** ELF of HCP Na at 80, 19 (unit length of 6.0 Å), 2.6 (unit length of 7.0 Å) and 0 GPa, corresponding to the vertical lines in **Da.** E | Evolution of electron localization in FCC Na subset. **Ea.** ELF values at centers as functions of unit lengths. **Eb – Ec.** ELF of FCC Na subset with the unit lengths of FCC Na at 110, 70, 12 (unit length of 4.4 Å) and 0 GPa, corresponding to the vertical lines in **Ea.** F | Evolution of electron localization in HCP Na subset. **Fa.** ELF values at centers as functions of unit lengths. **Fb – Fe.** ELF of HCP Na subset with the unit lengths of HCP Na at 110, 70, 12 (unit length of 6.25 Å) and 0 GPa, corresponding to the vertical lines in **Fa.**
Figure S3. Important features of high symmetry structures. a. The split of a BCC lattice into two SC lattices (subsets). No nearest neighboring atoms in the original BCC lattice are contained in the same SC lattice, showing a perfect partition. The yellow, green, blue and red balls represent the positions of body centers (B), edge centers (E), face centers (F) and the tetrahedral interstitial sites of the BCC ($E_{BCC}^T$). The lattice sites of the subsets (SC lattices) are also shown by yellow balls. The edge centers (E) and body centers (B) of the subsets are also the octahedral interstitial sites ($E^O$) of the original BCC lattice. b. The split of the FCC lattice into two subsets, represented by purple and grey balls. Among the 12 nearest neighbors in the original FCC lattice, 4 are kept in the same subset as shown by bonds. c. The split of the HCP lattice into two subsets, represented by brown and black balls. Among the 12 nearest neighbors in the original HCP lattice, 4 are kept in the same subset as shown by bonds. d. The split of the SC lattice into two FCC lattices, represented by yellow and black balls. No nearest neighboring atoms in the original SC lattice are contained in the same FCC lattice, showing a perfect partition. e. The tetrahedral interstitial sites (white balls) form pairs in an HCP lattice. f. The tetrahedral interstitial sites (white balls) form a SC lattice in an FCC lattice.
Figure S4. Evolution of subset interactions in BCC and FCC K under pressure. a. ELF of BCC K subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC K at 30, 12, and 0 GPa. b. ELF of FCC K subset as function of unit lengths. The vertical lines show the unit lengths of original FCC K at 30, 12, and 0 GPa. c. The schematic of the changes of electron localizations in the subsets of BCC and FCC K under pressure. From right to left, the top row shows the ELF of BCC subset at 10, 5, 1 (perfect matching), and 0 GPa. The bottom row shows the ELF of FCC subset at 30 and 10 GPa.
Figure S5. Evolution of subset interactions in BCC and FCC Ca under pressure. a. ELF of BCC Ca subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC Ca at 30, 10, and 0 GPa. b. ELF of FCC Ca subset as function of unit lengths. The vertical lines show the unit lengths of original FCC Ca at 30, 10, and 0 GPa. c. The schematic of the changes of electron localizations in the subsets of BCC and FCC Ca under pressure. From right to left, the top row shows the ELF of BCC subset at 0, 10 (perfect matching), and 30 GPa, and the ELF of FCC Ca that is the subset of an SC Ca at 40 GPa. The bottom row shows the ELF of FCC subset at 0, 10, and 30 GPa.
Figure S6. Evolution of subset interactions in BCC and FCC Ba under pressure. 

a. ELF of BCC Ba subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC Ba at 20, 5.5, and 0 GPa. 
b. ELF of FCC Ba subset as function of unit lengths. The vertical lines show the unit lengths of original FCC Ba at 20, 5.5, and 0 GPa. 
c. The schematic of the changes of electron localizations in the subsets of BCC and FCC Ba under pressure. From right to left, the top row shows the ELF of BCC subset at 0 (perfect matching), 5.5, and 30 GPa. The bottom row shows the ELF of an HCP subset and an FCC subset at 10 GPa. It reveals a large subset repulsion in FCC lattice since the ELF of one subset locates at the atomic positions of another subset. This structure destabilization feature is largely avoided in HCP structure, since the ELF maxima of one subset are shifted away from the atomic positions of another subset due to its lower symmetry.
Figure S7. Subset interactions in transition metals in BCC structure. **a.** ELF values at the high symmetry points in BCC subsets of 3\(d\) transition metals. **b.** ELF values at the high symmetry points in BCC subsets of 4\(d\) transition metals. **c.** ELF values at the high symmetry points in BCC subsets of 5\(d\) transition metals. **d and e.** (110) view of the ELF of Zr and Mo in BCC structure. To compare precisely, the isosurfaces are set at 0.25 and the color code ranges are set as 0 to 0.6, for both metals. **f and g.** (110) view of the ELF of Zr and Mo in HCP structure. To compare precisely, the isosurfaces are set at 0.35 and the color code ranges are set as 0 to 0.6, for both metals.
Figure S8. Evolution of subset interactions in BCC Hf and W under pressure. 

a. ELF of BCC Hf subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC Hf at 80 and 0 GPa.

b. The schematic of the changes of electron localizations in the subsets of BCC Hf under pressure. From right to left, the top row shows the ELF of BCC subset at 0 and 80 GPa, corresponding to the vertical line in ELF graph.

c. ELF of BCC W subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC W at 200 and 0 GPa.

d. The schematic of the changes of electron localizations in the subsets of BCC W under pressure. From right to left, the top row shows the ELF of BCC subset at 0 and 200 GPa, corresponding to the vertical line in ELF graph.
Figure S9. Chemistry inside metal structures. a. The ELF of Na in c116 structure under 110 GPa. The yellow balls show the positions of the Na atoms. b. The structure of Ba4As3 in I43d structure. The yellow and the red balls represent the Ba and the As atoms. c. The ELF of Na in t119 structure under 150 GPa. d. Structure of Ti5CuSb2. The light blue balls represent Ti atoms, the dark blue and the brown balls represent Cu and Sb atoms. e. The ELF of Na in hP4 structure under 200 GPa. f. Structure of Na2S at 20 GPa. The yellow and brown balls represent the Na and S atoms respectively. g. The calculated Integrated Charge Differences (see methodology section for definition) of quasi-atoms in various structures of Na as functions of pressure.
Figure S10. Electron localizations and structure change of Al under high pressure. **a.** Structural evolution of Al under compression up to 4 TPa. **b.** ELF of BCC Al subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original BCC Al at 3200, 1780, 380 and 0 GPa. **c.** ELF of FCC Al subset (SC) as function of unit lengths. The vertical lines show the unit lengths of original FCC Al at 3200, 1780, 380 and 0 GPa. **d – g.** ELF of BCC Al subset with the unit lengths of BCC Al at 0, 380, 1780 and 3200 GPa, corresponding to the vertical lines in the ELF graph. **h.** ELF of HCP Al as function of unit lengths. The vertical lines show the unit lengths of HCP Al at 220, 50, 20 and 0 GPa. **i – l.** ELF of HCP Al at 0, 20, 50 and 220 GPa, corresponding to the vertical lines in the ELF graph.
Appendix. Electron localization map of metal lattices and subsets

Figure A1: Critical positions in whole/subset BCC, whole/subset HCP, and whole/subset FCC lattice. The symbols on the left denote the critical position in the structures and the right ones represent the corresponding symbols shown in the following ELF graphs.
Figure A2: ELF values of critical positions in the BCC structure of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing unit lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.
Figure A3: ELF values of critical positions in the FCC structure of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing unit lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.
Figure A4: ELF values of critical positions in the HCP structure of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing unit lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.
Figure A5: ELF values of critical positions in the BCC subset of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing lattice lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.
Figure A6: ELF values of critical positions in the FCC subset of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing lattice lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.
Figure A7: ELF values of critical positions in the HCP subset of metals. In each subgraph, the vertical dash lines from right to left side denotes the decreasing lattice lengths with increasing pressure. The applied pressures for Li are 0, 10, 40 GPa; for Na are 0, 70, 120 GPa; for K are 0, 12, 30 GPa; for Rb are 0, 7, 15 GPa; for Cs are 0, 2.5, 5 GPa; for Mg are 0, 50, 100 GPa; for Ca are 0, 10, 40 GPa; for Sr are 0, 3.5, 30 GPa; for Ba are 0, 5.5, 20 GPa; and for other metals are 0, 100 GPa, respectively.