

Anionic Chemistry of Noble Gases: Formation of Mg–NG (NG = Xe, Kr, Ar) Compounds under Pressure

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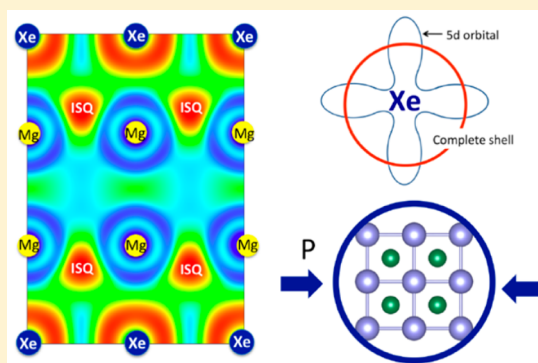
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S Supporting Information

ABSTRACT: While often considered to be chemically inert, the reactivity of noble gas elements at elevated pressures is an important aspect of fundamental chemistry. The discovery of Xe oxidation transformed the doctrinal boundary of chemistry by showing that a complete electron shell is not inert to reaction. However, the reductive propensity, i.e., gaining electrons and forming anions, has not been proposed or examined for noble gas elements. In this work, we demonstrate, using first-principles electronic structure calculations coupled to an efficient structure prediction method, that Xe, Kr, and Ar can form thermodynamically stable compounds with Mg at high pressure (≥ 125 , ≥ 250 , and ≥ 250 GPa, respectively). The resulting compounds are metallic and the noble gas atoms are negatively charged, suggesting that chemical species with a completely filled shell can gain electrons, filling their outermost shell(s). Moreover, this work indicates that Mg₂NG (NG = Xe, Kr, Ar) are high-pressure electrides with some of the electrons localized at interstitial sites enclosed by the surrounding atoms. Previous predictions showed that such electrides only form in Mg and its compounds at very high pressures (>500 GPa). These calculations also demonstrate strong chemical interactions between the Xe 5d orbitals and the quantized interstitial quasiatom (ISQ) orbitals, including the strong bonding and electron transfer, revealing the chemical nature of the ISQ.



INTRODUCTION

The electronic shell structure of atoms is paramount for interpreting the chemical properties of elements, including reactivity and periodicity.^{1,2} At ambient pressure, elements on the left side of the periodic table that have fewer electrons in their outermost shells tend to oxidize and become positively charged ions, whereas the opposite occurs for elements on the right side of the table. Upon filling these electronic shells, atoms are classically considered to become inert to chemical reactions. Although noble gases (NGs) are the quintessential full-shell elements, the first noble gas compounds were synthesized by Bartlett,^{3–5} 30 years after Pauling's prediction that noble gases could form stable compounds. In XeF₂, Xe is oxidized to the +2 state and forms covalent bonds with F by sharing its 5p electrons. Theoretical work has also demonstrated that Xe may react with transition metals such as Fe and Ni at pressures and temperatures present at the Earth's core, showing the power of pressure in modifying the chemical reactivity of elements.⁶ Additionally, Xe can form van der Waals compounds while

mixed with H₂ under high pressure.^{7,8} Pressure has also been shown to enhance the oxidation of some elements and therefore the formation of the corresponding compounds, including, for example, mercury tri- and tetrafluorides,⁹ xenon oxides,¹⁰ and xenon suboxides.¹¹ In a recent study, we showed that the completely filled Cs 5p electrons can be activated at high pressure to form CsF_n ($n > 1$) compounds.¹² In contrast to the unique oxidative chemistry of noble gases, the possibility for these elements to gain electrons and become formally anionic has not been previously explored.¹³ Here we demonstrate that Xe, Kr, and Ar can react with Mg under high pressure, forming compounds of Mg–Xe, Mg–Kr, and Mg–Ar. In these compounds, the NG gains electrons from the alkaline earth metal, Mg, and becomes negatively charged.

Furthermore, these results indicate that the presence of Xe can help the localization of electrons at interstitial sites, causing

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the formation of Mg-based high-pressure electrides (HPEs) at lower pressure than previously predicted.^{14,15} A HPE is a phenomenon recently demonstrated for alkali metals^{16–21} where the quantized orbitals of the interstitial quasiatoms (ISQs) have the same (energetic) response to external pressure as atomic orbitals.²³ However, the inner core electron repulsion causes the energy of the atomic orbitals to increase significantly with external pressure compared to the ISQ. Therefore, with high enough applied pressure, the electrons of the frontier orbitals will move into the energy-space of the ISQ orbitals and form a HPE. The ionization energy of the element and the pressure dependence are key in forming a HPE. So far, only Li and Na HPEs have been observed by diamond anvil cell (DAC) experiments, while Mg is predicted to become a HPE at 800 GPa.¹⁴ Forming nonstoichiometric compounds with oxygen can lower the HPE pressure to 500 GPa.¹⁵ Our work indicates that forming compounds with Xe reduces the HPE formation pressure for Mg to 125 GPa. These results highlight the potential to form alkali-earth-metal HPEs using current DAC experiments, while reacting with noble gas elements.

COMPUTATIONAL METHODS

To obtain stable structures for Mg–NG compounds, we conducted an unbiased structure prediction based on the particle swarm optimization algorithm as implemented in CALYPSO (crystal structure analysis by particle swarm optimization).^{23,24} The structure predictions were performed using a unit cell containing up to four Mg–NG units and at pressures ranging from 0 to 300 GPa. The underlying ab initio structural relaxations and the electronic band-structure calculations were performed within the framework of density functional theory (DFT) as implemented by VASP (Vienna Ab Initio Simulation Package).²⁵ The generalized gradient approximation (GGA) within the framework of Perdew–Burke–Ernzerhof (PBE)²⁶ was used for the exchange–correlation functional, and the projector augmented wave (PAW) potentials²⁷ were used to describe the ionic potentials. In the PAW potential for Xe, the 5s, 5p, 5d, and 6s orbitals were included in the valence. The cutoff energy for the expansion of the wave function into plane waves was set at 1200 eV, and Monkhorst–Pack *k*-meshes were chosen to ensure that all enthalpy calculations converged to better than 1 meV/atom. The maximally localized Wannier functions are constructed by using the wannier90 code.²⁸ The integrated crystal orbital Hamiltonian populations (ICOHP) are calculated by the Stuttgart TB-LMTO package.²⁹

RESULTS AND DISCUSSION

Computational Approach. Density functional theory (DFT) calculations³⁰ have been successfully employed to predict novel compounds and structures under high pressures.^{12,16,31} Since the crystalline structures of Mg–NG compounds are unknown, we employ a nonbiased automatic structure search method based on the particle swarm optimization (PSO) algorithm. This method can search for energetically favorable structures across the entire potential energy surface derived from DFT calculations.^{23,24} This method has recently been successfully applied to predict atomic structures of many systems.^{32–35} In this work, six compositions are studied in the Mg–NG (NG = Xe, Kr, Ar) system, including MgNG₂, MgNG, Mg₃NG₂, Mg₂NG, Mg₅NG₂, Mg₃NG. A thorough structure search for pressures from 0 to 300 GPa is conducted using PSO algorithm with steps of 50 GPa.

Stability of Mg–NG compounds under pressure. To compare the formation energy of Mg–Xe and Mg–Kr compounds with different composition, the enthalpy of

formation per atom, H_f , is calculated using the following formula for Mg–NG:

$$H_f(\text{Mg}_n\text{NG}_m) = \frac{[H(\text{Mg}_n\text{NG}_m) - nH(\text{Mg}) - mH(\text{NG})]}{(n + m)}$$

in which H is the enthalpy of the lowest energy structure of specified composition at the given pressure. The results are shown in the form of convex hulls in Figure 1a–c, which

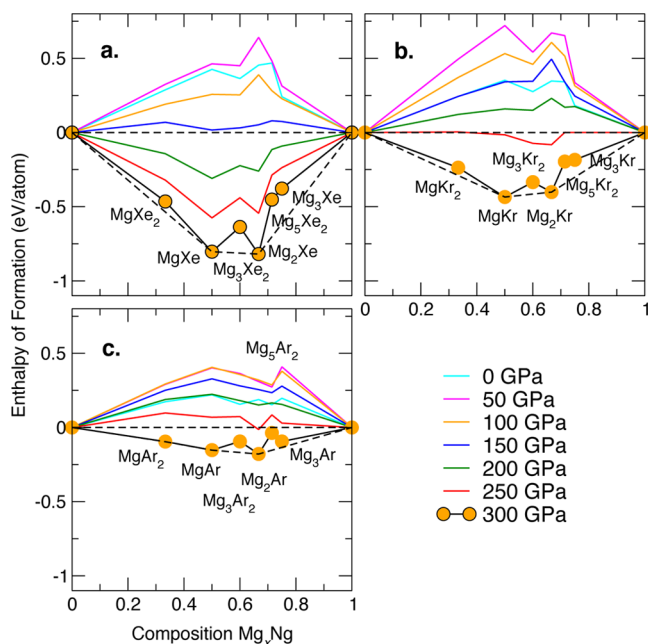


Figure 1. Stability of Mg–Ng compounds under high pressures and elevated temperatures. (a–c) The enthalpies of formations per atom of Mg–Xe, Mg–Kr, and Mg–Ar compounds under a series of pressures. The colors cyan, pink, orange, blue, green, red, and black represent the results under pressures of 0, 50, 100, 150, 200, 250, and 300 GPa. The dashed line connecting points for 300 GPa show the convex hull. The compounds locating on the convex hull are stable against decomposition into other compositions.

presents the stability of Mg–Xe, Mg–Kr, and Mg–Ar compounds at high pressure and zero temperature. The phases lying on the convex hull are stable against decomposition into other compositions, whereas phases above the convex hull are not stable and will decompose into the phases lying on the hull.

As shown in Figure 1a, all calculated Mg–Xe compounds have negative enthalpies of formation above 125 GPa; however, only MgXe and Mg₂Xe locate on the convex hull and therefore are stable against decomposition. Mg–Kr and Mg–Ar compounds show a similar trend, except they require pressures approaching 250 GPa to stabilize compound formation (Figure 1b,c). By calculating the phonon spectra, the dynamic stability of the compounds and structures at a given pressure are also confirmed [Figure S4, Supporting Information (SI)]. The effect of the zero-point energies (ZPE) on the enthalpy of formation is negligible, less than 2 meV/atom (~0.1 kJ/mol) for all compounds. The insignificant magnitude of the ZPE is typical for compounds that do not contain light elements, such as H and Li. Increasing temperature can also stabilize Mg–NG compounds, as revealed by the enthalpies of formation of MgXe and MgKr as functions of pressure and temperature, which are presented as contour plots in Figure S8 (SI). At 1000

K, MgXe and MgKr become stable at pressures of 50 and 150 GPa, respectively.

Since van der Waals interactions are known to be important for Xe, we performed calculations beyond the standard DFT. The random phase approximation (RPA) adopted here offers a balance between accuracy and efficiency.^{36,37} The DFT results were checked for the formation enthalpy of MgXe at 250 GPa. The pressure–volume curves predicted by the RPA are nearly identical to DFT for Mg and MgXe, whereas a slight increase (0.20 Å³/atom) of the volume is predicted for Xe at 250 GPa. The internal energy differences, as well as the enthalpy of formation, favor MgXe by an additional 30 meV compared to DFT. This indicates that the results are robust with respect to the electronic structure method employed.

Structure Features of Predicted Mg–NG Compounds.

The PSO structure search produces compounds with similar structural motifs, such as stacked square lattices (Figure 2a), in

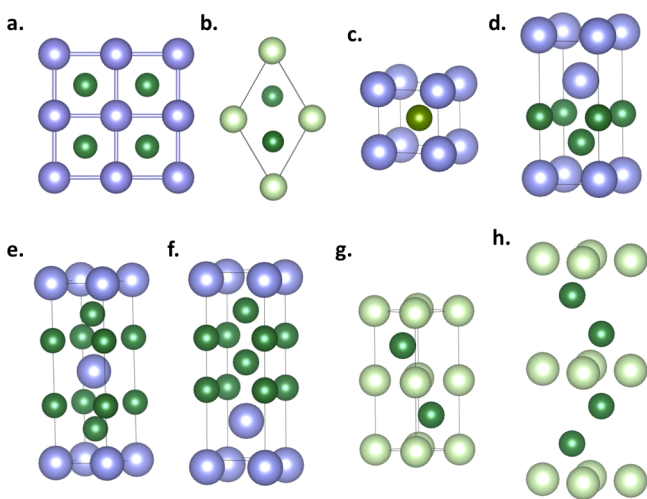


Figure 2. Selected structures of MgXe and Mg₂Xe compounds. (a) Top view of two intercalated square lattices (green and blue lattices). (b) Top view of hexagonal lattice of Mg–Ar compounds. (c) MgXe in CsCl structure, which is the simplest case of stacked square lattices. (d) MgXe in *P4/nmm* structure. (e) Mg₂Xe in *I4/mmm* structure. (f) Mg₂Xe in *P4/nmm* structure. (g) MgAr in *P6₃/mcm* structure. (h) Mg₂Ar in *P6₃/mcm* structure. In parts a–h, the large blue balls, the large light green balls, and the smaller green balls represent Xe, Ar, and Mg atoms, respectively.

the Mg–Xe and Mg–Kr systems. The simplest structure is the CsCl structure (Figure 2c; *Pm3m*), which is adopted by MgXe and MgKr at pressures higher than 100 and 250 GPa, respectively (Figure 1b). At lower pressure (<100 GPa for MgXe and <250 GPa for MgKr), the structure of MgXe and MgKr with lowest enthalpy (Figure 2d; *P4/nmm*) contains alternating square nets of Mg and NG stacked along the *c*-direction that are capped by the additional Mg or NG atom also in an alternating fashion. The resulting coordination appears as a series of edge- and corner-sharing square bipyramids. Mg₂Xe and Mg₂Kr contain coordination environments under high pressure that are similar to those of the MgNG compounds. Crystallizing in space group *I4/mmm*, as illustrated in Figure 2e, this structure contains square nets of Xe that are capped by Mg atoms, forming the edge-sharing square bipyramids. Sandwiched between these layers is a NG-centered CsCl-like cube. At lower pressure (<100 GPa), Mg₂Xe also crystallizes in space group *P4/nmm* (Figure 2f), where a capping atom and the NG

centering the cube are switched. Comparing all of these structures, it is interesting to note that under higher pressure the Mg and NG layers tend to form intercalated layers, whereas at lower pressure they appear to segregate (Figure 2f) and show a tendency to decompose into the elements.

Many binary intermetallic compounds adopt structures containing stacked hexagonal lattices; however, Mg–Xe and Mg–Kr are the first to be found adopting structures of stacked square lattices. Under increasing pressure, not only are the volumes of these compounds reduced, but the unit cell axial ratio (*c/a*) also changes with *c/a* > 1 at ambient pressure. Increasing pressure reduces the elongation in the *c*-direction, approaching the cubic value of *c/a* = 1. For some structures, the unit cell becomes more compressed in the *c*-direction than in the *a*- and *b*-directions (e.g., *c/a* < 1) under pressures higher than 150 GPa (Figure S2, SI).

In contrast to Mg–Xe and Mg–Kr, the Mg–Ar compounds are predicted to adopt hexagonal symmetry; correspondingly, the coordination number (CN) is 6. From 250 to 300 GPa, MgAr is stable in the anti-NiAs structure, consisting of an intercalated simple hexagonal lattice formed by Ar (the anion) atoms and a hexagonal close-packed (hcp) lattice formed by Mg (the cation) atoms (Figure 2b,g). At 300 GPa, MgAr transforms into the CsCl-type structure. Mg₂Ar at >250 GPa is isostructural with anti-NiAs structure (space group *P6₃/mcm*; Figure 2h). Here, two Mg layers are intercalated into the simple hexagonal lattice formed by Ar. The trend of increasing coordination number from MgAr to MgKr and MgXe compounds violates Pauling's first rule on crystal structure formation,¹ where the decreasing cation/anion radius ratio should lead to lower coordination. The mechanism of this violation is analyzed later in the paper.

Origin of the Stability. To identify the origin of the stability for the formation of Mg–NG compounds, the enthalpy of formation (ΔH) of MgXe and its energy components, including the internal energy (ΔE) and $P\Delta V$ term, as functions of increasing pressure are calculated. As shown in Figure 3a, at lower pressures (<100 GPa), the decrease in the MgXe enthalpy of formation is mainly caused by the reduction of volume. Following the reaction $\text{Mg} + \text{Xe} \rightarrow \text{MgXe}$ as a function of pressure, Figure 3b highlights changes in the ΔV with increasing pressure. At ambient pressure, MgXe has a larger volume than the sum of volumes for elementary Mg and Xe.

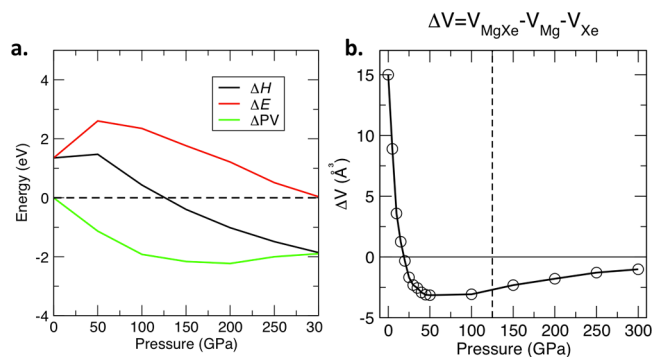


Figure 3. Origin of the stability of MgXe under pressure. (a) The change of enthalpy (ΔH), of internal energy (ΔE), and of PV while forming MgXe under increasing pressure. (b) The change of volume while Mg and Xe form MgXe under increasing pressure. The dashed line shows the pressure at which MgXe become stable against decomposition into Mg and Xe.

This is mainly because Mg is in a close-packed structure; however, as pressure increases, ΔV decreases quickly, becoming negative at about 20 GPa. At the transition pressure of 125 GPa, the volume of MgXe is approximately 10% smaller than the volume of Mg and Xe combined. It has been noticed that some alkali and alkaline metals have large compressibility due to the charge transfer from *s* to *d* orbitals under pressure.³⁸ Because of this volume reduction, the change in the electronic structure can have significant effect on the chemical stability. For example, a recent study revealed that the large volume change of Ca under pressure leads to charge transfer from the 4*s* orbital to the 3*d* orbital at around 200 GPa that causes a decomposition of Ca–Si compounds, which are stable at ambient condition.³⁹ The large compressibility calculated for MgXe is attributed to 3*s* orbital to 5*d* orbital charge transfer from Mg to Xe. Although the energies of both orbitals increase with pressure, the Xe 5*d* orbital energy is less sensitive to this perturbation and therefore is lower than that of Mg 3*s* orbital, allowing the charge transfer. This also gives rise to an internal energy decrease, which contributes to the stability of MgXe, especially under a pressure higher than 125 GPa (Figure 3a).

Electronic Structure of Mg–NG Compounds. The electronic structure of MgXe at 100 GPa, illustrated in Figure 4a,b, shows a nonzero projected density of states (PDOS) at

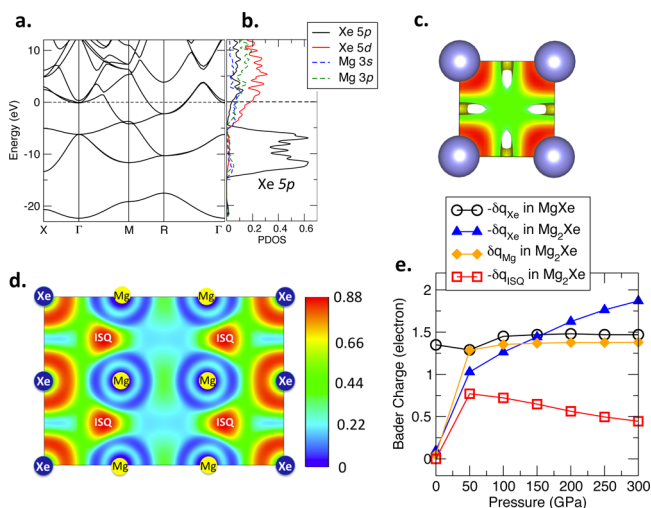


Figure 4. Electronic structure of MgXe under pressure. (a) Band structure of MgXe under 100 GPa in CsCl structure. (b) Projected density of states (PDOS) of MgXe under 100 GPa and in CsCl structure. The black and red solid lines represent Xe 5*p* and 5*d* states; the blue and green dashed lines represent the Mg 3*s* and 3*p* states. (c) The calculated electron localization functions (ELF) for MgXe in CsCl structure at 200 GPa showing at (100) cutoff plane. (d) Similar as in panel c, but for Mg₂Xe in *I4/mmm* showing at (100) cutoff plane. (e) The Bader charges for Xe in MgXe and Xe, Mg, and ISQ in Mg₂Xe, as a function of pressure. The absolute values are shown for Xe charges, which are negative in both compounds.

the Fermi level, suggesting metallic character. The states around the Fermi level consist mainly of Xe 5*d* states mixed with Mg 3*s* and 3*p* states. This suggests that charge transfer from the Mg 3*s* orbital to the Xe 5*d* orbital is the electronic mechanism of forming these compounds under pressure.

The electron localization function (ELF)⁴⁰ is often used to describe the charge redistribution and the bonding feature of molecules and solid materials. Larger ELF values usually correspond to inner shell or lone pair electrons and covalent

bonds, whereas the ionic and metallic bonds correspond to small ELF values. As shown in Figure 4c,d, both MgXe and Mg₂Xe are quite ionic in nature. Other Mg–Xe compounds and Mg–Kr and Mg–Ar compounds are also metallic, showing similar features as MgXe in their electronic structures.

The ELF plot for Mg₂Xe (Figure 4d) also reveals an exceptional feature in its electronic structure: there are electrons localized at the interstitial sites between the two adjacent Mg layers. Similar features are also found for ELF of Mg₂Kr and Mg₂Ar (Figure S5, SI). This is the signature of the recently discovered HPE.^{14,16,18,41} The formation of this localized electron density is due to the presence of quantized orbitals in the interstitial space that are confined by the surrounding atoms.²² The HPE energy increases with pressure due to the reduction of the size of the interstitial space. Because the orbital energy of the ISQ changes less significantly with pressure than the atomic orbital energy, electrons will transfer from atoms to the ISQ orbitals. Thus, at extreme pressures the formation of an electride becomes energetically favorable. Nevertheless, the actual presence of such isolated electrons can be concluded from a single electronic structure feature.⁴²

Using Bader's quantum mechanics atom-in-molecule (QMAIM) charge analysis⁴³ for MgXe and Mg₂Xe under pressure from 0 to 300 GPa (Figure 4e), we find that the charge transfer is quite large (1.5e per Xe in MgXe under 100 GPa), indicating that the compound is strongly ionic. The Bader charge is usually much smaller than the nominal charge, even for typical ionic compounds. For example, the Bader charge of MgO in the rocksalt structure at 100 GPa is calculated to be 1.73e, which is only slightly larger than the charge transfer in MgXe. It is interesting that a large charge transfer from Mg to Xe is present even at 0 GPa for MgXe in CsCl structure, although the compound is not stable and will decompose into Mg and Xe. By checking the orbital occupation, the electron transfer mainly occupies the Xe 6*s* orbitals. Increasing the pressure, however, changes the occupation of the Xe orbitals, with the 5*d* orbitals populated before the 6*s* orbitals, which is in direct violation of Aufbau's principle.

Three charges are also shown in Figure 4e for Mg₂Xe: Xe, Mg, and the ISQ. At 0 GPa, all three charges are close to zero. At 50 GPa, the charges on Xe, Mg, and ISQ are −1.03e, 1.29e, and −0.77e, respectively, showing a propensity for charge transfer at elevated pressures. Increasing the pressure beyond 50 GPa causes the charge on Mg to vary slightly, whereas the absolute charges on Xe increases and the ISQ decreases. Further increasing pressure to 300 GPa leads to an additional increase in the Xe charge and a decrease of the ISQ charge, indicating electron transfer from ISQ to Xe. Mg₂Xe is the first system that shows an electron transfer between ISQ and *d* orbitals under pressure. We also extended the calculation of the Bader charges up to 600 GPa for Mg₂Xe in the *I4/mmm* structure (Figure S6, SI). The change of the Bader charges becomes very small at pressures beyond 350 GPa. However, this result cannot exclude the possibility of total charge depletion from the interstitial sites (suppression of the electrides), since it is based on a structure that is found at lower pressure.

The formation of the high-pressure electrides is due to the occupation of electrons at the quantized orbitals of ISQ. This can be directly examined by showing the wave functions of the occupied bands. A more efficient way is the construction of the optimally localized Wannier functions. Such functions are constructed for Mg₂Xe (Figure S7, SI). Some of them are well-

localized at the ISQ sites and some others at Xe atoms, showing typical d orbital features. Furthermore, we also studied the bonding strength among Xe, Mg, and ISQ by calculating their integrated crystal orbital Hamiltonian population (ICOHP). The results reveal a mixed feature of ionic and covalent bonding for the Mg_2Xe compound. At a pressure of 200 GPa, the ICOHP values are -0.57 , -0.35 , -0.06 , -0.40 , -0.17 , and -0.04 eV/pair for Xe–Xe, Xe–ISQ, ISQ–ISQ, ISQ–Mg, Mg–Xe, and Mg–Mg pairs. These values are significantly smaller than that of a typical covalent bond, for example -1.819 eV/pair for Xe–F bonds in XeF_2 at 10 GPa, as calculated by the same method.¹²

DISCUSSION

The NG elements possess a complete atomic shell and therefore are classically inert to chemical reactions. The first Xe compound, $\text{Xe}[\text{PtF}_6]$, was found by Bartlett,³ 30 years after the theoretical prediction of Xe reactivity by Pauling. Since then, many compounds of Xe and other noble gas elements have been obtained or predicted by reacting them with strong oxidizing agents. In these compounds, the noble gas elements are positively charged.

In this work, we show a new effect of pressure, namely, reducing a chemical species with completed atomic shells. These calculations show that NG elements can be reduced, becoming negatively charged and forming intermetallic compounds with Mg under pressure. The mechanism of this phenomenon is that the energy of outer shell d orbitals (5d for Xe) increases less significantly under pressure than the 3s orbital of Mg. If the pressure is sufficiently high, electrons will transfer from the Mg 3s orbital to the NG d orbitals. As shown in our study, the charge transfer happens for Mg–Xe at pressures much lower than the pressure at which MgXe becomes energetically favorable.

The charge transfer from Mg to NG atoms and the corresponding population of the d orbitals cause strong chemical interactions between the NG atoms. Although there are many examples of chemical bonds between NG and other atoms, the interactions between NG atoms are often limited to weak van der Waals forces. This is due to the fact that the valence orbitals of neutral NG atoms are completely filled, excluding any chemical bonding between them. In a small number of NG compounds, such as XeF_2 and XeO_2 , the NG will form covalent bonds with the oxidant atoms, but the interaction between NG atoms is very weak. In all cases, the NG is the cation in these compounds. In contrast, the work presented here indicates that NG atoms can also gain electrons to become negatively charged. They are also predicted to show strong chemical interactions between the NG atoms. As shown in the ELF for MgXe (Figure 4c) and for Mg_2Xe (Figure 4d), large values can be seen between the Xe atoms, indicating strong chemical interactions with a large covalent component.

One striking feature of Mg–NG compounds is the exhibition of HPE at comparatively low pressure. The presence of the ISQ²² in Mg_2Xe can be clearly seen in Figure 4d. The ELFs of Mg_2Kr and Mg_2Ar show similar features (Figure S5, SI). Although the HPE in elemental Li and elemental Na were observed in diamond anvil cell (DAC) experiments, the similar transformation into HPE for elemental Mg was predicted to happen at pressures higher than 800 GPa. This is partially because the filled Mg 3s orbital is significantly lower in energy than Li and Na frontier s orbitals. The predicted Mg HPE adopts the MgB_2 structure with ISQ located in the place of the

boron atoms. The lower-pressure HPE formation calculated here is due to noble gases for two reasons. First, the NG atoms deplete a large amount of Mg charge, reducing the number of ISQs to accommodate the electrons. A larger number of ISQs, corresponds to larger volume, therefore is not favored by increasing pressure. Second, the presence of a large size of NG atoms increases the volume of the interstitial space, which leads to the reversion of ISQ and Mg 3s levels at lower pressure. Because the Xe 5d and ISQ levels are close in energy, they also show strong chemical interactions. The ELF in the regions between neighboring Xe and ISQ is as high as 0.5, indicating strong covalent components.

Recent work on HPE showed that, in contrast to s and p orbitals, the energy of d orbitals decreases relative to the ISQ level with increasing pressure.²² As a result, the elements containing unoccupied low-energy d orbitals do not exhibit HPE phenomena. Interestingly, the involvement of the $(n - 1)d$ orbitals in heavier alkali and alkaline metals, such as K, Ca, and Cs, prevent them from forming HPE under high pressure, although their ionization energies are even lower than Li and Na at ambient condition, due to the high energy of their frontier s orbitals. Mg_2Xe is a unique system that shows that the electrons gradually transfer from ISQ to Xe 5d under increasing pressure (Figure 4e). It is also interesting that the ISQ charge decreases from Mg_2Ar to Mg_2Kr and to Mg_2Xe . At 300 GPa, the ISQ charge values are 0.89e, 0.58e, and 0.45e for the above three compounds, respectively. This is due to the fact that the d levels of later NG are lower in energy and can then deplete more electrons away from ISQ.

The energy shift of s and d orbitals under pressure is a general trend, and the large charge transfer and the population of the outer shell orbitals are not limited to NG elements and Mg. In other calculations we have found that Xe can form stable compounds with Li at a pressure much lower than that required for stable Mg–Xe compounds. The effect of the s and d orbital ordering under pressure has been observed in experiments for some alkali and alkaline metals. For example, at sufficiently high pressure (>30 GPa), the s electrons of K will transfer to the d shell, causing K to behave like a transition metal with a partially filled d band.⁴⁴ Because of the competition of their own outer shell d orbitals, Xe cannot oxidize heavy alkali and alkaline earth metals.

The formation of xenon compounds at high pressures may have implications for the chemistry of the terrestrial planets and exoplanets. Compared to the other noble gases, in Earth's atmosphere, Xe is deficient by a factor 2–4 relative to values on the Sun and by a factor of 10 relative to values for chondritic meteorites, a signature shared with the atmospheres of Mars and Venus.⁴⁵ Recent work exploring novel Xe behavior has argued that Xe compounds in the deep Earth may constitute a reservoir hosting the Xe that is not observed in the atmospheres of the terrestrial planets.^{46–49} While comparing Figure S8 (SI) with the mantle adiabat,⁵⁰ we find that MgXe becomes stable at depths ~ 1500 km in the lower mantle. At the core–mantle boundary ($T \sim 3500$ – 4500 K, $P \sim 135$ GPa), the enthalpy of formation of MgXe can be as high as 1.25 eV (121 kJ/mol). Although Mg in the Earth's mantle is primarily hosted in silicate and oxide phases, a trace amount of Mg–Xe compound is enough to form a chemical reservoir of Xe, with concentrations on the order of parts per quadrillion.⁵¹

SUMMARY

Using accurate DFT calculations in conjunction with automatic crystal structure search techniques, this work demonstrates a new chemical phenomenon of the noble gases: they can gain electrons, becoming negatively charged, and form thermodynamically stable compounds with Mg under high pressure. The resulting metallic compounds adopt very simple structures, such as CsCl-type, and show striking chemical features. For instance, the population of the outer shell d levels of noble gases not only lead to anionic noble gases but also the strong chemical interaction among them. Of particular interest from this discovery is the formation of high-pressure electrified at relatively low pressure, which is caused by the presence of noble gas atoms. We also observe a direct interaction between the atomic orbitals, such as Xe 5d, and the interstitial quantum orbitals, which demonstrates the quantum nature of the HPE. The propensity of forming metallic Mg–NG compounds increases with increasing size. The identification of these phases may provide an alternative explanation for the puzzle of the missing Xe in earth science.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08162.

Figures and tables giving structures, enthalpy, and physical properties calculated at different pressures of the Mg–Xe and Mg–Ar compounds (PDF)

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Notes

The authors declare no competing financial interest.

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