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TOPICAL REVIEW — CALYPSO structure prediction methodology and its applications to materials discovery

Pressure-induced new chemistry*

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It has long been recognized that the valence electrons of an atom dominate the chemical properties, while the inner-shell electrons or outer empty orbital do not participate in chemical reactions. Pressure, as a fundamental thermodynamic variable, plays an important role in the preparation of new materials. More recently, pressure stabilized a series of unconventional stoichiometric compounds with new oxidation states, in which the inner-shell electrons or outer empty orbital become chemically active. Here, we mainly focus on the recent advances in high-pressure new chemistry including novel chemical bonding and new oxidation state, identified by first-principles swarm intelligence structural search calculations. The aim of this review is to provide an up-to-date research progress on the chemical bonding with inner-shell electrons or outer empty orbital, abnormal interatomic charge transfer, hypervalent compounds, and chemical reactivity of noble gases. Personal outlook on the challenge and opportunity in this field are proposed in the conclusion.

Keywords: high pressure, oxidation state, stoichiometry, structural prediction

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1. Introduction

At ambient conditions, the valence electrons of an atom dominate the chemical properties, rooted in the well-accepted atomic shell structure.[1,2] In general, atoms react with other atoms by losing, obtaining, or sharing their valence electrons. However, the inner-shell electrons or outer empty orbital are not involved in chemical bonding. Thus, the number of the valence electrons of an element is closely related to the oxidation state in its compounds. On the other hand, the preparation of compounds with new oxidation states is a rather attractive topic in condense-mater physics and chemistry.[3–6] This is because compounds with new oxidation states usually contain new types of chemical bonding and exhibit interesting physical and chemical properties.[6–10]

Pressure, like temperature and volume, is a basic thermodynamic parameter, but it exhibits unique advantages in finding new materials[11–15] and stabilizing unexpected stoichiometric compounds with new oxidation states.[16,17] This can be attributed to the fact that pressure can shorten the interatomic distance,[18] overcome the reaction barrier,[19,20] rearrange the atomic orbital energy level,[21] and modify the electronegativity.[22] In particular, the chemical properties of elements are strongly correlated with the relative orbital energy levels. Although pressure increases the atomic orbital energy levels, the elevated magnitudes of various elements are different.

High-pressure experiments are expensive. Moreover, many attempts are needed to determine the experimental conditions before obtaining the desirable compounds. However, first-principles structure prediction method has become an alternative way to explore potential experimental conditions and identify new functional materials at high pressures.[23–28] For instance, the recent breakthrough in the field of superconductivity was achieved by a direct investigation on a theoretical prediction of compressed solid H_2S with remarkable large superconductive transition temperature.[29,30] This method has also been successfully applied to the discovery of new chemical reactions and oxidation states, not accessible at ambient pressure.[31–34] Some of the research results break through the understanding of atomic shell structure, and realize the chemical bonding involved in inner-shell electrons or outer space orbital.[35–37] Although there have been many important advances in the field of high-pressure new chemistry,[38–42] in this review, we mainly focus on the recent progress discovered by first-principles unbiased structure search (CALYPSO) calculations.

2. New oxidation states of gold

Gold (Au) is a magic element in the periodic table and shows unusual physical and chemical properties, mainly originated from the strong relativistic effect.[43–46] Its electron configuration is $5d^{10}6s^1$. The extension of 5d orbital results in the high reactivity of 5d electrons and the tendency to form higher oxidation states. The contraction of 6s orbital leads

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to the high electronegativity comparable to halogen and the obtainment of electrons from the other atoms, showing a negative oxidation state.[44,47] Au has become a rare representative of negative oxidation state among the metal elements. On the other hand, Au compounds with different oxidation states exhibit interesting properties and wide applications. For example, the negative oxidation state of Au leads to a series of exotic properties, such as ferroelectricity, electric polarization, and catalysis.[48] F-rich Au compounds can be used as strong oxidants originated from their large electron affinity.[49] However, the long-desirable target AuF_6 has not been reported thus far.[50,51] In the oxidative addition reactions, Au in different oxidation states induces diverse catalytic activity.[52–54] Therefore, the investigation of Au oxidation state has always been the most interesting and active fields in chemistry and material.[47,52,55,56]

Lithium (Li) and fluorine (F) have strong inclination to lose and acquire electrons in chemical reactions due to their strong electropositivity and electronegativity, respectively. Once pressure stabilized the Li-rich or F-rich Au compounds, they might show new negative or positive oxidation states. In the Li–Au binary compounds, several of Li-rich aurides (e.g., Li_4Au and Li_5Au) become stable at megabar pressures.[59] Their common structural feature is the Au-center polyhedrons (Fig. 1(a)). The distance between the two nearest Au atoms is significantly longer than the aurophilic interaction distance, indicating that the interatomic Li–Au interaction is dominant. Bader charge analysis shows that Au gains more than one electron from Li, occupying the 6s + 6p orbitals. Thus, Au in Li-rich aurides ($n \geqq 3$) behaves as a 6p-element. More interestingly, the negative oxidation states of Au can be effectively tuned from −1 to −3 (or even higher) by modulating the Li compositions. For F-rich Au compounds, AuF_4 and AuF_6 were identified under high pressure,[57] exhibiting typical molecular crystal characters (Fig. 1(b)). Thus, the oxidation state of Au can be unambiguously assigned as +4 and +6, respectively. The molecular orbital analysis of AuF_4 shows an obvious Au $5d^7$ electronic configuration, which is consistent with the assignment of the +4 oxidation state in Au. Besides these, two hitherto unknown mixed-valence states of Au have been found in AuO_2 (+3 and +5) and AuS (+1 and +3) (Fig. 1(c)).[58] These studies not only provide a controllable method for achieving the diverse oxidation states of Au, but also widen the understanding of Au element.

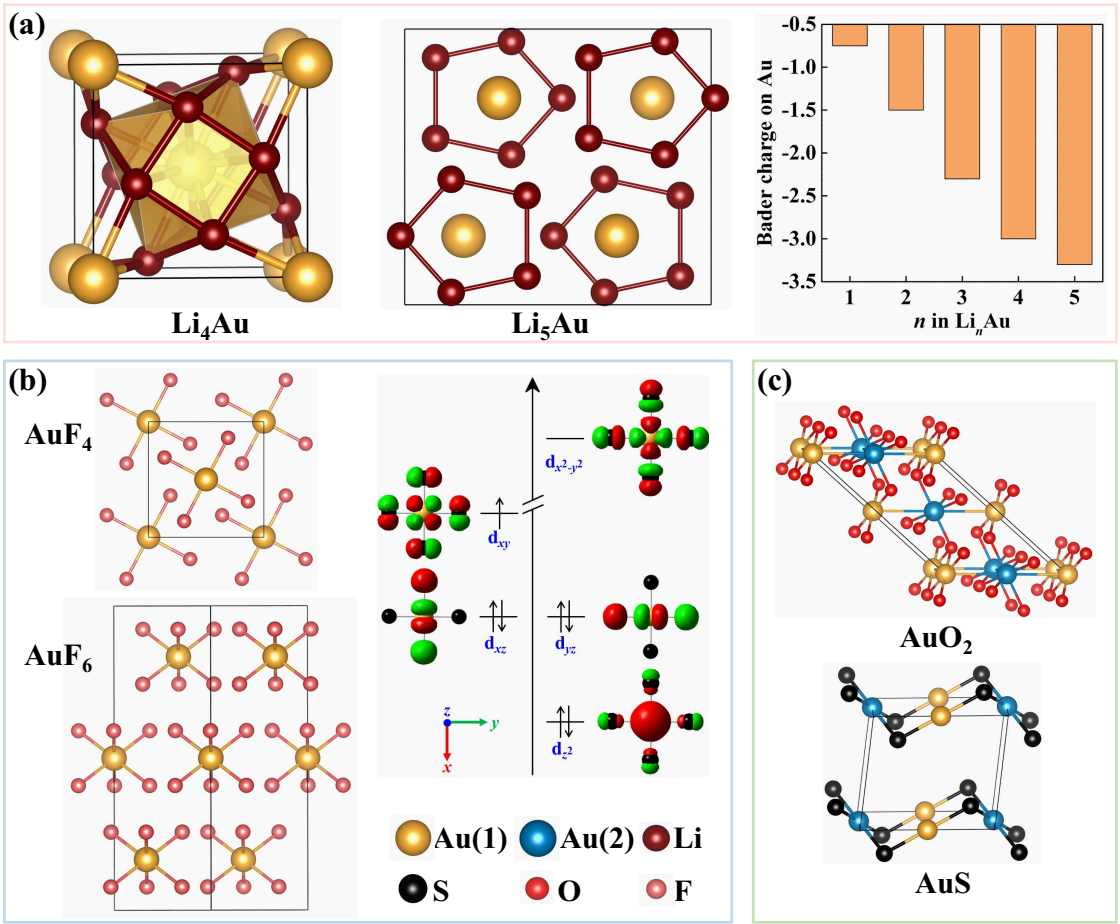


Fig. 1. (a) Crystal structure of *I*4/*m* Li_4Au and *Cmcm* Li_5Au at 50 GPa. The Bader charge of Au in various Li_nAu (n = 1–5) compounds, showing that the negative oxidation state of Au is beyond −3 in Li_4Au and Li_5Au. (b) Crystal structures of *I*4/*m* AuF_4 and *R*-3 AuF_6; molecular orbital plots of Au 5d orbitals in *I*4/*m* AuF_4. Adapted with permission from Ref. [57]. Copyright (2018) American Chemical Society. (c) The two mixed-valence compounds *C*2/*m* AuO_2 and *P*-1 AuS. Adapted with permission from Ref. [58]. Copyright (2018) Wiley.

3. New oxidation states of alkali and alkali-earth metal

Alkali metals, with ns^1 valence electron configurations, have strong reaction activity and can form ionic compounds with other elements. Thus, for a long time, it has been believed that alkali metals prefer to lose the outermost electron, forming +1 oxidation state,[60] and their core electrons are not involved into chemical bonding. It becomes a huge challenge for alkali metals to form a higher oxidation state.[61–63] On the other hand, since the first discovery of alkali metal anions (named alkalides) in the 1970s,[64,65] there has been much interest in obtaining more electrons of alkali metals from other atoms.[66,67] However, the negative oxidation state of alkali metals is limited to −1 at ambient pressure.

Caesium (Cs), with the exception of Fr, is the least electronegative element in alkali metal group. Moreover, its 5p level becomes broadened and even increases to the states around the Fermi level under high pressure.[68–72] Miao *et al.* predicted that Cs can open its inner shell through the reaction with F at high pressures, allowing its 5p electrons to participate in the chemical reaction and exhibiting the oxidation state beyond +1.[36] Cs in CsF_2, CsF_3, and CsF_5 molecular crystals show the formal oxidation states of +2, +3, and +5 (Figs. 2(a) and 2(b)). This is the first example to announce that inner shell electrons can become reactive at high pressures, breaking through the classical understanding that inner-shell electrons cannot participate in chemical bonds.

In an opposite way, Cs obtaining electron from Li, at high pressures, shows a new chemical inclination that is not accessible at ambient conditions. At ambient pressure, Li and Cs only exist in the form of alloys.[73] However, LiCs, Li_3Cs, Li_4Cs, and Li_5Cs become stable intermetallic compounds at high pressures.[74] LiCs is stabilized into a CsCl-type structure (Fig. 2(d)). For other compounds, Cs–Li polyhedrons are connected with each other through face- or vertice-sharing. Intriguingly, Cs can gain more than one electron from Li, and extend its negative oxidation state beyond −1. This is due to the fact that the energy increase of Li 2s is much faster than that of Cs 5d, and eventually reordering them with pressure. This character is favor of the charge transfer from Li 2s to Cs 5d, reducing the total energy and stabilizing the Li–Cs compounds. To be noted, the metastable LiCs phase shows superconductivity with a T_c of 21.4 K at 25 GPa. Its superconductivity comes from the charge transfer from Li 2s to Cs 5d, and from 6s to 5d in Cs, inducing a strong electron–phonon coupling.[75]

Alkali metals can open up the inner electrons at high pressures. It is a natural thought that whether alkaline earth metals have similar properties. However, the electron screening effect on the inner electrons in alkali-earth elements is much stronger than that in alkali elements. As a result, opening up the inner shell of alkali-earth metals might be more difficult with respect to alkali metals.[76] In the periodic table, barium (Ba) is adjacent to Cs, and nonradiative in alkali-earth metal group. Under high pressure, Ba can open up its inert 5p shell through the reaction with F, exhibiting the oxidation states greater than +2 in its F-rich compounds BaF_3, BaF_4, and BaF_5 (Fig. 2(c)).[77] Alkali and alkali-earth metals in their compounds are usually ionic at ambient pressure. Under high pressure, Cs–F bond are covalent (Fig. 2(e)) in Cs–F compounds,[36] whereas Ba–F bond are ionic (Fig. 2(f)).

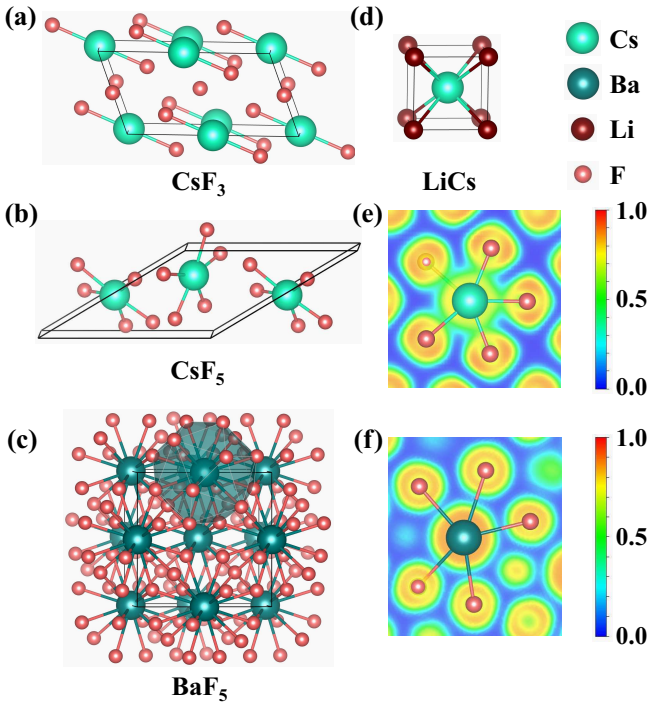


Fig. 2. (a) CsF_3 at 100 GPa in a $C2/m$ structure. (b) CsF_5 at 150 GPa in an $Fdd2$ structure. (c) F-43m-BaF_5 at 200 GPa. (d) LiCs in the CsCl structure at 150 GPa. ELF maps of CsF_5 (e) and BaF_5 (f).

4. Unusual F-rich compounds

As can be seen above, F is essential in achieving extremely high oxidation states in both transition metals and main group elements.[78] On the other hand, F-rich compounds often exhibit strong oxidating power, serving as fluorinating agents or oxidants.[8,78] For instance, PtF_6 can oxidize xenon, producing the first noble gas compound, $XePtF_6$.[79] Thus, design and preparation of F-rich compound are rather important from both fundamental and applicable standpoints.[80–82]

Mercury (Hg), one of the post-transition metals, has a fully filled 5d shell. Its typical oxidation state is +2. When Hg reacts with F under high pressure, its 5d electrons become active, forming HgF_3 (Fig. 3(a)) and HgF_4 (Fig. 3(b)) compounds, showing +3 and +4 oxidation states in Hg.[83] This discovery resolved the long-standing dispute over whether Hg could be included into transition metals.[84] Moreover, the electronic structure analysis shows that HgF_3 is metallic and

ferromagnetic, resulting from the $5d^9$ electron configuration of Hg. Notably, the Hg–F bond in HgF_4 is covalent.

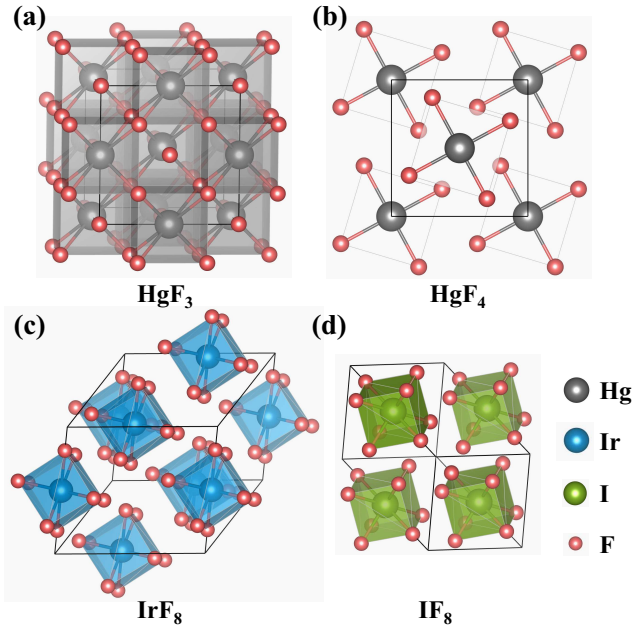


Fig. 3. Crystal structures of (a) *Fm*-3*m* HgF_3 at 100 GPa. (b) *I*4/*m* HgF_4 at 50 GPa. (c) *R*-3 IrF_8 at 200 GPa. Adapted with permission from Ref. [85]. Copyright (2019) American Chemical Society. (d) *R*-3 IF_8 at 300 GPa.

One of the key factors in the formation of F-rich compounds is that the central atoms can provide more valence electrons. Iridium (Ir) contains nine valence electrons ($5d^76s^2$), which can be fully utilized in its compounds, showing the highest oxidation state of +9.[6] However, the high oxidation states of Ir are all in its oxides (e.g., $[(\eta^2\text{-}O_2)Ir^{VII}O_2]^+$, $Ir^{VIII}O_4$, $[Ir^{IX}O_4]^+$),[6,86] existing in molecular forms. Thus far, the highest known F stoichiometry in Ir fluoride is only IrF_6. Very recently, three IrF_8 molecular crystals (Fig. 3(c)) have been predicted to be stable at high pressures, which become the first bulk solid containing the +8 oxidation state in Ir.[85] The spatial symmetry of the basic building block in the three IrF_8 phases enhances with the increase in the pressure (e.g., dodecahedron → square antiprism → quasicube). The pressure-induced faster elevation of Ir 5d orbital energy level with respect to F 2p facilitates the charge transfer from Ir 5d to F 2p, reducing the total energy, so that F-rich compounds become stable. Since F-rich compounds are potential oxidants, the oxidizing power of the predicted compounds was evaluated by calculating their electronic affinities. The oxidizing power of the three identified IrF_8 phases is close to or exceeds PtF_6, a recognized strong oxidant.

As the next transition metal of Ir, platinum (Pt) has one more valence electron than Ir. Thus, we have explored the F-rich compounds of Pt at high pressures in order to obtain a higher F stoichiometry. However, the most F-rich compound is PtF_6 up to 300 GPa (Fig. 4(c)). The known PtF_4 and PtF_6 undergo structural phase transitions (Figs. 4(a) and 4(b)) with pressure. Overall, although Pt, Au, and Hg have more valence electrons than Ir, their most F-rich stoichiometries are PtF_6, AuF_6, and HgF_4. The pressure-induced different increase of their 5d atomic orbital energy levels might be responsible for the observations (Fig. 4(d)).[85]

The coordination number of an atom in compound has great effect on the structure and property.[87,88] Thus, hypercoordination has become one of the most active research fields.[89–91] Among the halogen elements, except astatine,

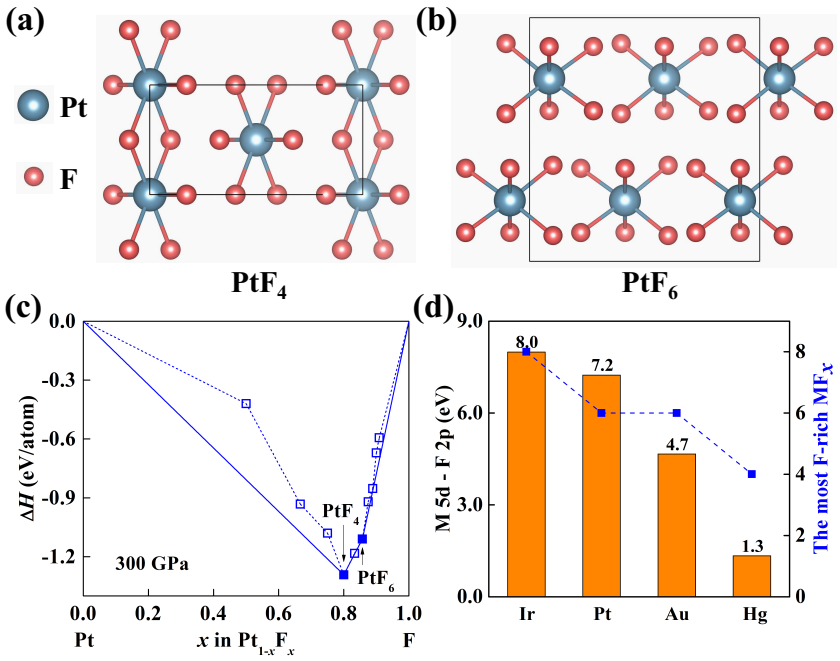


Fig. 4. (a) PtF_4 in *C*2/*m* symmetry at 300 GPa. (b) PtF_6 in *C*2/*c* symmetry at 300 GPa. (c) Phase stabilities of the considered PtF_x ($x = 1$–10) compounds with respect to elemental Pt and F_2 solids at 300 GPa. (d) The energy difference between *M* 5d and F 2p orbital at 100 GPa, and the stable F-richest stoichiometry of *M* (*M* = Ir, Pt, Au, Hg).

iodine (I) has the largest atom radius, the weakest electronegativity, and the largest polarizability. These characters might allow more atoms in its coordination sphere. On the other hand, available hypercoordinated I compounds can be applied for the environmentally benign catalysis and the highly selective oxidization.[92–94] Up to now, the highest coordination number of I in neutral compound is seven (e.g., IF_7).[95] The known anionic octafluoride (IF_8^-) shows square antiprismatic. Pressure-induced stable neutral IF_8 molecule having a quasi-cube molecular configuration (Fig. 3(d)), has been identified through swarm intelligence structural search calculations.[37] At ambient pressure, the I 5d orbital level is much higher than that of I 5p, making the hybridization impossible. Under high pressure, the I 5d orbitals in IF_8 come down and are split by the cubic ligand field into lower-lying e_g and higher-lying t_{2g} sets, so that the hybridization with filled F-centered orbitals becomes possible.[96] Thus, I in IF_8 is not only hypercoordinated, but also hypervalent. Moreover, IF_8 shows metallic, coming from a hole contribution of F 2p bands. Interestingly, IF_8 and IrF_8 exhibit similar quasi-cubic structure with the R-3 symmetry.

5. Unexpected chemical activity of noble gases

Noble gases (Ng's) are the most stable elements due to their closed outer shell. Among them, xenon (Xe) is most likely to be involved in the chemical reactions because of its large atomic size, showing weak binding ability of nuclei to outer electrons. Strong oxidizers with high electron affinity might open the full shell of Xe. As expected, the first noble gas compound, $XePtF_6$, was synthesized in 1962,[79] and three Xe fluorides, XeF_2, XeF_4, and XeF_6, were found in the same year.[97–99] On the other hand, it becomes more active and forms various compounds with other atoms at high pressures.

Recent investigation on Xe–F binary compounds has found several of new phases, displaying interesting structural characters under high pressure.[100] Besides the synthesized XeF_2, XeF_4, and XeF_6 at ambient pressure, the other two Xe-rich stoichiometries, such as Xe_2F (Fig. 5(a)) and Xe_3F_2, have been discovered at high pressures. Intriguingly, there appear Xe–Xe covalent bonds in these Xe–F compounds, becoming the first evidence of Ng–Ng bond in compound after in Ng cations (e.g., Xe_2^+ and Xe_4^+).[101–103] Moreover, Xe atoms form intercalated graphitic layers in Xe_2F.

Chlorine (Cl), with a weaker electronegativity than F, can also break the closed shell of Xe. However, the known Xe chloride ($XeCl_2$) cannot be isolated outside a matrix. Under high pressure, a series of Xe–Cl compounds become stable in solid states, such as XeCl, $XeCl_2$, and metastable $XeCl_4$ (Fig. 5(b)).[104] F can oxidize Xe to +6 oxidation state,[99] while Cl only leads to the formation of $XeCl_4$ with +4 oxidation state. The predicted Xe–Cl compounds show diverse electronic properties, ranging from metallicity to semiconducting.

Except for the high electronegative halogen elements, nitrogen (N), which is chemically inert at normal conditions and stabilizes into the N_2 molecule, can form compounds with Xe under high pressure. XeN_6 has been predicted to be the product of Xe and N_2 at megabar pressures ($\geqq$ 146 GPa).[105] The XeN_6 phase (Fig. 5(c)) exhibits intriguing structural characteristics containing the chaired N_6 hexagons and 12-fold coordination of Xe bonded with N. It is a semiconductor with a band gap of $\sim$ 1.5 eV. XeN_6 becomes the potential high energy density material due to its remarkable large energy density of 2.4 kJ·g^{-1}. Unlike the ionic bonds between Xe and F[100] or Cl,[104] Xe–N bond is covalent.

Transition metals, such as iron (Fe) or nickle (Ni), can also react with Xe under high pressure, forming sable compounds of XeFe, $XeFe_3$ (Fig. 5(d)), $XeFe_5$, $XeNi_3$ (Fig. 5(e)), and $XeNi_5$.[106] This breakthrough finding resolves the problem that Xe disappears in the Earth's core, and provides an opportunity to re-recognize the chemical properties of transition metals. It is well known that transition metals are usually serving as reducing agents and lose their electrons showing positive oxidation states. However, Fe/Ni gains electrons from Xe at high pressures. This is completely different from the understanding of traditional chemical knowledge. The charge transfer from Xe to Fe/Ni under high pressure may be the result of pressure-induced alternation of atomic electronegativity.[22,107]

For alkali metals, the inclination of losing electrons is less likely to be changed. Alkali metal Ng compounds have been investigated under high pressure, such as Cs–Xe[108] and Li–Ar[109] systems. Cs–Xe compounds (Fig. 5(g)) exhibit weak ionicity, in which Xe gains electrons from Cs. The charge transfers become more intriguing in Li–Ar compounds (Fig. 5(f)), as well as alkali earth metal Ng compounds (e.g., Mg–Xe (Fig. 5(h)), Mg–Kr, and Mg–Ar).[110] In these cases, alkali metals transfer electrons not only to Ng's, but also to interstitial sites forming electrides. Perhaps, it is not easy to add large amount of electrons to Ng's, so the excess part is localized in the interstitial regions of the crystal.

Finally, the most stable inert gas, helium (He), becomes chemically active at high pressures. Several of stable helium compounds have been obtained through reacting with ionic compounds at high pressures.[112] Intriguingly, the electrons of He atoms do not participate in any chemical bonds, but He atom plays a key role in reducing the strong repulsive Coulomb interactions between the majority ions with the same charge, and decreasing the Madelung energy. Based on the identified compounds and the composition of the Earth's minerals, a large quantity of He could be stored in the Earth's lower mantle.

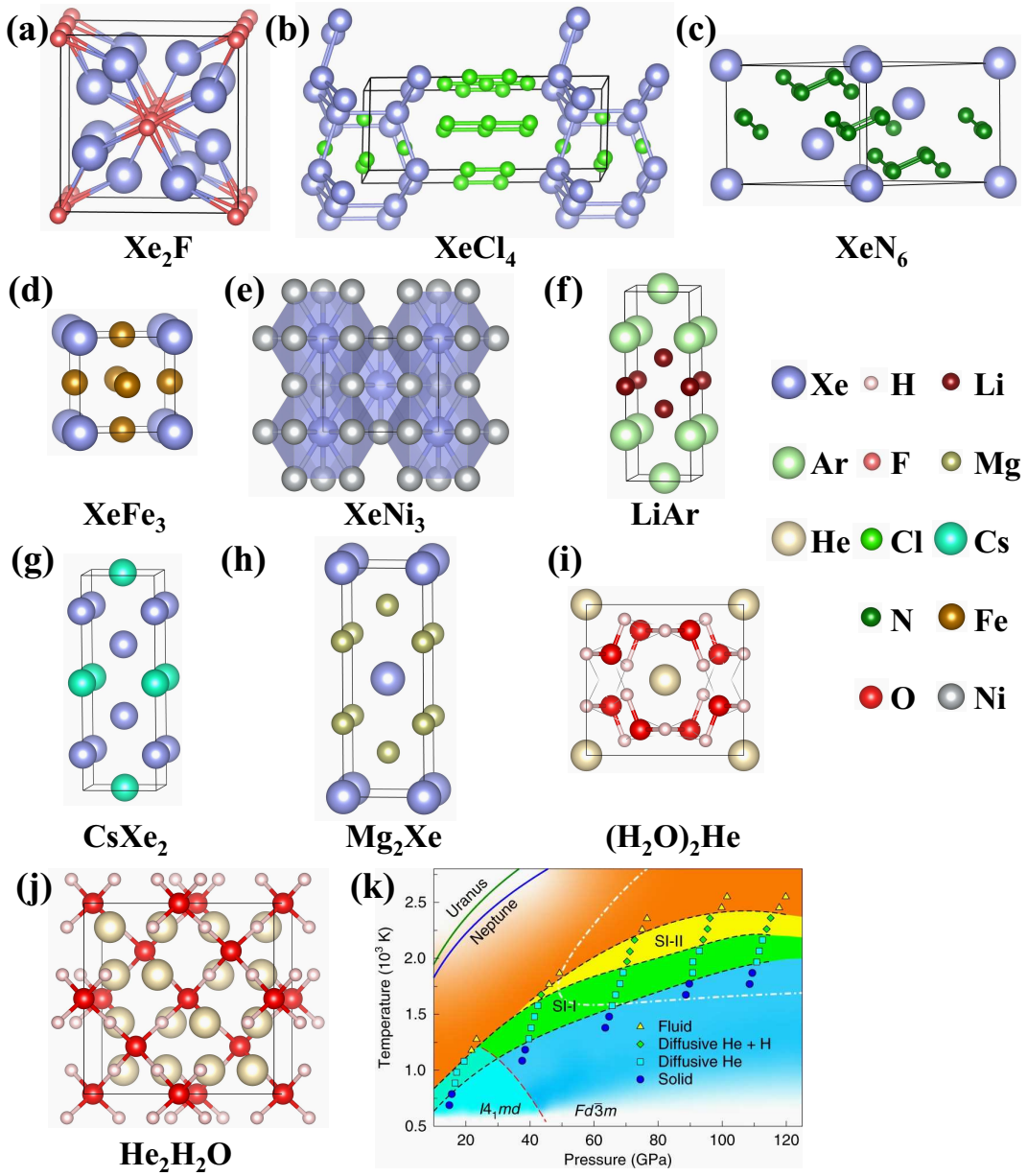


Fig. 5. Crystal structures of (a) *I*4/*mcm* Xe_2F at 200 GPa. (b) *P*-6*m*2 $XeCl_4$ at 100 GPa. (c) *R*-3*m* XeN_6 at 150 GPa. (d) *Pm*-3*m* $XeFe_3$ at 250 GPa. (e) *Pmmn* $XeNi_3$ at 250 GPa. (f) *P*4/*mmm* LiAr at 160 GPa. (g) *I*4/*mmm* $CsXe_2$ at 200 GPa. (h) *I*4/*mmm* Mg_2Xe at 200 GPa. (i) *Ibam* $(H_2O)_2He$ at 300 GPa. (j) *Fd*-3*m* He_2H_2O at 70 GPa. (k) Phase diagram of the helium-water system at high pressures. Adapted with permission from Ref. [111]. Copyright (2019) Nature.

Ng's can also combine with H_2O molecule at high pressures. He was predicted to form compound with H_2O.[113] The only stable stoichiometry is $(H_2O)_2He$ (Figure 5(i)), in which the strong bonding interaction between He and O atoms (denoted as He…O interaction) plays a major role of the stabilization. The He…O interaction originates from the closed-shell of He and O atoms and the strengthen is similar to hydrogen bonding. In $(H_2O)_2He$, H_2O transfers little charge to He, so that it shows semiconducting property. However, the reactions of Xe and H_2O under high pressure and high temperature produces $Xe_4H_{12}O_{12}$.[114] More recently, unusual superionic states have been observed in He–H_2O compounds through the reaction of He and H_2O under high pressure and high temperature with the aid of machine learning method.[111] This breakthrough finding provides important theoretical evidences for understanding the physical and chemical properties of He at high pressures and the structural evolution of the celestial bodies such as Uranus and Neptune (Figs. 5(j) and 5(k)).[111] More interestingly, He and Ne guests can be trapped by alkali-metal oxide and sulfide under pressure, suggesting a new strategy for gas storage.[115] Moreover, Ng's can also combine with each other to form stable compounds, such as $XeHe_2$,[116] $ArHe_2$,[117] and $NeHe_2$.[118,119]

6. Conclusions and outlook

Pressure has led to the discovery of numerous unusual chemical reactions, not accessible at ambient pressure. Some

of them indicate (i) the inner shell electrons or outer empty orbital participate in the chemical bonding, (ii) abnormal interatomic charge transfer occurs, (iii) noble gases become chemically active and form various kinds of compounds with other elements. Part of the compounds show interesting structures and properties. These findings extend the understanding and cognition of traditional chemistry. However, the research in this field is just beginning. Only a few elements in the periodic table have been studied, and there is still a vast space for exploration. On the other hand, more and more systemic research is needed urgently to explore the reaction mechanism, and establish the basic theory of chemical reaction under high pressure. To be noted, most of these studies are carried out from the standpoint of theoretical calculations. This might originate from some difficulties in high pressure experiments. For instance, strong oxidizing or reducing agents (e.g., F and Li) are harmful to experimental instruments.[35] Thus, more experimental studies are highly demanded. Theory and experiment complement and verify each other, promoting the development of high-pressure new chemistry.

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