First-Principles Study of Hg under High-Pressure

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We calculate bulk Hg under various compression conditions using first-principles molecular dynamics (FPMD) and all-electron methods. A calculated crystal structure of Hg is hexagonal close-packed (crystal symmetry $P6_3$/mmc). Electronic and lattice properties are obtained under hydrostatic, uniaxial and biaxial compression conditions. A norm-conserving pseudopotential is used in the FPMD calculations with the partial core correction(PCC) and scalar relativistic effects. In this study, we investigate a variation of $5d$ states and a relation of $6s$, $6p$ and $5d$ states under compression. $5p$ core states calculated by the all-electron method are quite deep and do not contribute to valence states.

Key Words: first-principles, electronic structure, $5d$ states, high-pressure

1. INTRODUCTION

In this paper, we investigate the electronic and lattice properties of bulk Hg under high-pressure conditions using the electronic structure calculations. We focus on behavior of $5p$ and $5d$ states under various compression conditions. We consider a hexagonal close-packed (hcp) structure (crystal symmetry $P6_3$/mmc) of Hg which is one of the high-pressure phases[1] as shown in Fig. 1. Some theoretical studies of the hcp and other crystal phases of Hg were reported previously.[2-5] Other phases (α, β-Hg, etc.) are not considered in this study. The purpose of this study is to investigate electronic structure changes in $5p$ and $5d$ states of Hg and their contributions to $6s$ and $6p$ valence states around the Fermi level under high-pressure conditions. The important point to note is that it is possible to optimize the structure of Hg under various compression conditions using the first-principles molecular dynamics (FPMD) method with a norm-conserving pseudopotential. On the other hand, $5p$ core states are treated by using the all-electron calculation method (WIEN2k).[6] At the first, we calculate the electronic and lattice properties of Hg under various compression conditions ($P = 0$, 200, 400 GPa as hydrostatic, $Pxy = 50$ GPa as biaxial a, b-axis, $Pz = 50$, 100 GPa as uniaxial c-axis) using FPMD. The electronic structure calculations using WIEN2k use the lattice parameters obtained by FPMD. $5d$ electrons of Hg need to be treated as the valence states. The $5d$ states of Hg are located at $5 \sim 7$ eV below the Fermi level at ambient pressure ($P = 0$ GPa). We investigate the change in the $5p$ and $5d$ states under high-pressure conditions. We treat the $5p$ core states using the all-electron calculation method. As a result, the $5p$ states are quite deep at over 60 eV below the Fermi level when $P = 200$ - 400 GPa. There are no contributions of the $5p$ states to the valence states. It is necessary to investigate the change in the $5d$ states under high-pressure conditions because they are shallower and have a larger contribution to the valence states than the $5p$ states. The contribution of the $5d$ states to the valence band may be more important than

that of the $5p$ core states and may increase if the $5d$ states will close to the Fermi level under compression.

It is expected that first principles calculations may predict novel physical properties and behavior of materials under high-pressure conditions. We believe that it will be very important to investigate the electronic and lattice properties under various compression conditions in high-pressure physics.

2. METHOD OF CALCULATION

The present calculation (FPMD) is based on the local density approximation in the density functional theory.[7,8] The exchange-correlation formulae of Wigner,[9] and Perdew and Zunger[10,11] are used. The optimized pseudopotentials by Troullier and Martins (TM)[12,13] are used. Nonlocal parts of the pseudopotentials are transformed to the Kleinman-Bylander separable forms[14] without ghost bands. A partial core correction (PCC)[15] is considered. Scalar-relativistic effects are included in the Hg pseudopotential. Spin-orbit coupling is not considered in this study. The number of sampling k-points (N_k) is 95 in the irreducible Brillouin zone (BZ). Part of the calculations is performed with 259 k-points to achieve higher numerical accuracy. The wave function is expanded in plane waves, and the energy cutoff (E_{cut}) is 100 Ry with the maximum number of plane waves being about 6000. The number of atoms in a unit cell is 2. The number of k-points is fixed during the cell optimization. We apply hydrostatic, uniaxial (c-axis) and biaxial (a, b-axis) compressions. All systems maintain the crystal symmetry (hcp) under compression. The details of the calculation process with the cell optimization were reported in our previous works.[16,17]

We perform the all-electron calculation using WIEN2k code[6] in order to compare with calculated results of the FPMD method and treat the $5p$ core states. The lattice constants obtained by the FPMD method are used in the all-electron calculations.

3. RESULT AND DISCUSSION

Table I. Optimized lattice constants[nm], the c/a ratios of Hg. "W" indicates the Wigner formula of exchange-correlation. "PZ" indicates the Perdew and Zunger formula of exchange-correlation. "PZ2" indicates the number of k-points is 259 with the Perdew and Zunger formula

	GPa	c	a	c/a
Hg(W)	$P = 0$ GPa	0.5454	0.3388	1.610
Hg(PZ)	$P = 0$ GPa	0.5399	0.3349	1.612
Hg(PZ2)	$P = 0$ GPa	0.5388	0.3354	1.606
Hg(W)	$P = 200$ GPa	0.4450	0.2723	1.634
Hg(W)	$P = 400$ GPa	0.4200	0.2574	1.632
Hg(W)	$Pxy = 50$ GPa	0.6635	0.2802	2.368
Hg(W)	$Pz = 50$ GPa	0.2503	0.5508	0.4545
Hg(W)	$Pz = 100$ GPa	0.2357	0.5539	0.4256

The lattice properties (lattice constant, c/a ratio) are optimized by FPMD. The optimized lattice properties in the present calculation are tabulated in Table I. Lattice constant a in this study is larger than that (0.3196 nm) of other theoretical calculation.[4] An ideal value is used for the c/a ratio in the previous work.[4] There are no lattice anomalies of Hg as previous works[17-21] under anisotropic compression. Lattice constants a and c in the exchange-correlation formula of Perdew and Zunger reduce slightly in comparison with those in the Wigner formula. Furthermore, lattice constant c reduces with increasing the number of k-points (95 → 259). The reduction of lattice constant c at 259 k-points is small with 0.001 nm from Table I. Lattice constant a at 259 k-points expands slightly. From Table I, the c/a ratios of Hg when $P = 200$, 400 GPa are slightly larger than that when $P = 0$ GPa. In contrast, the change in the c/a ratio under anisotropic compression is remarkably large. Lattice constant c is very sensitive under c-axis compression. Unit cell volumes of Hg under hydrostatic and a, b-axis compressions decrease. In contrast, volumes (443.89, 422.60 a.u.^{3}) when $Pz = 50$, 100 GPa increase, which are larger than that (365.86 a.u.^{3}) when $P = 0$ GPa.
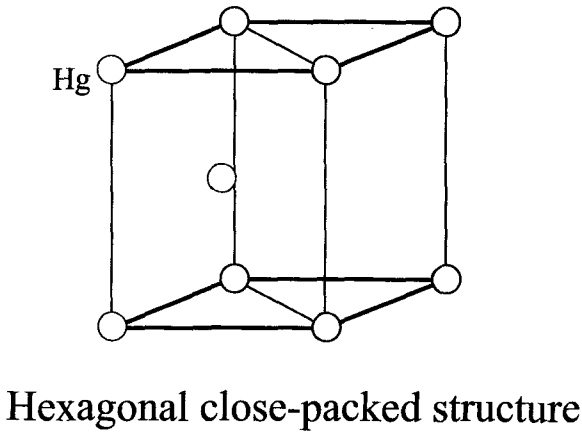

Hexagonal close-packed structure

Fig. 1. Hexagonal close-packed (hcp) structure of Hg.

Hg(hcp, Wigner) $P = 0$ GPa   Hg(hcp, Wigner) $Pxy = 50$ GPa

Hg(hcp, Wigner) $P = 200$ GPa   Hg(hcp, Wigner) $Pz = 100$ GPa
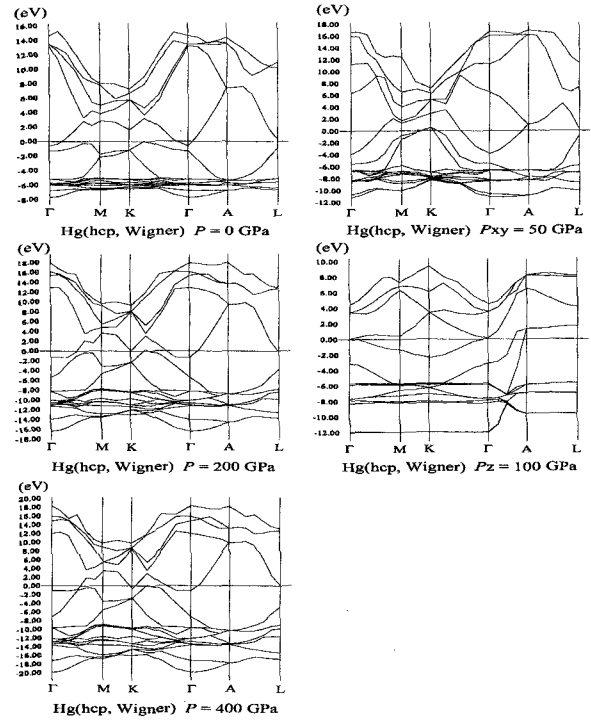
Hg(hcp, Wigner) $P = 400$ GPa

Fig. 2. Electronic band structures of Hg when $P = 0$, 200, 400 GPa, $Pxy = 50$ GPa and $Pz = 100$ GPa. The Fermi level is indicated by the horizontal line.
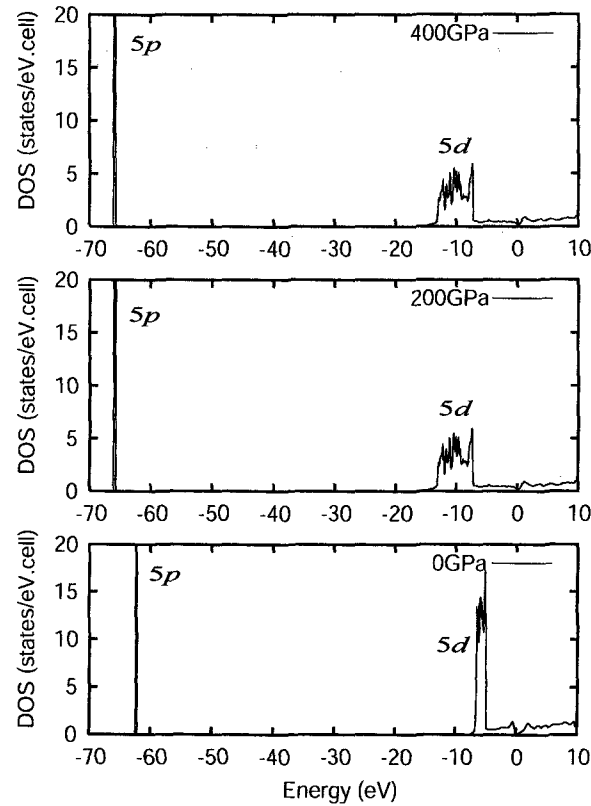

Fig. 3. Density of states of Hg when $P = 0$, 200, 400 GPa. The Fermi level is set at Energy $= 0$ eV.
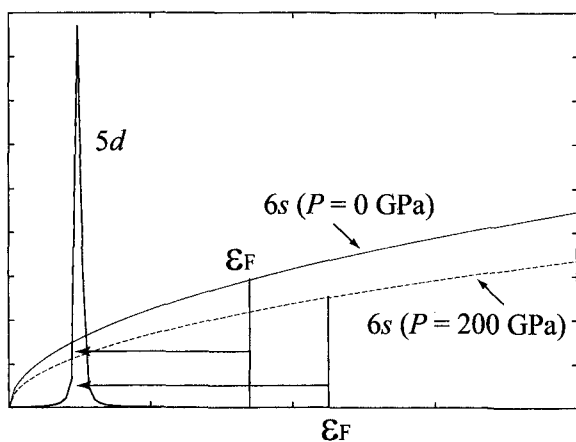
Fig. 4. Schematic view of the broadening DOS of 6s states and shifting upward for the Fermi level under hydrostatic compression.

The electronic band structures of Hg when $P = 0$, 200, 400 GPa, $Pxy = 50$ GPa and $Pz = 100$ GPa are shown in Fig. 2. Densities of states (DOS) when $P = 0$, 200, 400 GPa are shown in Fig. 3. The bandwidths increase as pressure increases in all cases. Dense and less dispersive $5d$ bands are situated at $5 \sim 7$ eV below the Fermi level when $P = 0$ GPa. As a result, the metallic character of Hg is invariable under various compression conditions. Although hydrostatic compression does not modify the electronic band structure totally, the $5d$ states of Hg become more dispersive as pressure increases. Therefore, mixing of $6s$- and $6p$-$5d$ increases when $P = 200$, 400 GPa. The bandwidth of the $5d$ states increases as pressure increases. This can be seen from the DOS of $5d$ states under hydrostatic compression as shown in Fig. 3. However, the $5d$ states do not close to the Fermi level under hydrostatic compression. They shift to lower as increasing hydrostatic compression. The trends of the electronic band structures when $P = 0$, 200, 400 GPa agree with those obtained by all-electron calculations. However, it is reasonable to think that this downward shift of the $5d$ states under hydrostatic compression is relative. The origin of this lowering of $5d$ states will be explained as follows. Although the $5d$ states become more dispersive under hydrostatic compression, average energies of the $5d$ states are mostly invariant because the $5d$ states under compression are fully occupied. In contrast, a bandwidth and the DOS of $6s$ states are broadened under hydrostatic compression. Therefore, the Fermi level shifts upward relatively due to broadening the DOS of $6s$-states as shown schematically in Fig. 4. This means the $5d$ bands shift downward if the Fermi level is set at 0 eV in all compression conditions. In these schematic view and treatment, the $6p$ states are not considered for simplicity.

The change in the electronic band structure under uniaxial c-axis compression is remarkable as shown in Fig. 2. In contrast, the change under biaxial compression is relatively small in comparison with that when $Pz = 100$ GPa. The electronic band structure when $Pz = 100$ GPa

is less dispersive in comparison with those under hydrostatic and biaxial compressions. Many bands when $Pz = 100$ GPa become flat at the Γ-M-K-Γ lines. Actually, it seems that a transformation from hcp to other phases occurs at lower c-axis compression if no symmetry constraint is given.

The DOS of Hg including the $5p$ states are obtained by all-electron calculations. In the all-electron calculation, the $5p$ core states can be treated easily and they are drawn in Fig. 3. The $5p$ core states lie around $60 \sim 70$ eV below the Fermi level when $P = 0$, 200, 400 GPa. Therefore, the $5p$ states do not influence to the valence states.

4. SUMMARY

We have calculated the electronic and lattice properties of bulk Hg (hcp) under various compression conditions using the FPMD and all-electron methods. The $5p$ core states are quite deep at over 60 eV below the Fermi level and they have no contributions to the valence states. The $5d$ states are located at $8 \sim 14$ eV and $10 \sim 16$ eV below the Fermi level when $P = 200$ and 400 GPa, respectively. Although the $5d$ states are valence bands and the s-d and p-d hybridizations increase as pressure increases, they do not close to the Fermi level. It is concluded that the contribution of the $5d$ states to the valence states around the Fermi level does not increase under hydrostatic compression. The Fermi level shifts upward under hydrostatic compression because of broadening the $6s$ states mainly. We can see the $5p$ and $5d$ states shift downward relatively under hydrostatic compression when the Fermi level is set at 0 eV in all compression conditions. The changes in the electronic band structures under anisotropic compression is larger than those under hydrostatic compression. Particularly, it is remarkably large when $Pz = 100$ GPa due to the large change in lattice properties under c-axis compression. More detailed calculations are necessary to perform in future.

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