Prediction of the Reactivity of Argon with Xenon under High Pressures
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ABSTRACT: Pressure significantly modifies the microscopic interactions in the condense phase, leading to new patterns of bonding and unconventional chemistry. Using unbiased structure searching techniques combined with first-principles calculations, we demonstrate the reaction of argon with xenon at a pressure as low as 1.1 GPa, producing a novel van der Waals compound XeAr2. This compound is a wide-gap insulator and crystallizes in a MgCu2-type Laves phase structure. The calculations of phonon spectra and formation enthalpy indicate that XeAr2 would be stable without any phase transition or decomposition at least up to 500 GPa.

INTRODUCTION

Due to the stable closed-shell electronic configuration, noble gas (NG) elements (e.g., He, Ne, Ar, Kr, and Xe) were historically believed to be chemically unreactive. However, Pauling† predicted that Xe and Kr may bond to electronegative atoms, which was proved experimentally by Bartlett‡ with the synthesis of the first NG compound XePtF6. This seminal discovery led to a recognized renaissance in NG chemistry in the past few decades.†‡

Under ambient conditions, the heavier NG element Xe and, to some extent, Kr and Ar have been known to be oxidized by halogen and oxygen, forming halide and oxide compounds, respectively.‡† Under high pressures, the reactivity of NGs was drastically altered.

On one hand, application of high pressure makes NGs easier to be oxidized; for example, NGs can be oxidized not only by fluorine, oxygen, and nitrogen, but also by sulfur, and even metal elements such as iron and nickel.‡† Theoretical predictions revealed that Xe reacts with S and N at 146 and 191 GPa, respectively. Direct reactions of Xe with Fe/Ni were predicted to occur under the pressures of Earth’s inner core. A subsequent experimental study reported the synthesis of a Xe–Ni compound at a pressure around 150 GPa. Of special attention, the Fe/Ni atoms in the Xe–Fe/Ni compounds play the role of anions instead of cations that behave as usual metals. In addition, Xe has also been observed to react with water ice at pressures above 50 GPa. In these NG compounds, Xe bonds to other elements chemically by sharing its closed-shell electrons. On the contrary, NG elements can also become oxidants and gain electrons from alkali and alkaline earth metals such as Li, Cs and Mg.

On the other hand, NGs also form van der Waals (vdW) compounds under lower pressures wherein the NG atoms do not lose or gain electrons. For instance, the Laves phase compounds NeHe2, Ar(H2)2, ArHe2, Xe(O2)2, and Xe(N2)2 can be synthesized at pressures of a few gigapascals. The stabilities of such compounds can be explained in terms of packing rules analogous to binary crystals of hard spherelike particles for intermetallic compounds. Other classes of vdW compounds have also been discovered. The structure of (N2)6Ne7 clathrate with the centers of the N2 molecules forming distorted dodecahedron cages, each enclosing 14 Ne atoms. XeHe2 stabilizes at 12 GPa, adopting a hexagonal AlB2-type structure. Some other stoichiometries such as the Xe–H2O, Xe–H2O, He–H2O systems have also been observed. The origin of the stability for these compounds was not well understood.

In a few cases, unexpected chemistry in Xe–F compounds stabilized by covalent Xe–Xe bonding has also been reported recently. It is obvious that the bonding of NGs in compounds under high pressures exhibits strong uncertainty, which provides a broad scenario waiting for further investigation. In this paper, we theoretically explore the phase diagram and bonding of the Xe–Ar binary system under high pressures. Our results demonstrate the existence of a Xe–Ar compound with the stoichiometry of XeAr2.

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RESULTS AND DISCUSSION

To obtain the most energetically favorable structures for the Xe–Ar binary system, the stoichiometries of XeAr\textsubscript{n} (n = 1–8) containing up to 4 formula units (fu) per simulation cell are systematically searched under pressures of 0, 100, 200, and 500 GPa. The calculated formation enthalpies (H\textsubscript{f}) of each stoichiometry at different pressures are shown in the form of convex hulls as depicted in Figure 1. From this figure, the thermodynamic stability of XeAr\textsubscript{n} can be determined. The results indicate that each stoichiometry of XeAr\textsubscript{n} has a small positive H\textsubscript{f} at 0 GPa. As the pressure increases to 100, 200, or 500 GPa, the convex hulls are dominated by a well-developed minimum at XeAr\textsubscript{2} stoichiometry, indicating that only XeAr\textsubscript{2} is stable against decomposition into elemental Xe and Ar. The other stoichiometries are thermodynamically unstable due to the fact that the increase of pressure would promote their formation enthalpies to be larger positive values. The stable XeAr\textsubscript{2} compound is predicted to crystallize in the MgCu\textsubscript{2}-type Laves phase structure (Figure 2a), wherein the Xe atoms occupy the Mg (8a) sites, forming a diamond-type sublattice, and the Ar atoms reside in the voids of the Xe framework, occupying the Cu (16d) sites. At 100 GPa, the lattice parameter of XeAr\textsubscript{2} is 7.08 Å in the unit cell. By representing its constituents as hard spheres, the stability of AB\textsubscript{2}-type Laves phase can be understand by the packing rule, i.e., a hard-sphere radius ratio R\textsubscript{A}/R\textsubscript{B} close to 1.25 will achieve the maximum packing efficiency (0.71%) when crystallized in Laves phase. The ratio R\textsubscript{A}/R\textsubscript{B} of XeAr\textsubscript{2} is 1.13, which is close to the ideal value of a Laves phase. Our structural search simulations reveal that the increase of pressure will further stabilize the Laves phase XeAr\textsubscript{2} instead of any phase transition or decomposition, which is in sharp distinction with other NG compounds such as XeHe\textsubscript{2}, NeHe\textsubscript{2}, and ArHe\textsubscript{2}. As shown in Figure 1, the pressure-dependent formation enthalpy of MgCu\textsubscript{2}-type XeAr\textsubscript{2} wherein it is shown that XeAr\textsubscript{2} becomes stable at 1.1 GPa. The effect of vDW interactions on the stability of XeAr\textsubscript{2} is also calculated by using the PBE-D2 method. The results indicate that the stable pressure shift to 2.6 GPa with the inclusion of vDW corrections. To determine the dynamical stability of MgCu\textsubscript{2}-type XeAr\textsubscript{2}, the phonon dispersion spectra are calculated based on the quasi-harmonic model, and the selected results are shown in Figure 3. It is found that XeAr\textsubscript{2} is dynamically stable without showing any imaginary phonon frequency in the pressure range from 10 to 500 GPa.

Figure 1. Formation enthalpies (H\textsubscript{f}) of XeAr\textsubscript{n} (n = 1–8) with respect to decomposition into constituent elemental solids under different pressures. Solid lines denote the convex hull, where the data points located on represent stable species against any type of decomposition. Inset: Pressure-dependent formation enthalpy of XeAr\textsubscript{2} obtained with (Perdew–Burke–Ernzerhof (PBE) + D2) and without (PBE) vDW corrections.

Figure 2. (a) Crystal structure of XeAr\textsubscript{2}. The big and small spheres represent Xe and Ar, respectively. (b) Pressure-dependent band gap of XeAr\textsubscript{2} and Xe (face-centered cubic). (c) Pressure-dependent Bader charge on the Xe atoms in XeAr\textsubscript{2}. (d) Electron localization function (ELF) of XeAr\textsubscript{2} at 500 GPa.

Figure 3. Phonon dispersion spectrum of XeAr\textsubscript{2} at 10 and 500 GPa.

It is known that the Gibbs free energy (\(G = H - TS\)) reduces to enthalpy (\(H = U + pV\)) when temperature is 0 K. The formation enthalpy of a compound is determined by the relative internal energy \(\Delta U\) and \(p\Delta V\) terms with respect to elemental solids. Figure 4 displays the calculated pressure-dependent \(\Delta U\) and \(p\Delta V\) of XeAr\textsubscript{2}. It is shown that the large gain in negative \(p\Delta V\) term effectively tunes the formation enthalpies to be negative, although the relative internal energies \(\Delta U\) are positive at 0–150 GPa, leading to the reaction of Xe with Ar above 1.1 GPa. The negative \(p\Delta V\) of XeAr\textsubscript{2} is attributed to the smaller volume compared to the mixing volume of elemental Xe and Ar. For comparison, we also calculated the pressure-dependent \(p\Delta V\) for MgCu\textsubscript{2}-type XeS\textsubscript{2} and AlB\textsubscript{2}-type XeHe\textsubscript{2}. As shown in Figure 4, the
However, for XeHe$_2$, the values of both being negative in the whole pressure region considered.

The states of Ar 3s and 3p and Xe 5s and 5p are highly localized, suggesting a weak atomic interaction in XeAr$_2$. The obtained smaller ELF values (0.32) between the nearest Xe atoms in XeAr$_2$ at 500 GPa are presented in Figure 2b. It is shown that the gap of XeAr$_2$ decreases more slowly than that of Xe. XeAr$_2$ metallizes at approximately 500 GPa, which is substantially higher than that of Xe (~130 GPa). At 500 GPa, the PDOS plotted in Figure 5b shows that the electronic states are widely broadened, indicating that the relevant valence electrons become more delocalized. The PDOS also reveal a significant overlap between the 5p states of Xe and 3p states of Ar. Additionally, Bader analysis$^{43}$ reveals a charge transfer of 0.43 e/atom from Xe to Ar at 500 GPa (Figure 2c).

To study the electronic properties, we calculate the projected density of states (PDOS) under high pressures. As shown in Figure 5, XeAr$_2$ is a wide-gap insulator under low pressures. At 10 GPa (Figure 5a), the band gap is about 8 eV. The states of Ar 3s and 3p and Xe 5s and 5p are highly localized, suggesting a weak atomic interaction in XeAr$_2$. The calculated pressure-dependent band gaps of XeAr$_2$ in comparison to those of elemental Xe$^{42}$ are presented in Figure 2b. It is shown that the gap of XeAr$_2$ decreases more slowly than that of Xe. XeAr$_2$ metallizes at approximately 500 GPa, which is substantially higher than that of Xe (~130 GPa). At 500 GPa, the PDOS plotted in Figure 5b shows that the electronic states are widely broadened, indicating that the relevant valence electrons become more delocalized. The PDOS also reveal a significant overlap between the 5p states of Xe and 3p states of Ar. Additionally, Bader analysis$^{43}$ reveals a charge transfer of 0.43 e/atom from Xe to Ar at 500 GPa (Figure 2c). These features of electronic properties indicate that strong chemical interactions may exist in XeAr$_2$ under high pressures.

The fact that both Xe and Ar possess closed-shell electronic structures makes them chemically inert at ambient conditions. In the XeAr$_2$ compound, the atoms are bound by vdW forces under low pressures. At 500 GPa, the nearest-neighbor Xe–Xe, Xe–Ar, and Ar–Ar distances in XeAr$_2$ are 2.56, 2.45, and 2.09 Å, respectively. It appears that these atomic distances are close enough for them to form covalent bonds compared with the proposed covalent radii of Xe (1.40 Å) and Ar (1.06 Å) atoms.$^{44}$ To detect the chemical bonding in XeAr$_2$, we calculate the crystalline orbital Hamiltonian population (COHP) for nearest-neighboring Xe–Xe, Xe–Ar, and Ar–Ar pairs. As can be seen from Figure 5c, the contributions from bonding states are larger than those from antibonding in the occupied states of the Xe–Xe pair. As a result, the integrated COHP (ICOHP) up to the Fermi level is −1.20 eV/pair for bonded Xe–Xe. In the view of crystal orbital Hamilton populations,$^{45}$ this value suggests a conspicuous contribution of the Xe–Xe contact to the band energy and always relevant to covalent bonding. In addition, we also calculate the electron localization function (ELF).$^{46}$ As a rule, an ELF value larger than 0.5 usually corresponds to covalent bonds. However, some untypical covalent bonds have been found to have lower ELF values.$^{47}$–$^{49}$ As displayed in Figure 2d, the obtained ELF value between the nearest Xe atoms in XeAr$_2$ at 500 GPa is 0.5, which also suggests the possible presence of covalent Xe–Xe bonds. With regard to the Xe–Ar pair, the COHP plots show large occupation of the antibonding states and the ICOHP up to the Fermi level is −0.36, suggesting a weak atomic bonding. The obtained smaller ELF values (0.32) between the neighboring Xe–Ar atoms also confirm this. For the neighboring Ar–Ar pair, the obtained ICOHP is only −0.07, indicating nonbonding interaction between the relevant atoms.

**CONCLUSIONS**

In summary, we have theoretically explored the stability of XeAr$_n$ (n = 1−8) under high pressures up to 500 GPa using the effective CALYPSO structure searching method combined with first-principles calculations. The results shown that Xe reacts with Ar at a pressure as low as 1.1 GPa, producing a MgCu$_2$-type Laves phase XeAr$_2$ compound. This compound is a wide-gap insulator that would metallize at about 500 GPa. Analysis of the electronic structures and COHP under 500 GPa suggests a possible presence of covalent Xe–Xe bonds in XeAr$_2$. Our results shed light on the chemical bonding between NG elements and enrich the NG chemistry.

**COMPUTATIONAL DETAILS**

We perform a systematic structural search for the XeAr binary system based on a particle swarm optimization methodology as implemented in the CALYPSO code,$^{50,51}$ which has been successfully employed in predicting a large variety of crystal structures.$^{52}$–$^{58}$ The underlying total energy calculations and structural relaxations are carried out within the framework of density functional theory using the projector augmented wave method$^{59}$ as implemented in the VASP code.$^{60}$ We adopt the Perdew–Burke–Ernzerhof of generalized gradient approximation$^{61}$ to describe the exchange–correlation functional.
The electron-ion interaction is described by pseudopotentials with $5s^25p^6$ and $3s^23p^6$ as valence electrons for Xe and Ar, respectively. The use of a cutoff energy of 650 eV and dense enough $k$-point sampling grids gives excellent convergence of the calculated enthalpy (~1 meV/atom). The dynamical stability of predicted structures is determined by phonon calculations using the finite displacement approach as implemented in the Phonopy code. To quantify the chemical bonding, the crystal orbital Hamilton population (COHP) is calculated by using the program Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction.

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Notes
The authors declare no competing financial interest.

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