Structural behavior of uranium dioxide under pressure by LSDA+U calculations

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Structural behavior of UO$_2$ under high-pressure up to 300 GPa has been studied by first-principles calculations with LSDA+U approximation. The results show that a pressure induced structural transition to the cotunnite-type (orthorhombic $Pnma$) phase occurs at 38 GPa. It agrees well with experiment observed ~42 GPa. A new iso-structural transition following that is also predicted taking place from 80 to 130 GPa, which has not yet been observed in experiments. Further high compression beyond 226 GPa will result in a metallic and paramagnetic transition. It corresponds to a volume of 90 Å$^3$ per cell, in a good agreement with previous theoretical analysis in the reduction of volume required to delocalize 5$f$ states.

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I. INTRODUCTION

Uranium dioxide (UO$_2$) is widely used as fuel material in nuclear reactors. It was extensively studied from 1940th in physical, chemical and thermodynamic properties by experimental and theoretical methods (especially during last decade) due to its important applications. The shortage of energy around the world makes us ask for more contribution from nuclear power, where the burn-up efficiency of nuclear fuels is a bottle-neck. In order to tackle this difficulty, understanding the detailed behavior of fuel materials under burning-up and irradiation is important. Recent use of fuel materials to high burn-up shows many microstructure formations, which is not possible to access by empirical approach and atomic scale theoretical analysis is highly requested.

Previous theoretical studies on UO$_2$ mainly focused on defects effects arised from irradiation damages and thermodynamic properties near ambient pressure with semi-empirical approaches. Electronic properties and large scale intrinsic structural behavior under disturbance (say, compression, tension and distortion of lattice) were rarely investigated in despite of its importance in most properties of UO$_2$. This partly is due to the lacking of a reliable method to deal with this kind of complex materials before. The development of density functional theory (DFT) changed the situation greatly and provides a quantum mechanics based theoretical approach to tackle this problem.

However, to our knowledge only a few $ab$ initio electronic structure studies have been published on UO$_2$, most of which were based on conventional LDA or GGA approximation of the exchange-correlation energy. It is well recognized that strong Coulomb correlation among partly filled $f$ electrons of uranium atoms makes these approximations failed. Usually a metallic ground state is predicted for UO$_2$ instead of the experimental observed antiferromagnetic semiconductor. The same problem exists for transition metal oxides, and raises questions about the applicability of DFT approach to these materials. Fortunately, a method combining spin-polarized local density approximation (LSDA) and on-site Coulomb repulsion among localized $d$ or $f$ electrons namely, LSDA+U method was proposed and has shown its capability to treat this problem.

Usually a Hubbard Hamiltonian with two empirical parameters is employed to describe the Coulomb interaction between $5f$ electrons localized on uranium sites in UO$_2$. Adding this Hamiltonian to the conventional LSDA (or GGA) energy functional, one arrives at a point where all orbitals except those included in the model Hamiltonian are treated within the framework of LSDA (or GGS) while the localized $5f$ states are treated by the unrestricted Hartree-Fock (UHF) approximation, namely,

$$E_{LSDA+U} = E_{LSDA}[(\varepsilon_i)] + \frac{(U - J)}{2} \sum_{l,j,\sigma} \rho_{lj}^\sigma \rho_{lj}^{-\sigma},$$

(1)

where $\rho_{lj}^\sigma$ is the density matrix of electrons occupying a partly filled electron shell ($5f$ in UO$_2$), $\sigma$ refers to spin direction, and $\{\varepsilon_i\}$ is the Kohn-Sham eigenvalues. Self-consistent solution of DFT with this energy functional gives that strong correlation effects associated with $5f$ states are going to affect all other states as well, in particular though $2p$ states of oxygen do not influenced by Hubbard correlations directly, they are really linked to localized $5f$ states via hybridization terms. It is necessary to point out that LSDA+U method is not a self-determined approach. The results depend on model parameters $U$ and $J$ very much, which should be chosen carefully by comparing with experimental
data. Fortunately this can be done very well with just a small set of data and preserve the predictability of the method mostly.\textsuperscript{20,21,22}

There have been several works with LSDA+U approximations on uranium dioxide published. All of them were near the equilibrium volume at ambiance pressure for fluorite structure and focused mainly on electron energy loss spectra\textsuperscript{21,22,23} and magnetic structure\textsuperscript{24} These calculations showed that the results of LSDA+U in a well agreement with experiments. However, no attempt was made to investigate the structural behavior of UO\textsubscript{2} under pressures with LSDA+U method, which may be fundamental for understanding the behavior of nuclear fuel under irradiations. By far the validity of LSDA+U method beyond fluorite structure for UO\textsubscript{2} has not been confirmed yet. Recent hydrostatic compression experiment\textsuperscript{25} makes it possible to check it by comparing with measured equation of state. On the other hand, first principles calculations without Hubbard correction on GGA(S) approximation showed that it can give almost correct energy information for UO\textsubscript{2} regardless a wrong electronic band structure was predicted. Specially, by calculating the lattice parameter and bulk modulus of fluorite structure UO\textsubscript{2} with various approximations, J. C. Boettger argued that density gradient corrections, spin polarization and spin-orbit coupling effects are equally important, and suggested when only structural properties are concerned LSDA+U is not necessary.\textsuperscript{25} However the predicted wrong ferromagnetic ground state weakened the creditability of his argument. Other calculations ignored spin-orbit coupling also gave reasonable lattice parameter and bulk modulus\textsuperscript{25,26} indicates spin-orbit coupling is not so important for this case (though a large impact on magnetic property is expected). We will show in this paper that it should be careful when GGA(S) approximation is used because the coincidence of cohesive energies of UO\textsubscript{2} calculated by GGS with LSDA+U approximations is valid only for fluorite phase. An energy difference will appear if other structures are involved.

In this paper we will study the structural stability of fluorite phase (with \textit{Fm\overline{3}m} space group) and cotunnite phase (\textit{Pnma} space group) of uranium dioxide under hydrostatic pressures using DFT method based on LSDA and GGS approximations plus Hubbard correction. Calculation methodology is presented briefly in next section. We will discuss a little bit about the widely used rule of common tangent of energy curves to determine the transition pressure of pressure-induced structural transition, because this rule fails in a case when an energy barrier existed. A more general rule is proposed, which can give the energy barrier when experimental transition pressure is available. Finally, a detailed comparison of our results with static high-pressure experiments is given, associating with a discussion on ultra-high pressure behavior of UO\textsubscript{2} crystal.

II. METHODOLOGY

Total energy curves of both phases (\textit{Pnma} and \textit{Fm\overline{3}m}) at different volumes are computed with VASP code.\textsuperscript{26,27} The \textit{Pnma} structure is fully relaxed to get all Hellman-Feynman forces smaller than 0.002 eV/Å, while fluorite structure keeps the ideal geometry due to all coordinates are completely determined by the symmetry. For comparison, both spin-polarized generalized gradient approximation (GGS)\textsuperscript{28} and local density approximation (LSDA)\textsuperscript{29} with/without Hubbard \textit{U} term energy functional are used. The parameters of Hubbard term are taken as \textit{U} = 4.5 eV and \textit{J} = 0.51 eV, which was checked carefully by S. L. Dudarev \textit{et al.} for fluorite UO\textsubscript{2}.\textsuperscript{20,21,22} Calculations employ projector-augmented wave (PAW) pseudopotentials\textsuperscript{20,21,22} with a cutoff kinetic energy for planewaves of 400 eV. Integrations in reciprocal space are performed in the first Brillouin zone with 18 irreducible \textit{k}-points for fluorite structure and at least 28 irreducible \textit{k}-points for cotunnite phase generated with the Monkhorst-Pack\textsuperscript{22} scheme. Its convergence is well checked. The energy tolerance for the charge self-consistency convergence is set to \textit{1 \times 10^{-5}} eV for all calculations. Cohesive energies at different volumes are extracted from the total energies by subtracting spin-polarized isolated atom contributions. Then, they are fitted to a Morse-type energy function

\[
E(V) = D \left[ \left( e^{-2[(V/V_0)^{1/3}-1]} - 1 \right)^2 - 1 \right]
\]

(2)

to facilitate post-analysis. It is necessary to point out that for \textit{Pnma} phase we also used a different \textit{U} value obtained by fitting to experimental data of \textit{Pnma} phase since \textit{U} = 4.5 eV fails to predict the correct transition pressure. This implies that structure or lattice distortions would have considerable impact on on-site coulomb interaction. For the same structure, however, we find the dependence of \textit{U} on pressure is ignorable.

The equation of state (or compression curve) at zero-Kelvin is calculated directly by an infinitesimal variation of cohesive energy with respect to volume given by \textit{P} = -\partial E/\partial V. Usually the phase transition pressure is determined by the common tangent of their energy curves, which can be derived simply as follows. At thermodynamic equilibrium state under finite pressure, the enthalpy must be minimized, i.e., \textit{\delta H} = 0. In a case two phases in equilibrium, there is a variation of enthalpy with respect to the concentration of each phase besides with respect to volumes. The latter gives \textit{P}_i = -\partial E_i/\partial V (where \textit{i} is phase label) and the former results in \textit{P} = -\Delta E/\Delta V = (E_2 - E_1)/(V_1 - V_2) with \textit{\delta H} = \delta x(\Delta E + P\Delta V), where \delta x is the concentration variation of, say, the first phase and \Delta E (\Delta V) is the energy...
TABLE I: Cohesive energies of uranium dioxide at 0 GPa.

| Phase     | approach     | $D$(eV/atom) | $g$     | $r_0$(Å) | $B_0$(GPa) |
|-----------|--------------|--------------|---------|----------|------------|
| $Fm\bar{3}m$ | LSDA         | 9.044        | 6.122   | 5.323    | 239.99     |
| $Fm\bar{3}m$ | GGS          | 7.956        | 6.195   | 5.432    | 203.53     |
| $Fm\bar{3}m$ | LSDA+U      | 8.194        | 6.198   | 5.444    | 208.32     |
| $Fm\bar{3}m$ | GGS+U       | 7.212        | 6.336   | 5.552    | 180.68     |
| $Fm\bar{3}m$ | Other calc. | 7.41$^a$; 8.2$^c$ | 5.37$^a$; 5.24$^b$; 5.4$^c$ | 173$^a$; 252$^b$; 194$^c$ |
| $Fm\bar{3}m$ | Exp.         | 7.44$^d$     | 5.46$^d$; 5.473$^e$ | 207$^c$; 208.9$^f$ |
| $Pnma$    | LSDA+U($U$=4.5 eV) | 8.154        | 5.787   | 5.331    | 192.5      |
| $Pnma$    | LSDA+U($U$=6.0 eV) | 8.020        | 5.972   | 5.340    | 200.6      |

$^a$LMTO+LSDA+U$^{21}$
$^b$PW+LDA$^{17}$
$^c$PW+GGA$^{18}$
$^d$Taken from $^{21}$
$^e$See Ref.$^{25}$
$^f$See Ref.$^{36}$

(volume) difference between these two phases. The balance condition of pressure requires $P = P_i$ (for $i = 1, 2$), namely,

$$-\frac{\partial E_i}{\partial V} \bigg|_{V=V_i} = \frac{E_2 - E_1}{V_1 - V_2}.$$  

(3)

It is exactly the common tangent rule for transition pressure of pressure induced structural transitions. Evidently, $P\Delta V$ provides the least energy $\Delta E$ required to drive a transition from phase 1 to phase 2. The transition pressure equals to $P$ if no energy barrier exists, which is a common case for usual metals and alloys. However, when an energy barrier with an amplitude of $\Delta w$ is involved, the work done by external pressure $P'$ should be large enough to get over the barrier in addition to the energy difference $\Delta E$. Then the variation of enthalpy with respect to phase concentration should be $\delta H = (\Delta E + \Delta w + P'\Delta V) \cdot \delta x \equiv 0$. Obviously the common tangent rule becomes invalid here. The hysteresis pressure is given by $\Delta P = P' - P$. Without knowledge about the energy barrier, one cannot determine the transition pressure $P'$ by energy curves itself. However, in contrast, one can deduce the energy barrier amplitude with measured transition pressure $P'$ by

$$\Delta w = -(\Delta E + P'\Delta V).$$  

(4)

III. CALCULATIONS AND DISCUSSIONS

A. Cohesive energy

Calculated cohesive energies with different approximations for fluorite ($Fm\bar{3}m$) and cotunnite ($Pnma$) structures of uranium dioxide as well as the parameters fitting to Eq.(2) are listed in table I where the energy is for per atom and equilibrium cell volume is given by $V_0 = r_0^3$. The cohesive energy for a cell of $U_4O_8$ is given by multiplying $D$ with 12. For comparison purpose, other calculated and observed values$^{17,18,21,25,36}$ are also listed. It should be noticed that $Pnma$ phase has a smaller effective cubic lattice constant and bulk modulus than fluorite phase at zero-pressure, which implies it will become stable under compression.

Variation of cohesive energy of $Fm\bar{3}m$ phase along cubic lattice constant ($V^{1/3}$) is shown in figure I. It is interesting to see that GGS and LSDA+U give quite similar energy curves, confirming previous calculations that GGS also can give reasonable energy information for fluorite phase of $UO_2$ in spite of the corresponding electronic density of state (DOS) is wrong$^{4,15,18,37}$. However, we should emphasize here that it is just a coincidence. Analogous to the case without Hubbard correction, LSDA-U overestimates the binding energy slightly and GGS+U underestimates it. On the other hand $U$ term uplifts the binding energy wholly, and results in this coincidence. We can also see from table I that PAW method outperforms ordinary pseudo-potentials both for GGS and LSDA approximations in terms of equilibrium volume, cohesive energy and bulk modulus$^{4,17,18}$. Furthermore, Our LSDA+U calculations with PAW potentials give results in perfect agreement with experiments$^{21,25,36}$ (in particular the calculated equilibrium lattice constant of 5.44 Å vs observed 5.46 Å and bulk modulus of 208.3 GPa vs 208.9 GPa). It also predicts an antiferromagnetic ground state.
with a band gap of \(~1.45\,\text{eV}\), agrees with previous calculation very well.\(^{21}\) To reproduce the X-ray photoelectron spectroscopy\(^{38}\) observed band gap of \(~2\,\text{eV}\), Dudarev et al. argued that to take spin-orbit coupling into account is necessary. We confirmed this by a spin-orbit coupling calculation implemented in VASP which gives a band gap of \(2.04\,\text{eV}\). GGS+U approximation, however, gives a larger equilibrium lattice constant and smaller bulk modulus, despite the cohesive energy is more close to the observed value, as well as a band gap of \(1.6\,\text{eV}\). Totally speaking, LSDA+U outperforms GGS+U approximation for this set of \(U\) term parameters. It is necessary to point out that the discrepancy with previous LMTO calculation should be owing to their convergence precision is not so good. Their calculation gave quite poor mechanical properties\(^{39}\) that implying the force is inaccurate. Later calculation by the same authors improved this.\(^{22}\) The spin-orbit coupling is ignored in our following calculations. The resulting error can be estimated at a lattice constant of \(5.44\,\text{Å}\) for fluorite phase, where spin-orbit coupling decreases the cohesive energy about \(0.3\,\text{eV}\) for per atom, very close to the energy difference between GGS and LSDA+U at the same volume. Thus we can expect that neglect spin-orbit coupling will gives an error of \(0.012\,\text{Å}\) in lattice constant and \(3\,\text{GPa}\) in bulk modulus, the same difference as GGS.
FIG. 3: Calculated compression curves of uranium dioxide along relative volume compared with experimental measurements. An unexpected large discrepancy of transition pressure between measurement (point B) and theoretical prediction (point A) is obtained for \( U=4.5 \text{ eV} \) case. However, a better result is recovered with \( U=6.0 \text{ eV} \).

B. Cotunnite phase

To optimize the geometry of \( Pnma \) phase at different pressure, LSDA+U method with \( U = 4.5 \text{ eV} \) is employed. To avoid the Pulay stress problem (which arised from the fact that the plane wave basis set is not complete with respect to changes of the volume), structure relaxation calculations are performed at fixed volumes rather than under constant pressures. Then pressure is derived from the energy-volume relation. The structure is fully relaxed to optimize all internal coordinates and cell shape, while the symmetry of \( Pnma \) space group is kept. Calculated cohesive energy curve is shown in figure 2. For comparison the curve of fluoride phase is also given as dash-dotted line. It shows that under high pressure \( Pnma \) phase becomes stable. A transition pressure of 7.8 GPa is given by the slope of common tangent as showing in the inset. This value is quite unexpected because it is less than \( \frac{1}{5} \) of the experiment observation as \( \sim 42 \text{ GPa} \). It is very small even if compared with another early measurement that predicted a pressure-induced phase transition to orthorhombic \( Cmcm \) phase at \( \sim 29 \text{ GPa} \) (which has not yet been repeated by other authors). Nevertheless, the calculated volume reduction of 6.4\% agrees well with the observed 7% at the beginning of cotunnite phase.

Then one may ask what is the matter with it? Is the LSDA+U approximation wrong? From table I and the comparison of its results at equilibrium volume with experimental data for fluoride phase, we do not think so. Actually, as figure 2 shows, LSDA+U gives a compression curve that agrees very well with experiment for \( Fm\bar{3}m \) phase, which means that the Hubbard \( U \) parameter is reasonable and insensitive to pressure. Clearly we cannot attribute this deviation to the failure of density functional theory or LSDA+U approximation. Figure 3 also shows the P-V curve calculated with GGS approximation. It is worse than LSDA+U and the transition pressure is also as low as 32 GPa. A hysteresis pressure about 34 GPa is estimated by using the transition pressures observed in experiment and calculated with \( U = 4.5 \text{ eV} \), which are marked by arrows B and A in figure 3 respectively. As discussed in previous section, this hysteresis of transition pressure would imply an energy barrier existing. In fact it is very common for ionic crystal and semiconductors. For example a phase transition of GaN from wurtzite to rocksalt phase, where a large hysteresis of pressure is observed. By using Eq. (1), the cohesive energy curves of \( Pnma \) and \( Fm\bar{3}m \) phases (Eq. (2) and parameters listed in table I), and the experimental transition pressure of 42 GPa, we estimate an energy barrier as \( \sim 2.1 \text{ eV per cell (U}_4\text{O}_8) \). This value is large enough to survive \( Pnma \) phase to ambient condition. Unfortunately, no experiment shows this event.

Therefore, the only possibility is that the discrepancy in \( Pnma \) phase resulted from the dependence of \( U \) on structure (or lattice distortions). We obtained a different \( U=6.0 \text{ eV} \) by fitting to the measured P-V data of \( Pnma \) phase. The resulting energy curve and Morse function parameters are given in figure 2 and table I respectively. We can see \( U = 6.0 \text{ eV} \) gives a quite similar energy curve as \( U = 4.5 \text{ eV} \), except the wholly uplifting of the curve. Hereafter, all calculations will be performed for \( U=6.0 \text{ eV} \) and \( U=4.5 \text{ eV} \) separately, so we assign the former case as \( U6 \) and the latter as \( U45 \) for briefness. Although the improvement on P-V curve in \( U6 \) is limited, as figure 3 shows, the calculated transition pressure is corrected to \( \sim 38 \text{ GPa} \), almost five times of \( U45 \) case and in a good agreement with.
FIG. 4: Electronic density of state for $5f$ states of UO$_2$ at a cell volume of 131.4 Å$^3$. Transition to $Pnma$ will increase the band gap and shrink the energy region of localized states.

observed 42 GPa. The resulted hysteresis pressure is just 4 GPa, which ends up an energy barrier as 0.018 eV/atom and ignorable at room temperature. Obviously, $U_{6}$ is more credible than $U_{45}$ since it is compatible with the fact that no $Pnma$ phase has been observed under ambient condition. The calculated reduction of volume at transition from $Fm\bar{3}m$ to $Pnma$ phase is 6.2%, close to $U_{45}$ case, also agrees well with experimental data.

Figure 5 compares the density of state (DOS) of $5f$ states in $Fm\bar{3}m$ and $Pnma$ phases of UO$_2$ at a cell volume of 131.4 Å$^3$, close to the transition pressure of $U_{6}$ case. The most remarkable difference is the increase of band gap from 0.8 eV in fluorite phase to 2.4 eV in $Pnma$ phase. As a consequence, unoccupied states also move outwards. Below the Fermi level, different from fluorite phase where a nearly dispersionless band containing two well-localized $5f$ electrons that lies roughly from -1.8 to 0 eV, in $Pnma$ phase these localized states are further narrowed to start from -1.0 eV, while the valence $5f$ state is expanded from -3.7 to -1.0 eV, too. To completely delocalize the localized $5f$ states, a pressure above 121 GPa is required for $U_{45}$ and beyond 226 GPa for $U_{6}$, we will discuss this in next subsection.
C. High pressure behavior

The variation of local magnetic moment of uranium atoms with cell volume is almost the same for \textit{Pnma} and \textit{Fm\textoverline{3}m} phases in \textit{U\textsubscript{45}} case, implying the magnetic property is insensitive to structural transition in \textit{UO\textsubscript{2}}. As figure 5 shows, in spite of that GGS+U and LSDA+U approximations give much different cohesive energies for the fluorite phase, the calculated magnetic moment of uranium atoms is very close for a large range of volume, except for the highly expansion region ($V > 300 \text{\AA}^3$) where atoms trend to be isolated. At equilibrium volume, our calculation gives a moment of $\sim 1.93 \mu_B$ in a good agreement with previous calculation\textsuperscript{21} and slightly larger than observed $1.74 \mu_B$\textsuperscript{42}. It can be improved by including spin-orbit coupling to $1.88 \mu_B$ with an orbit contribution of $0.46 \mu_B$. This value is much smaller than all-electron calculation where an orbit moment of $3.6 \mu_B$ was predicted\textsuperscript{22}.

As shown in figure 5, there is a flat level for the local magnetic moment of uranium within moderate pressure range. A transition from antiferromagnetism to paramagnetism is observed at a volume between $102.1 \sim 108.4 \text{\AA}^3$ for \textit{U\textsubscript{45}} case (equivalent to 121 and 159 GPa in pressure). It corresponds to a volume of 63$\sim$66.4% of the equilibrium volume of fluorite phase and an effective cubic lattice constant as 86$\sim$88% of the latter phase. Increase $U$ to 6.0 eV postpones the paramagnetic transition to higher pressure as $226 \sim 294$ GPa, which has an effective cubic lattice constant that is 82$\sim$84% of the fluorite phase at ambient condition. It is worthwhile to point out that at the same volume a metallic transition also occurs due to completely delocalization of 5\textit{f} states.

As shown in figure 6, we can see the band gap disappear completely between $226 \sim 294$ GPa. The transition volume is in a good agreement with previous intuitive analysis that a reduction in the effective cubic lattice parameter to 82% of the equilibrium lattice parameter $a_0$ (of \textit{Fm\textoverline{3}m} phase) is required to have 5\textit{f} states in the conduction band\textsuperscript{43}. It is clear that the paramagnetic transition is driven by the delocalization of the two pre-localized 5\textit{f} electrons which become itinerant at this volume, and it is quite reasonable that the metallization is always accompanied by a paramagnetic transition for materials analogous to \textit{UO\textsubscript{2}} where both band gap and local magnetic moment are attributed to the same localized states. Below the metallic transition, we also find a new iso-structural transition occurring between $80 \sim 130$ GPa for \textit{Pnma} phase. Figure 7 shows the variation of relative lattice parameters of \textit{Pnma} phase starting from respective transition pressure of \textit{U\textsubscript{45}} and \textit{U\textsubscript{6}} cases. Drastic variations were observed for all lattice parameters between $75 \sim 121$ GPa for \textit{U\textsubscript{45}} and $80 \sim 130$ GPa for \textit{U\textsubscript{6}}, where the smallest axis $b$ has a strong rebound and the middle $a$ is collapsed. At higher pressure, the variations of relative lattice parameters become smooth and approaches isotropic compression. It is a typical structural transition. For \textit{U\textsubscript{45}} case one may wonder whether there is some relevancy between this transition and the metallic one because they adjoin closely in pressure. However calculation with \textit{U\textsubscript{6}} shows that they are irrelevant. By the way, at low pressure the calculated variation of relative lattice parameters is different from experimental observation, where the smallest axis $b$ is most compressible whereas the $a$ axis is most rigid. We do not know the exact reason for this discrepancy at present. But the experiment observed trend of relative lattice parameters cannot hold to high pressures because a stronger repulsive force will present along the shorter axis due to higher compression of electronic states. One can expect a rebound of the smallest axis at higher pressure.
As discussed in previous subsections, the value of $U$ depends on structure. This raises a question about the applicability of LSDA+$U$ method to intermediate process of structural transition, since the energy is affected by this term directly. It is impossible to fit the $U$ value for all intermediate structures with experimental data. Therefore, if one attempts to approximately model the transition (or lattice distortions) with just single or several values of $U$, evaluating the corresponding error becomes important. We do this job for UO$_2$ by calculating the energy variation along the linear interpolated intermediate structures between $Fm\bar{3}m$ and $Pnma$ phases under $\sim$8 GPa, namely, a candidate transition path for $U45$ case. In this calculation, no structure optimizing is performed.

The result is shown in figure 8, where the respective energy of $Fm\bar{3}m$ phase is set as reference point for GGS, LSDA and a classical pair potential model. For LSDA+$U$, only the energy of fluorite phase calculated with $U=4.5$ eV is set as reference energy, to take varying $U$ effect into account. Since $U6$ fails to model $Fm\bar{3}m$ phase and $U45$ fails to describe $Pnma$ phase, as the first level approximation, we interpolate the value of $U$ between these two phases linearly.
The result is given in figure 8 as the solid curve without symbol. As expected, \(U_6\) performs well for intermediate structures near \(P_{nma}\) phase while \(U_{45}\) becomes better for those close to fluorite phase. The largest error is 0.15 and 0.14 eV per atom for \(U_6\) and \(U_{45}\), respectively. What amazing is that the classical pair potential model outperforms GGS/LSDA approximation in this test. The former has an error as 0.18 eV per atom and the latter two are 0.32 and 0.34 eV per atom, respectively. It is about two times larger than LSDA+U approximation. This result of GGS/LSDA approximation is somewhat disappointed. For an unit cell of \(U_4O_8\), it would lead to an error about 4 eV in cohesive or formation energy. In this sense, the point defect formation energy calculated by M. Freyss et al.\({}^{18}\) is inaccurate and need further improvement with LSDA+U method in uranium defects case due to the large structure distortions. Finally, we would like to point out that the previous conclusion made by J. C. Boettger that “the strong correlation effects that are generally believed to produce the observed band gap do not have a significant impact on the binding properties of \(UO_2\)\(\) should be treated carefully depending on the studied structures and required precision.

IV. CONCLUSION

The structural behavior of uranium dioxide under pressure up to 300 GPa was investigated by DFT method with GGS/LSDA approximations plus (or not) Hubbard \(U\) correction for strong correlated on-site Coulomb interactions. Comparison with experiment showed that LSDA+U gives the best description for \(UO_2\) in fluorite phase. However the calculated transition pressure to \(P_{nma}\) phase with the same \(U\) parameter was quite low, indicating the value of \(U\) depends on structure or lattice distortions sensitively. A better value of \(U\) for \(P_{nma}\) phase is obtained, which removes the factitious energy barrier predicted by \(U=4.5\) eV. The error due to varying of \(U\) is estimated as just half of the error given by GGS/LSDA approximation, showing LSDA+U is more reliable. Higher pressure leads to an iso-structural transition followed by a metallic-paramagnetic transition, which takes place between 226∼294 GPa with an effective cubic lattice parameter as 82∼84% of the fluorite phase’s at zero pressure, in a good agreement with previous theoretical analysis.

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This is partially due to the fact that total energy is an integral of DOS and insensitive to its detailed profile structure. A quite similar situation holds for cluster expansion of DOS, where the convergence of DOS is not so good, but the resulted energy and electronic entropy have a good convergence with respect to cluster size. See, for example J. Chem. Phys. 122, 214706 (2005).

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From a point of view based on calculations in this paper and Ref.[22], the criticism of J. C. Boettger about LSDA+U method on this point is not pertinent.

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