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Mercury under Pressure acts as a Transition Metal: Calculated from First Principles**

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Abstract: *The inclusion of Hg among the transition metals is readily debated. Recently, molecular HgF_4 was synthesized in a low-temperature noble gas but the potential of Hg to form compounds beyond a $+2$ oxidation state in a stable solid remains unresolved. We propose high-pressure techniques to prepare unusual oxidation states of Hg-based compounds. Using an advanced structure search algorithm and first-principles electronic structure calculations, we find that under high pressure Hg in Hg–F compounds transfers charge from the d orbitals to the F, thus behaving as a transition metal. Oxidizing Hg to $+4$ and $+3$ yielded the thermodynamically stable compounds HgF_4 and HgF_3. The former consists of HgF_4 planar molecules, a typical geometry for d^8 metal centers. HgF_3 is metallic and ferromagnetic owing to the d^9 configuration of Hg, with a large gap between its partially occupied and unoccupied bands under high pressure.*

One of the most challenging and attractive topics in condensed-mater physics and chemistry is the preparation of compounds with high oxidation states beyond the naturally occurring forms.[1,2] Group IIB elements, including Zn, Cd, and Hg, are usually defined as post-transition metals[3] because they are commonly oxidized only to the $+2$ state.[4,5] However, it is possible that Hg could be stable in higher oxidation states owing to the large relativistic effects that perturb the position of the 5d energies.

Metastable, gas-phase planar molecules containing Hg^{IV} have been predicted by quantum chemistry calculations.[6–14] The previous studies predicted that HgF_4 molecules could resist dissociation to HgF_2 and F_2 molecules.[10,15,16] HgF_4 molecules has also been detected using matrix-isolation infrared (IR) spectroscopy.[1] Regarding Hg^{III}, it has been reported experimentally in a short-lived compound.[6] A Hg^{III} fluoride in molecular form has been recently studied by quantum chemistry calculations.[9] All these results clearly reveal the propensity of Hg to act as a transition metal while reacting with strong oxidizing agents, such as fluorine. However, Hg in a thermodynamically stable high-oxidation state, such as in HgF_4, has not been achieved.

Herein, we propose high-pressure as a viable method to stabilize Hg^{III} in molecular crystals and extended solids. High-pressure methods based on diamond anvil cells (DACs) have yielded novel structures for elements and compounds under extremely high pressures (beyond megabars). Recent developments on first-principles structure-search methods enhance our capability to predict unknown structures under high pressure.[17–21] Herein, we utilize these new methods together with a density functional theory (DFT) approach to find the most thermodynamically stable structures for each HgF_n compound and calculate their electronic ground state, in the range of pressures 0–500 GPa. With this information, we can construct the phase diagram that tells us the relative thermodynamic stability of each compound at a given pressure (see Supporting Information Section I for a more thorough overview on the computational methods used).

We have selected four different compositions for HgF_n ($n = 3$–6), and searched their structures at pressures from 50 to 500 GPa. Then we took the lower enthalpy structures for

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each pressure, and calculated their ground states throughout the pressure range from 0 to 500 GPa, and identified the most stable structure for each composition under pressure. To compare the stability of Hg–F compounds, we calculated the enthalpy of their formation reaction [Eq. (1)]

$$HgF_{2(s)} + \frac{n-2}{2}F_{2(s)} \rightarrow HgF_{n(s)} \qquad (1)$$

For the most stable structures at each pressure, the enthalpy of formation per atom is calculated as [Eq. (2)].[22,23]

$$h^f(HgF_n) = \frac{1}{n+1}\left(H(HgF_n) - H(HgF_2) - \frac{n-2}{2}H(F_2)\right) \qquad (2)$$

We choose to use the enthalpy of HgF_2 instead of Hg because of the exceeding stability of HgF_2.[23]

None of the high oxidation HgF_n ($n > 2$) compounds is thermodynamically stable at ambient pressure (see Supporting Information, section I). The 50 GPa convex hull (Figure 1) shows that HgF_4 is stable at this pressure. By interpolation, we found that HgF_4 becomes stable at 38 GPa. Similarly, HgF_3 becomes stable at 73 GPa. Interestingly, at pressures higher than 200 GPa, HgF_4 becomes unstable and decomposes into HgF_3 and F_2. According to our calculations, HgF_5 and HgF_6 are not stable in the studied pressure range. Therefore, our calculations reveal four different pressure regimes where the thermodynamic stability of new Hg–F compounds is concerned. From 0 to 38 GPa, none of these Hg–F compounds is stable; from 38 to 73 GPa, HgF_4 is stable; from 73 to 200 GPa, both HgF_3 and HgF_4 are stable; from 200 to 500 GPa, only HgF_3 is stable (the lowest enthalpy structures of $HgF_{5,6}$ can be found in the Supporting Information, section II; parameters of $HgF_{3,4}$ structures, in the Supporting Information, Section V).

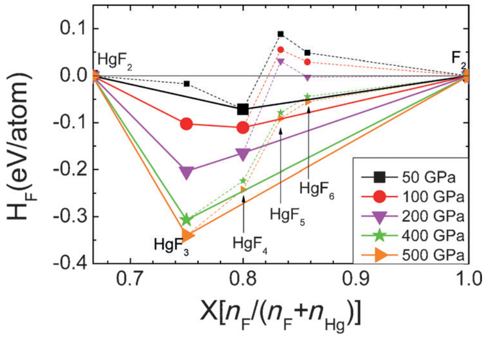

Figure 1. Diagram of the phase equilibrium between HgF_2 and F_2 and the intermediate compounds of HgF_n ($n = 3\ldots6$), with respect to the F abundance in the crystal. The convex hulls that determine the existing phase equilibriums at different pressures are plotted with solid lines. Dotted lines are used as a visual aid to plot the thermodynamic stability of the rest of phases.

Two low-enthalpy structures were identified for HgF_4 over the pressure range of 0–300 GPa. The most stable structure under ambient conditions had $Pca2_1$ symmetry and consisted of chain-like HgF_2 and F_2 molecules (Figure 2 a,b). This phase separation already indicates that HgF_4 will not be stable at ambient pressure. At 20 GPa, the system relaxes into *I*4*m* symmetry (Figure 2 c,d): the atoms form HgF_4 square-planar molecular units. The same square molecule structure has been found theoretically for the gas state[9,15,16] and experimentally in He matrix.[1] At 50 GPa, the Hg–F distance is 1.949 Å, much shorter than the average Hg–F distance of 2.215 Å in HgF_2 at the same pressure. On the other hand, the shortest F–F distance is 2.112 Å which is significantly longer than the F–F molecular bond length of 1.439 Å. This is evidence of the destruction of the molecular features of F_2 and the stability of the HgF_4 molecules.

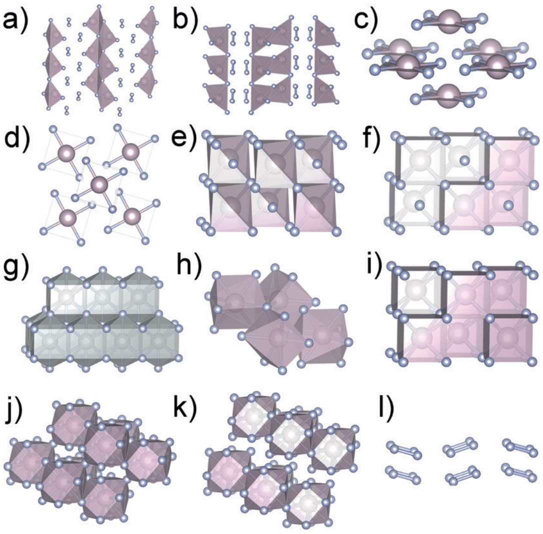

Figure 2. Real-space configuration of the crystalline structures used in this article: For HgF_4, a) side view and b) top views of the thermodynamically unstable *Pca*2₁ low-pressure structure and (c) and (d) are the same views for the stable high-pressure structure *I*4*m*. For HgF_3: e) is the low-pressure *C*2*m* and f) is *Fm*-3*m*. For AgF_2: g) is the result of applying 200 GPa. For HgF_2: h) is the low pressure *Pnma*, i) is the high pressure *Fm*-3*m*. For HgF_5, j) is the *C*2*m*. For HgF_6, k) is the *C*2*m*. For F_2, l) is the *C*2/*c* structure. Large and small spheres represent Hg and F atoms, respectively.

The phonon spectra of HgF_4 in the *I*4*m* structure, of HgF_2 in the *Pnma* structure, and of F_2 in the *C*2/*c* structure were calculated over the pressure range of 0–300 GPa. The results show that the structures of all three solids were dynamically stable up to 300 GPa.

The planar geometry of the HgF_4 molecules is typical of d^8 configurations, indicating the involvement of 5d electrons in the formation of Hg–F bonds. As shown in Figure 3 a b, the d orbitals split into four groups in a square-planar crystal field formed by surrounding F anions. $d_{x^2-y^2}$ was the highest in energy. The transition-metal cations could be energetically stabilized in this configuration in the event that eight electrons filled the four lower d states and left the $d_{x^2-y^2}$ states empty. The bonding features of HgF_4 were also examined by calculating the electron localization function (ELF)[24] using the VASP code. The results (Figure 3 c) clearly showed the equivalent covalent bonds of Hg and its four neighboring F atoms.

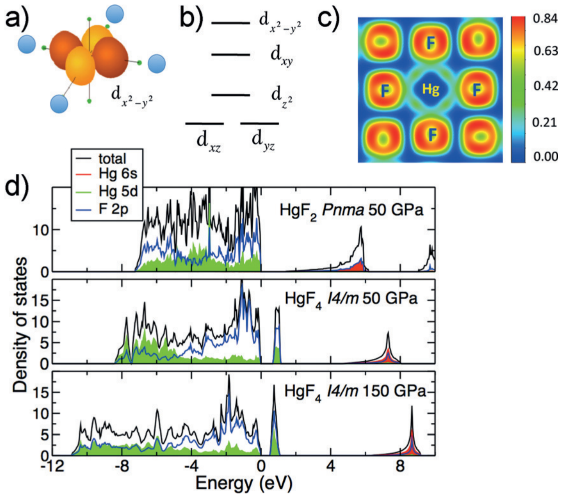

Figure 3. Electronic structure of the HgF$_4$: a) plot of the $d_{x^2-y^2}$ orbitals of the Hg, which are raised in energy according to the crystal-field splitting in a square-planar complex, as shown in (b). c) is the ELF for HgF$_4$ in the *I4m* structure at 150 GPa; Hg is the central atom and the rest are F. d) plot of the PDOS for HgF$_2$ in the *Pnma* structure at 50 GPa and for HgF$_4$ in the *I4m* at 50 and 150 GPa. In the PDOS plots, the black solid lines indicate the total DOS, the blue solid lines indicate the F 2p states and the red and green shaded areas indicate the Hg 6s and Hg 5d states.

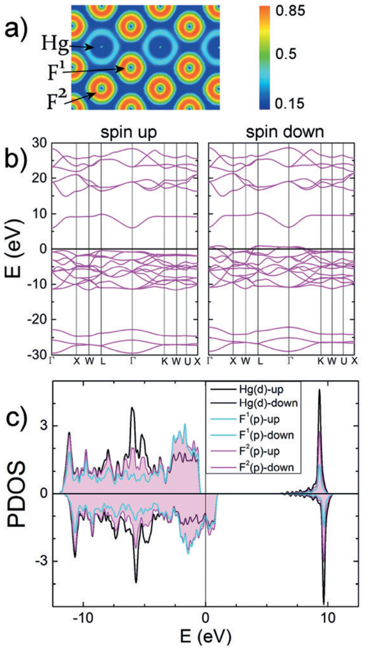

Figure 4. a) Plot of the ELF of the HgF$_3$ structure. ELF ranges from 0.15 (blue) to 0.85 (red); b) Plot of the band structure of HgF$_3$ at 200 GPa, separated for the majority (spin up) and minority (spin down) electrons; c) Projected DOS of HgF$_3$ at 200 GPa, where the sign indicate majority–minority electrons. The and lines and the line with shaded area show the PDOS of the Hg 5d (black), F^1 2p (cyan) and F^2 2p (magenta/shaded) states.

To further reveal the nature of Hg–F bonds, we calculated and compared the total and projected density of states (DOS and PDOS) for HgF$_4$ in the *I4m* structure and HgF$_2$ in the HgCl$_2$ structure at 50 GPa. HgF$_2$ shows a gap of 1.5 eV. The conduction bands consist mainly of the F p and Hg 6s states, whereas the valences bands consist of both F p and fully filled Hg 5d states (+2 state, see Figure 3d). On the other hand, HgF$_4$ displays a much smaller gap of only 0.71 eV. More importantly, the 5d band was split between the valence and the conduction bands, in agreement with the planar geometry of the HgF$_4$ molecules and the d^8 configuration analysis.

Our calculations show that HgF$_3$ can be thermodynamically stable at pressures higher than 73 GPa, adopting a structure with *Fm*-3*m* symmetry (see Figure 2f). In this structure, F atoms are located at two different sites, F^1 and F^2. Hg and F^1 atoms adopt the crystal lattice of the fluorite (CaF$_2$); this is identical to the structure of HgF$_2$ at ambient pressure.[25] On the other hand, the F^2 atoms occupy the octahedral interstitial sites. Hg–F^1 distances are significantly shorter than the Hg–F^2 distances: at 100 GPa, Hg–F^1 is 2.181 Å; whereas Hg–F^2 is 2.519 Å. Additionally the Hg–F^1 distance is comparable to the Hg–F distance of 2.133 Å in HgF$_2$ at 100 GPa. The phonon analysis of HgF$_3$ showed that in whole the pressure range where HgF$_3$ is thermodynamically stable, it is dynamically stable as well. For a pressure below 100 GPa, small lattice deformations occur to HgF$_3$ which lower the symmetry to *C*2*m* (Figure 2e).

Concerning to the electronic structure, we found that HgF$_3$ is metallic and magnetic (1 μ_B per Hg) throughout the studied pressure range. It is therefore a new example to add to the few fluorides that are metallic.[26] According to the band structure and the PDOS (see Figure 4b,c), the two highest valence bands in the valence group (Hg d-band and F p-band) are not fully occupied for spin-down channel, placing the Fermi level slightly below the valence band maximum (VBM). This is a natural result of Hg being in oxidation state of +3, which is d^9 configuration. Unlike most metals, the band structure of HgF$_3$ is similar to a semiconductor with heavy hole doping. The corresponding conduction bands locate from 2 to 6 eV above the valence bands. The lowest conduction band consists of mainly Hg 6s states and has a large dip with very large dispersion around Γ point. The magnetism in HgF$_3$ is also unexpected since 5d transition metals and their compounds are usually non-magnetic. Considering that pressure usually diminishes the spin-polarization in transition-metal compounds, the persistence of magnetism in HgF$_3$ is quite unusual. By comparing different spin configurations in extended unit cells, we found that HgF$_3$ is ferromagnetic. Note that to obtain spin-polarized state of HgF$_3$ a hybrid functional in the frame work of Heyd–Scuseria–Ernzerhof[27] is employed because the GGA functionals only yield non-magnetic states. The change of the enthalpy due to spin polarization is very small (see Supporting Information, section IV), around 30 meV/atom, under high pressure, so its inclusion should not cause significant revision to the convex hull. However, we cannot rule out the possibility that a systematic structure search using hybrid functionals would yield a structure featuring mixed valence of Hg^{II} and Hg^{IV}.

An increase on the external pressure has two effects on the electronic structure: the reduction of the width of the conduction band (around 0.4 eV) and the increase of the band-gap between the conduction band minimum (CBM) and the VBM (from 1.4 eV at 0 GPa to 6 eV at 500 GPa). At about 300 GPa, the gap between CBM and VBM is larger than 3 eV, making HgF_3 transparent to visible light. However, because of the presence of high-density holes in the valence bands, the conductivity of HgF_3 should remain high. Thus, HgF_3 should behave like a transparent conductor owing to its unique electronic structure.

The remarkable features of the electronic structure of HgF_3 can also be seen in other d^9 elements, such as Ag^{II}.[28] The electronic structure of its derivatives has been intensely studied.[29,30] AgF_2 structure has the symmetry *Pbca* at low pressure,[31] which is very different to HgF_3. However, under high pressure, its electronic structure is similar to that of HgF_3 and can be viewed as a heavily hole-doped semiconductor.[30] Similar atomic and electronic structure features can also be found in another Ag^{II} compound, $(AgF)(BF_4)$.[26] Its structure consists of chains of AgF^+ molecules with a very strong ionic component.

Considering the bands and PDOS of the F^1 and F^2 atoms, the d-bands of Hg appear to overlap in energy with the p-bands of F^1, but not much with the F^2. Additionally, the ELF plot (see Figure 4 a) shows that the F^2 atoms are surrounded by regions with very low ELF, indicating that these atoms are not covalently bonded to other atoms. By analyzing the orbital occupation, we find that at ambient pressure the d orbitals have $9.49\,e^-$. This places the HgF_3 chemically between HgF_4 and HgF_2, as a d^9 element. A Bader charge analysis assigns the Hg atoms a net charge of $+1.63$ e at 100 GPa and $+1.84$ e at 500 GPa, in agreement with a formal oxidation state of $+3$. F atoms show a net charge of -0.54 e at 100 GPa, and at 500 GPa the net charge is -0.56 e for F^1 and -0.71 e for F^2. According to this description, HgF_3 has a strong ionic character. It consists of a three-dimensional lattice of HgF_2^+ and fixed F^- ions in the interstitial sites.

Keywords: ab initio calculations · crystal structure search · high oxidation state · high-pressure chemistry · mercury

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