Regulation of Ionic Bond in Group ⅡB Transition Metal Iodides

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Using a swarm intelligence structure search method combining with first-principles calculations, three new structures of Zn–I and Hg–I compounds are discovered and pressure-composition phase diagrams are determined. An interesting phenomenon is found, that is, the compounds that are stable at 0 GPa in both systems will decompose into their constituent elements under certain pressure, which is contrary to the general intuition that pressure always makes materials more stability and density. A detailed analysis of the decomposition mechanism reveals the increase of formation enthalpy with the increase of pressure due to contributions from both ΔU and $\Delta[PV]$. Pressure-dependent studies of the ΔV demonstrate that denser materials tend to be stabilized at higher pressures. Additionally, charge transfer calculations show that external pressure is more effective in regulating the ionic bond of Hg–I, resulting in a lower decomposition pressure for HgI_2 than for ZnI_2. These findings have important implications for designs and syntheses of new materials, as they challenge the conventional understanding on how pressure affects stability.

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Pressure, as an important thermodynamic quantity, can effectively influence the electronic structure and chemical reactivity of elements, and produce materials that are unattainable under ambient conditions. Noble gas (NG) elements with closed-shell electronic configurations are difficult to react with other elements under normal pressure, but recent research has shown that pressure can lead to successful formation of NG compounds. For example, Xe can be oxidized by Fe/Ni to form stable compounds under Earth's core pressure[1] and can be reduced to a negatively charged anion by alkaline earth metal Mg under a pressure of 150 GPa.[2] Successfully predicting that Be,[3] Au,[4] and Zn[5] can form Li compounds under pressure indicates that it is an effective method for regulating the chemical reactivity of Li. In 2018, Binn *et al.* synthesized a compound of lithium and copper, LiCu-R39, for the first time under pressures lower than 1 GPa by compressing a mixture of elements in a diamond anvil cell. They found that above 5 GPa, LiCu-R39 transformed into a new stoichiometric compound, Li_2Cu, accompanied by a reduction in Cu–Cu bonding from two-dimensional layers to one-dimensional chains, demonstrating the strong effect of pressure on the reactivity of lithium.[6] In addition, in 2023, Li *et al.* investigated silver iodide under compression conditions using synchrotron x-ray diffraction experiments and first-principles calculations. Their study reveals the effective regulation of ionic bonds by pressure, where the strong ionic bond Ag–I is broken under pressure, leading to the recovery of elemental solids from the decomposition reaction.[7]

Group ⅡB transition metal di-iodides (ZnI_2, CdI_2, HgI_2) have attracted great research interest in basic applications due to their unique properties. ZnI_2 has gained attention in industrial applications and has been the subject of numerous studies exploring its structure,[8–10] thermochemistry,[11] and thin film properties.[12–15] The sensitivity of CdI_2 to photochemical radiation has attracted significant attention in both theoretical and experimental settings.[16–24] This makes it a promising candidate for use in UV photochromic materials, scintillation detectors, and photography.[17] HgI_2 has a large bandgap (300 K, $E_g = 2.13$ eV) and high ionization efficiency (52%), making HgI_2 detectors most efficient among the most common semiconductors detectors (HgI_2, CZT, CdTe).[25–27] The study of the high-pressure behavior of group ⅡB transition metal di-iodides has received attention experimentally and theoretically. In 2020, extensive studies on the high-pressure behavior of CdI_2 were conducted, combining theoretical calculations with experimental techniques such as x-ray diffraction and Raman scattering.[24] This effort led to the determination of the phase transition sequence $P6_3mc$–$C2/m$–$I4/mmm$ for CdI_2 and the discovery of changes in its insulator-semiconductor-metal properties under compression. Especially, a surprising finding was also reported by us in 2022, which revealed the decomposition of CdI_2 under a pressure of 61.5 GPa, a physical phenomenon that contradicts the common understanding that pressure always results in material densification and stability.[16] While the high-pressure phase diagram of HgI_2 has been explored by various researchers, the max-

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imum pressure studied is still around 10 GPa,[28–30] and there have been no studies on the high-pressure behavior of ZnI_2. Importantly, pressure can also promote the synthesis of new chemical reactions, leading to the formation of unusual stoichiometric compounds that cannot be obtained under ambient conditions. Therefore, further exploration and investigation of the high-pressure behavior of the Zn–I and Hg–I systems are necessary.

In this Letter, we investigate Zn–I and Hg–I systems up to 100 GPa using first-principles calculations combined with CALYPSO structure search, revealing that 1/2 is the most stable stoichiometry. Both systems exhibit pressure-induced decomposition phenomena, and an exploration of the decomposition mechanism suggests that pressure hinders charge transfer between atoms and weakens the ionic interaction.

The CALYPSO search method,[31,32] in combination with *ab initio* total-energy calculations, has proven to be an efficient tool for finding stable structures under specific conditions and chemical ratios. This approach has been widely used in high-pressure studies and has contributed significantly to the field.[33–38] For this study, the CALYPSO search method was applied to the Zn_xI_y (x/y = 1/3, 1/2, 1/1) and Hg_xI_y (x/y = 1/3, 1/2, 1/1, 2/1) systems at 0 K and over a pressure range of 0–100 GPa using a 1–4 formula units. Structural relaxations were performed in the framework of density functional theory (DFT), using the Vienna *ab initio* simulation package (VASP) with the Perdew–Burke–Ernzerhof generalized gradient approximation.[39,40] To ensure that the enthalpy calculation can converge well within the range of 1 meV/atom, the Monkhorst–Pack scheme was used with a plane-wave energy cutoff of 600 eV and a dense k-point grid of spacing $2\pi \times 0.03$ Å. We used the projection-enhanced wave potential,[41] and the valence electrons of Zn, Hg, and I were $3d^{10}4s^2$, $5d^{10}6s^2$, and $5s^25p^5$, respectively. The dynamical stability of the structures was confirmed by calculating the phonon spectrum using the PHONOPY code.[42] In addition, electronic properties and bonding characteristics were analyzed. Charge transfer in the crystal was investigated using Bader's quantum theory of atoms in molecules[43] and bonding properties were determined through the calculation of the crystal orbital Hamilton population using the LOBSTER package.[44,45] The Madelung energy of the crystal was obtained using the VESTA software.[46]

We conduct extensive structural searches of the Zn–I and Hg–I systems in the pressure range of 0–100 GPa. Our calculations reproduce the experimental phase of α-HgI_2 ($P4_2/nmc$) and HgI ($I4/mmm$),[47,48] which means that the reliability of the results is proved. We also find the theoretically proposed $P6_3mc$ phase of ZnI_2 and the $P6_3mc$ phase of HgI_2.[29,49] In addition, there are three new phases discovered: an $I\bar{4}2d$ phase of ZnI_2, an $I4/mmm$ phase of HgI_2, and a $Pm\bar{3}m$ phase of HgI. Detailed information about all phases was proved in the Supplementary Materials (Table S1).

An effective way to probe the relative thermodynamic stability of various stoichiometries under high pressure is to construct a convex hull diagram, the formation enthalpies of compounds relative to constituent elements are calculated with

$$\Delta H(M_xI_y) = [H(M_xI_y) - xH(M) - yH(I)]/(x+y),$$

where H is the calculated enthalpy of each composition per formula unit and M represents metallic zinc and metallic mercury. We present our calculation results in Figs. 1(a) and 1(b). Compounds, aligned vertically to the data lying on the solid lines, are thermodynamically stable, while those to the data lying on the dotted lines are unstable or metastable, and will decompose. For the Zn–I and Hg–I systems, $x/y = 1/2$ is the most stable in the stoichiometric ratio studied because Zn and Hg easily form +2 valence when forming compounds. Particularly, the formation enthalpy of the compounds in all ratios considered increases under compression, leading to the pressure-induced decomposition of the two systems. ZnI_2 will decompose above 50 GPa, and HgI and HgI_2 will decompose above 30 GPa.

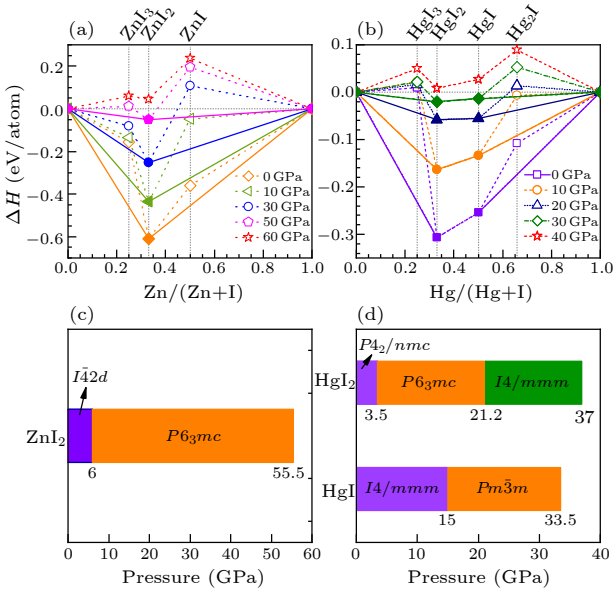

Fig. 1. Calculated formation enthalpy (ΔH) at different pressures: (a) Zn–I system, (b) Hg–I system. The pressure composition phase diagram of (c) Zn–I system, (d) Hg–I system. The $P6_3/mmc$ phase for element Zn,[50,51] $I4/mmm$ (β), $C2/m$ (γ), and $P6_3/mmc$ (δ) phases for element Hg,[51–55] and $Cmca$, $Immm$, $Pm\bar{3}m$, and $I4/mmm$ phases for element I[56] are used to calculate the formation enthalpy.

To elucidate the phase transition sequence and accurate decomposition pressure of stable compounds, we conduct a thorough investigation of the enthalpy difference of the obtained structures relative to the constituent elements as a function of pressure (Fig. S1 in the Supplementary Materials). ZnI_2, the $I\bar{4}2d$ phase obtained by structural search under 0–6 GPa, is more stable than the previously reported $P6_3mc$, and the $P6_3mc$ phase maintains after 6 GPa until the decomposition occurs at 55.5 GPa. HgI, the searched $Pm\bar{3}m$ phase, becomes the most stable structure at 15 GPa and decomposes at 33.5 GPa. We observed two distinct phase transitions for HgI_2 occurring at

3.5 GPa and 21.2 GPa, with a phase transition sequence of $P4_2/nmc$–$P6_3mc$–$I4/mmm$. The $I4/mmm$ phase was found to decompose at 37 GPa. Our findings on the phase transition sequence of HgI_2 are slightly different from those obtained in the 2005 room-temperature experiments,[29] likely due to temperature differences. We have included the pressure-composition phase diagrams in Figs. 1(c) and 1(d) for an easy understanding of our results.

In the present study, we investigate the high-pressure induced decomposition mechanism of ZnI_2 and HgI_2, which have the most stable ratios in their systems. At 0 K, the Gibbs free energy expression simplifies to the enthalpy expression as the TS term is zero. Thus, we utilize the enthalpy difference ΔH to determine the direction of the reaction. ΔH is calculated as $\Delta H = \Delta U + \Delta[PV]$, where ΔU and $\Delta[PV]$ represent the differences in the internal energy and PV terms between the compound and its constituent elements, respectively, and P represents the external pressure. We calculate the changes in ΔU and $\Delta[PV]$ as functions of pressure and present the results in Fig. 2. The nonlinear variations of ΔH, ΔU, and $\Delta[PV]$ with pressure are attributed to the phase changes in both the compound and constituent elements. Remarkably, $\Delta[PV]$ of ZnI_2 increases substantially from 0 GPa to the decomposition pressure ($\sim$0.52 eV/atom) compared to a negligible change in ΔU ($\sim$0.08 eV/atom). Conversely, for HgI_2, both ΔU and $\Delta[PV]$ increase, but with different amounts. Specifically, ΔU increases by $\sim$0.2 eV/atom, and $\Delta[PV]$ increases by $\sim$0.1 eV/atom. Thus, our study suggests that the mechanisms causing the decomposition of the compounds ZnI_2 and HgI_2 are distinctly different. The decomposition of ZnI_2 primarily results in an increase in ΔH due to the increase in $\Delta[PV]$, while both ΔU and $\Delta[PV]$ of HgI_2 contribute to the increase in ΔH.

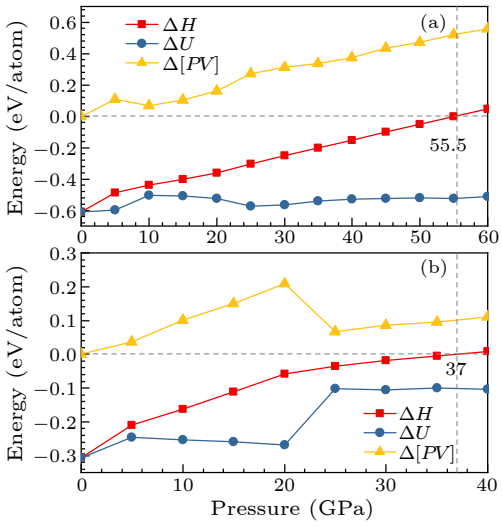

Fig. 2. ΔH, ΔU, and $\Delta[PV]$ versus pressure for (a) ZnI_2, $Zn + 2I$ mixture, (b) HgI_2, $Hg + 2I$ mixture.

To provide insights into the physical mechanisms of decomposition, we examine the pressure dependence of the difference in the average volume per atom occupied by a compound and its constituent elements, denoted as ΔV. The results presented in Figs. 3(a) and 3(b) reveal that both ZnI_2 and HgI_2 compounds have larger volumes than their respective elemental mixtures at 0 GPa, resulting in a positive ΔV. However, due to the high-pressure phase transition, the variation in ΔV is rugged and exhibits an overall decrease from 0 GPa to decomposition for both the compounds, but remains positive at the decomposition pressure. The variation in $\Delta[PV]$ for ZnI_2 is more pronounced than that of HgI_2, owing to the greater ΔV of ZnI_2 at the corresponding pressure.

Further analysis of the ΔV variation is conducted by calculating the difference between the volumes of the material at finite pressure and at 0 pressure, as shown in Figs. 3(c) and 3(d). The results indicate that all materials are compressed under pressure, and the response to pressure varies with different compounds. Notably, ZnI_2 is found to be more compressible as elemental mixtures than as a compound before the phase change at 6 GPa. This observation is attributed to the high compressibility of I, which results in a large volume change even with a small pressure increase, causing an increase in ΔV. The phase changes to the $P6_3mc$ structure, and the compound compresses more easily than the elemental mixture, resulting in ΔV below 0 GPa. The HgI_2 compound is more compressible than its elemental mixtures before decomposition, leading to a decrease in ΔV relative to 0 GPa. Despite this change, both ZnI_2 and HgI_2 have positive ΔV values at decomposition pressure, which means that the elemental mixture is denser than the compound at high pressure. Therefore, our analysis of volume shows that dense materials tend to be more stable under high pressure.

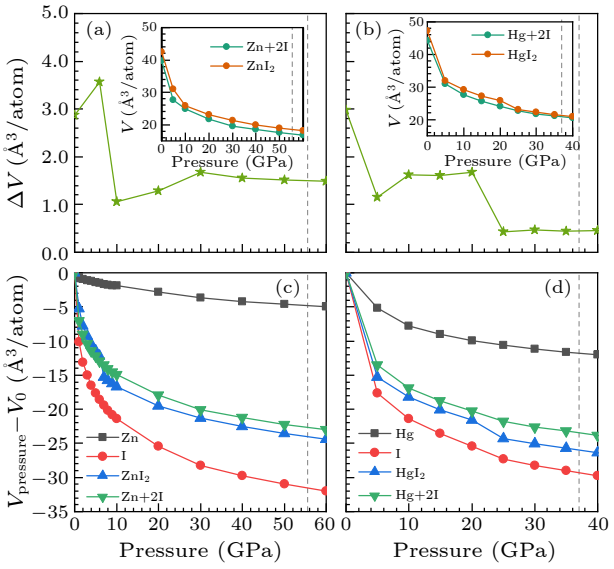

Fig. 3. [(a), (b)] Volume differences between the compounds (ZnI_2, HgI_2) and $M + 2I$ (M = Zn, Hg). [(c), (d)] Pressure dependence of the calculated volume difference between the finite pressure and ambient pressure for ZnI_2 and HgI_2.

We compute the electronic properties and chemical bonding to understand the effect of pressure on interatomic interactions. The interaction in ionic compounds

is primarily due to electrostatic forces arising from charge transfer, which is caused by the electronegativity difference. The higher the electronegativity is, the stronger the electron-attracting ability is. The calculated charge transfer as a function of pressure is shown in Fig. 4(a). At 0 GPa, the electronegativity of the metal atoms is lower than that of the I atom, and the electronegativity difference between Zn and I (1.01) is greater than that between Hg and I (0.66), so more electrons are transferred from Zn to I. It is evident that pressure weakens the charge transfer, revealing the hindering effect of pressure on charge transfer. Specifically, the effects of pressure on charge transfer in ZnI_2 and HgI_2 compounds are different. From 0 GPa to 55.5 GPa, the electrons lost by Zn decrease by only 0.1, whereas from 0 GPa to 37 GPa, the electrons lost by Hg decrease by 0.2. Our calculations show that pressure regulates the Hg–I ionic bond more effectively, resulting in a lower decomposition pressure for HgI_2 compared to ZnI_2. The Madelung energy represents the electrostatic energy of the ionic crystal and can be used to measure the stability of compounds. As shown in Fig. 4(b), the Madelung energy of the crystal increases under pressure, indicating a decrease in stability. At the decomposition pressure, the change in Madelung energy for ZnI_2 is relatively smaller than that for HgI_2, which is attributed to the more effective regulation of the Hg–I ionic bond by pressure. In addition, the integrated crystal orbital Hamilton population reveals the presence of weak covalent interactions, which varies only slightly under pressure (the results are proved in Fig. S3 of the Supplementary Materials).

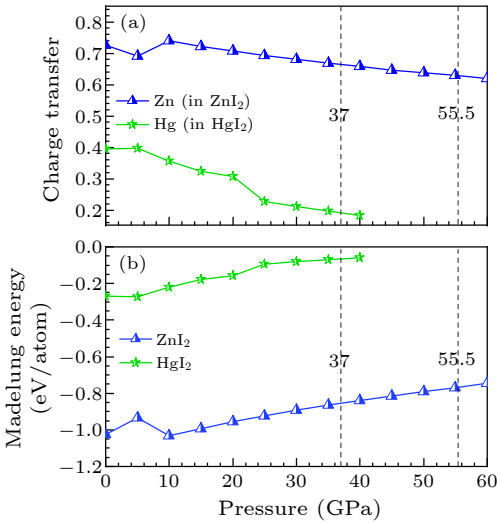

Fig. 4. The calculated (a) charge transfer and (b) Madelung energy versus pressure. The blue and green lines represent the compounds ZnI_2 and HgI_2, respectively.

In summary, we have established high-pressure phase diagrams at 0 K for the Zn–I and Hg–I systems by combining CALYPSO structure searches with first-principles calculations, and found three new phases.

Interestingly, we find that both ZnI_2 and HgI_2 decompose into their constituent elements under certain compression conditions. Through a detailed analysis of the variation of $\Delta[PV]$ and ΔU between compounds and constituent elements under pressure, we are able to elucidate the decomposition mechanisms of these compounds. Our findings suggest that the increase in $\Delta[PV]$ is related to the applied pressure P and the positive ΔV. Furthermore, according to the results of charge transfer calculations, external pressure is more effective in regulating the ionic bond of Hg–I, resulting in a lower decomposition pressure for HgI_2 than for ZnI_2. Overall, our work represents a significant advance in the high-pressure behavior of Zn–I and Hg–I systems and provides important insights into the decomposition mechanisms and electronic properties of these materials under compression.

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