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First-principles study of ground-state properties of U$_2$Mo

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By means of first-principles calculations, we have systematically investigated the structural, elastic, vibrational, and electronic properties of the ground-state phase for the intermetallic compound U$_2$Mo. Our results uncover that the previously synthesized $I4/mmm$ structure of U$_2$Mo is a metastable phase and unstable, neither thermodynamically nor vibrationally at the ground state. In combination with the evolutionary structural searches, our first-principles calculations suggest a new ground-state $Pmmm$ phase, which has been theoretically confirmed to be stable, both thermodynamically and vibrationally. Moreover, through the DFT+D technique we have discussed the van der Waals interactions on the structural, elastic and vibrational properties, revealing a weak effect in pure U and Mo solids and U$_2$Mo alloy. The analysis of the electronic band structures evidences its electronic stabilities with the appearance of a deep valley of the density of states at the Fermi level. Moreover, we have further investigated the temperature-dependent structural, thermal expansion and elastic properties of our proposed $Pmmm$ ground-state phase. These results are expected to stimulate further experimental investigations of the ground-state phase of U$_2$Mo.

1 Introduction

In comparison with the mixed-oxide (MOX) fuels, the metallic fuels exhibit significant potential advantages for fast reactors due to its superior properties. It has been applied for a rather long history. For instance, the first prototype fast breeder reactor, Clementine, became operational in 1949 at the Los Alamos National Laboratory using metallic fuel (i.e., δ-stabilized plutonium). The main concern of the metallic nuclear fuels is its irradiation performance and compatibility with cladding materials. However, the early metallic fuels (i.e., Pu-Fe and Pu-Al alloys) often suffered from high swelling rates and high smearing density. In the mid-1980s, fuels with U-Zr and U-Pu-Zr alloys showed a significantly better performance and were able to be operated at higher temperatures and higher burn-up. In the 1990s, a variety of U-Pu-X ternary alloys (X = Mo, Nb, Ti and Zr) have been tested as fuels for fast reactors in the USA and Europe with various degrees of success. In recent years, the developments of TRU-burning advanced fast nuclear reactors (the abbreviation TRU states for so-called transuranium and accelerator driven system (ADS) call for new concept of fuel types because those reactors share two different considerations, simultaneously: waste incineration and power generation. For them, U-based metallic fuels become promising candidates due to their high heavy metal densities and excellent thermal conductivities. Within this context, extensive studies on metallic fuels have been performed. Among them, U-Mo alloys have been thought to be the most prominent candidates because of their more stable irradiation performance compared with other high density uranium alloys and compounds (e.g., U$_3$Si, U$_6$Fe and U$_2$Mn). Interestingly, Mo has a high solubility (ca. 35at.%) in γ-U at high temperature above 833 K. However, below this temperature, the Mo-soluted γ-U alloy is decomposed into α-U and U$_2$Mo. The experimental measurement already revealed that U$_2$Mo crystallizes in the $C11_b$ (MoSi$_2$ prototype with the space group of $I4/mmm$) structure. To date, there have been experimental investigations on the thermodynamic properties for various U-Mo alloys. In particular, for U$_2$Mo some thermodynamic properties have been measured. Recently, using Mo doping combined with ultrafast cooling, Tkach et al. have investigated the fundamental electronic properties including Sommerfeld coefficient, magnetic susceptibility of γ-U. Their results have uncovered that the Mo-doped γ-U exhibits a conventional BCS superconductivity with $T_c$ ca. 2.1 K and a critical field exceeding 5 T for the 15 at%Mo-soluted alloy. Moreover, no magnetic properties have been observed for U$_2$Mo, indicating a possible paramagnetic state.

In fact, during the past few decades, many theoretical and computational results on U-based alloys have been published,
Despite of several crucial challenges on U and its alloy. One of the most crucial aspects is that the light-actinide metals, from Th to Pu, pose a severe challenge to modern electronic-structure theory partially due to the existence of highly directional and localized f-electron bonding states. Moreover, the heavy nuclei of the light-actinide metals induce a large relativistic effect on their valence-band structures, and usually require inclusion of the spin-orbit coupling (SOC) effects. Despite of those challenges, some basic properties (such as, zero-pressure zero-temperature equilibrium volumes and bulk modulus) can be successfully derived for the light-actinide metals\textsuperscript{16} using all-electron, full-potential, electronic-structure method: the full-potential linear augmented-plane-wave (FLAPW) and the linear combinations of Gaussian-type orbitals-fitting function (LCGTO-FF) methods. It has been recognized that for the ground-state orthorhombic α-U phase, the equilibrium and structural properties\textsuperscript{17}, elastic constants\textsuperscript{18}, phonon spectra\textsuperscript{19}, various defects\textsuperscript{20–22}, and even subtle electronic-structure details related to charge-density waves\textsuperscript{23} have been all well described within conventional DFT\textsuperscript{24}. However, for strongly correlated uranium dioxide\textsuperscript{25,26} and uranium mononitride\textsuperscript{27}, the DFT+U treatment has been applied to reproduce well the experimental findings. Some investigations also demonstrated that the standard DFT methods are validate in describing the point defect properties of UC\textsuperscript{28,29} and UN\textsuperscript{30}.

As yet there has only been a few attempts to perform \textit{ab initio} study of the formation enthalpy of Mo-soluted γ-U alloys. Through the cluster expansion technique\textsuperscript{31} within the Ising Hamiltonian formalism with a set of effective cluster interactions defined by the direct inversion method from the total energies of 16 bcc-based ordered structures, U\textsubscript{2}Mo was found to be stable because of its negative formation enthalpy. However, the temperature of phase equilibria transferred into a disordered phase was estimated to be excessively high, \textit{ca.} 2273 K for U\textsubscript{2}Mo, which is much higher than the experimental value of \textit{ca.} 853 K\textsuperscript{14}. Using the exact muffin-tin orbital method (EMTO) and full-potential linear muffin-tin orbital method (FP-LMTO), Landa \textit{et al.}\textsuperscript{32} have calculated the formation energy and electronic density of states (DOS) for the disordered Mo-soluted γ-U alloy in comparison with the ordered U\textsubscript{2}Mo. The results showed a significant reduction of the DOS in the vicinity of the Fermi level\textit{(Ef)} in the case of the ordered phase, which causes a decrease of the band-structure contribution to the total energy. Recently, S.Jaroszewicz \textit{et al.}\textsuperscript{33} have derived the thermal properties of the U\textsubscript{2}Mo by full-potential LPAW method.

Here, through first-principles calculations within the framework of standard density functional theory (DFT), DFT+\textit{U} and hybrid functional (HSE) by including the nonlocal exchange-interaction effect, we have calculated the thermodynamic, mechanical, elastic and vibrational properties of U\textsubscript{2}Mo. Our results demonstrated that the previously characterized tetragonal C\textit{11}_{4} phase of U\textsubscript{2}Mo is unstable, neither energetically nor vibrationally. Alternatively, utilizing the evolutionary search of USPEX\textsuperscript{34–36} we have found a new ground-state phase of U\textsubscript{2}Mo, which crystallizes in the orthorhombic structure (P\textit{mmm}). The derived phonon and elastic properties confirmed its dynamical and mechanical stability. It has also been found that the inclusion of the van der Waals interactions within the DFT+\textit{D} method does not alter those properties. In addition, we have analyzed its thermodynamical properties including thermal-expansion and specific heat properties as compared with the available experimental results. The paper is organized as follows. Pertinent details of the computational methods are described in section 2. Results and discussions of the density-functional calculations of the ground-state properties are provided in section 3. Lastly, concluding remarks are presented in Section 4.

2 Computational Method

We have employed the Vienna \textit{ab initio} Simulation Package (VASP)\textsuperscript{37–39} by utilizing the projector augmented wave (PAW) method\textsuperscript{40,41} within the framework of density functional theory (DFT)\textsuperscript{42,43}. The description of the exchange-correlation adopted the Perdew, Burke and Ernzerho (PBE)\textsuperscript{44} generalized gradient approximation (GGA). The \textit{k}-space integration with the incompletely filled orbitals has been performed with the tetrahedron method\textsuperscript{45} with Blöchl correction method\textsuperscript{46}. Optimizations are achieved by minimizing forces and total energies. The convergence criterion of the total energy and the force were set to be 0.01 meV and 0.001 eV/Å, respectively. The semicore 6s\textsuperscript{2}6p\textsuperscript{6}5f\textsuperscript{3}6d\textsuperscript{1}7s\textsuperscript{2} of U and the valence state 4d\textsuperscript{5}5s\textsuperscript{1} of Mo have been included in the PAW potentials. We used a plane wave cut-off energy of 400 eV, which has been found to be sufficient for precise energetics for all the elements considered in present work. For the calculations of elastic constants, the elastic tensor is determined by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship\textsuperscript{47}. The elastic tensor is calculated both, for rigid ions, as well as allowing for internal relaxation of the ionic Hessian matrix and multiplying with the internal strain tensor\textsuperscript{48}. The final elastic moduli including both, the contribution of distortions with rigid ions and the contributions from the ionic relaxations, are presented. In order to compute polycrystalline elastic moduli, the Voigt-Reuss-Hill approximation\textsuperscript{49–51} are applied. The polycrystalline mechanical properties calculated here include shear modulus (\textit{G}), Young’s modulus (\textit{E}), Poisson’s ratio (\textit{v}), and the Debye temperature (\textit{\Theta}_D)\textsuperscript{18}. For the bulk properties of the tetragonal and orthorhombic U\textsubscript{2}Mo, the 7×7×7 and 13×13×15 \textit{k}-mesh sampling has been applied, respectively, in the Brillouin Zone (BZ) according to the Monkhorst-Pack...
scheme\textsuperscript{52}. During our calculations, the spin-polarized calculation has been considered, but U\textsubscript{2}Mo is indeed nonmagnetic. Therefore, the nonspin-polarized calculation were adopted for all the calculations. To determine the ground-state enthalpy of formation, we have also calculated the total energies of bcc U and Mo metals with the 19×19×19 k-mesh sampling and 500eV cut off energy.

It is well-known that U often exhibits the localized f-electronic states we have hence introduced the hybrid functional (HSE)\textsuperscript{53,54} to calculate the total energies and electronic structure of U\textsubscript{2}Mo. The HSE employs an admixture of Hartree-Fock-like nonlocal exchange interaction and Perdew-Burke-Ernzerhof (PBE) exchange in the construction of the many-body exchange(x) and correlation (c) functional as follows,

\[
E_{xc}^{\text{HSE}} = \frac{1}{4}E_{x}^{\text{HF},sr,\mu} + \frac{3}{4}E_{x}^{\text{PBE},sr,\mu} + E_{x}^{\text{PBE},lr,\mu} + E_{c}^{\text{PBE}},
\]

where (sr) and (lr) refer to the short- and long-range parts of the respective exchange interactions whereas \(\mu\) controls the range separation of the Coulomb kernel, varying between 0.2 and 0.3 Å\textsuperscript{-1}. We have used \(\mu = 0.2\) Å\textsuperscript{-1}. The HSE functional is largely self-interaction free thus improving over the standard DFT description and enables us to achieve a correct understanding of strongly correlated electronic systems\textsuperscript{55–59}. In the case of HSE06 calculations, a 5×5×5 and 4×3×7 k-mesh sampling have been used for I\textsubscript{4}/mmm and Pmmn phases of U\textsubscript{2}Mo, respectively, and a 9×9×9 k-mesh sampling for bcc phases of U and Mo.

It has recently been recognized that the van der Waals interactions are necessary for accurately calculating bulk moduli and vibrational corrections in some solids\textsuperscript{60}. Therefore the DFT+D method\textsuperscript{61–63} has also been applied to the present cases and the role of the van der Waals interactions on the structural, elastic and vibrational properties has been discussed. In the case of DFT+D calculations, the parameters were obtained by using the dftd3\textsuperscript{62,63} program, and the rest parameters (\textit{i.e.}, cut off energy, k-mesh sampling) for the structure relaxation, elastic, vibrational properties are set as the same as standard DFT. The obtained results are listed in Table 1, along with available experimental data.

The phonon spectra and thermodynamic properties have been derived within the code of Phonopy\textsuperscript{64,65} by constructing the supercell approach within the conventional DFT framework. Real-space force constants of supercell was calculated by Parlinski-Li-Kawazoe method\textsuperscript{66} with a finite displacement (FD) method of 0.01 Å, and the phonon frequencies are calculated from the force constants. The 2×2×2 supercell are chosen to calculate thermodynamic properties using quasiharmonic approximations (QHA) at seven volumes.

### 3 Results and discussions

#### 3.1 Structural stabilities and enthalpies of formation of U\textsubscript{2}Mo

We have first performed a structural search for the ground-state phase of U\textsubscript{2}Mo by USPEX in conjunction with VASP codes within the standard DFT framework. Interestingly, the USPEX search has found that the most stable ground-state phase is the orthorhombic Pmmn structure for U\textsubscript{2}Mo,

![Fig. 1](color online) The structures of U\textsubscript{2}Mo (Left panel: I\textsubscript{4}/mmm and right panel: Pmmn). The red and green circles are Mo and U atoms, respectively.

![Fig. 2](Color online) Bulk modulus of Pmmn U\textsubscript{2}Mo as a function of temperature within standard DFT. The Black, red and green lines denote the shear modulus, bulk modulus and elastic modulus, respectively.
as shown in Fig. 1 (right panel). In contrast, the experimentally synthesized $I_{4}mmm$ phase (in Fig. 1 (left panel)) is not the energetically lowest one. Structurally, the proposed ground state $Pmmn$ phase is indeed closely related with the metastable $I_{4}mmm$ phase. As illustrated in Fig. 1, the structural distortion of the $I_{4}mmm$ phase by elongating the $a$ axis but shortening both the $c$- and $b$-axes, the $Pmmn$ structure will appear. The optimized lattice parameters (lattice constants and atomic positions) are compiled in Table 1 and the relaxed structural parameters of the $I_{4}mmm$ phase derived by standard DFT calculations with the PBE functional are in nice agreement with available experimental findings. However, the DFT+$D$ schemes underestimate the lattice parameters of $I43m$-U, $I4mcm$-Mo and $I4mmm$-U$_2$Mo, compared with the experimental findings.

In addition, their enthalpies of formation have been calculated according to the expression \(^\text{(2)}\) as follows,

\[ \Delta H_f = \frac{E_{U2Mo}^{total} - 2E_{U}^{t} + 1E_{Mo}^{t}}{3} \]

where $E_{U2Mo}^{total}$ is the total energy of the U$_2$Mo at the equilibrium state, and $E_{U}^{t}$ and $E_{Mo}^{t}$ are the energies of $bcc$ U and Mo, respectively. The obtained findings are listed in Table 1. As yet there has been no experimental enthalpy of formation reported for U$_2$Mo. Our calculated results within standard DFT-PBE calculations demonstrated that the $Pmmn$ phase has an enthalpy of $0.145$ eV/atom, which is more stable by about $0.042$ eV/atom than that of the $I_{4}mmm$ phase. Our calculated enthalpy of $-0.103$ eV/atom for the $I_{4}mmm$ phase is lower than the earlier theoretical data of $-0.064$ eV/atom and $-0.034$ eV/atom calculated by the cluster expansion in combination of FLAPW method and the EMTO-FPLMTO method, respectively. Through the HSE calculations, the proposed $Pmmn$ phase is still more stable by about $0.11$ eV/atom than the $I_{4}mmm$ phase, further evidencing that the $Pmmn$ phase is the ground-state phase. Furthermore, the HSE-derived enthalpies of formation of both $Pmmn$ and $I_{4}mmm$ phases are $0.144$ eV/atom and $0.037$ eV/atom, respectively. For the former the HSE-derived value is nearly the same as the result of the DFT-PBE derives, whereas for the latter the HSE-derived value is only about one third of the DFT-PBE data. It also needs to mention that the HSE-derived enthalpy of formation of the $I_{4}mmm$ phase almost equals to the value obtained using EMTO-FPLMTO method, as shown in Table 1. The DFT+$D$ derived enthalpies of formation of both $Pmmn$ and $I_{4}mmm$ phases are $0.161$ eV/atom and $0.090$ eV/atom, respectively; they suggest that the $Pmmn$ phase is the ground-state one.

### 3.2 Temperature-dependent elastic properties from 0 K to 880 K

We have further calculated the elastic constants of the single crystalline $I_{4}mmm$ and $Pmmn$ phases of U$_2$Mo in Table 2. We noted that the elastic constants of the $I_{4}mmm$ phase was also calculated by Jaroszewicz et al.\(^{33}\). Except for $C_{66}$, all other elastic constants are in good agreement to each other between our current data and the previous calculations. Interestingly, the $C_{66}$ value is about 20 GPa, which is very soft.\(^{33}\) However, using the same method of the Bloch correction (BC) as what Jaroszewicz et al. adopted, we have obtained a negative $C_{66}$ of -12 GPa, as shown in Table 2. In particular, it has been noted that because the $C_{66}$ itself is too small its value is very sensitive to the choice of how the partial occupation is set for each orbital during the calculations. If the Methfessel-Paxton method (MP) is used for the partial occupations with the small enough smearing-parameter, the $C_{66}$ and $C_{44}$ values are both small (9 GPa and 8 GPa, respectively). This fact demonstrated that the crystal of the $I_{4}mmm$ phase is very soft/unstable against the shear deformation along the directions of the $C_{66}$ or $C_{44}$ elastic tensors. Moreover, the DFT+$D$ scheme overestimates the elastic constants but does not change the instability of $I_{4}mmm$ phase, as shown in Table 2. Furthermore, we have also computed the elastic constants of the $Pmmn$ phase in Table 2, evidencing that both BC and MP methods yield very consistent data. In addition, those elastic constants derived both by standard DFT and DFT+$D$ schemes for the $Pmmn$ phase satisfy the mechanical stability criteria of the orthorhombic system: $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0$, $C_{11} + C_{22} - 2C_{12} > 0$, $C_{11} + C_{33} - 2C_{13} > 0$, and $C_{22} + C_{33} - 2C_{23} > 0$. These facts demonstrate the elastic stability of the $Pmmn$ phase. Based on the derived elastic constants, we further calculated their Young’s modulus, Shear modulus, Possion’s ratio, sound speed (transverse sound speed, $V_t$), longitudinal sound speed, $V_l$, average sound speed, $V_m$, and Debye temperature, as shown in Table 2. The Debye temperature($\Theta_D$) is known as an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. The $\Theta_D$ shows that, above this temperature, all the long-range acoustic modes will become active, but below it only a part of them can be evoked. The $\Theta_D$ is 265 K for $Pmmn$, being higher than the $\Theta_D$ of 195 K for $I_{4}mmm$. Moreover, the $\Theta_D$ for $Pmmn$, decreases from 265 K to 249 K with temperature increasing from 0 K to 880 K, as shown in Table 3. In addition, we have also derived the temperature-dependent shear modulus, isothermal bulk modulus and elastic modulus of the $Pmmn$ phase of U$_2$Mo in Fig. 2, as well as the temperature-dependent elastic constants, as shown in Table 3. It can be seen that with increasing temperature the three moduli and elastic constants decrease slowly.
3.3 Vibrational properties

We further calculated the phonon dispersions for both $I4/mmm$ and $Pnmm$ phases of $U_2Mo$. Figure 3 compiled the derived phonon dispersions and the phonon densities of states of both $I4/mmm$ and $Pnmm$ phases of $U_2Mo$ using the $3 \times 3 \times 3$ and $2 \times 2 \times 2$ supercells, respectively. For the $I4/mmm$ phase, it can be seen that, around the high-symmetry P-N direction, the two acoustical phonon branches exhibit highly large imaginary frequencies, in particular, being close to the boundary of the BZ. This fact indicates that this $I4/mmm$ structure is dynamically unstable, agreeing well with the above analysis of the elastic constants. The DFT+D scheme derived phonon dispersions of both $I4/mmm$ and $Pnmm$ phases do not significantly change (see Supplementary Fig. S1). These results reveal that the van der Waals interactions on pure U solid and its alloy is very weak. The detailed analysis demonstrates that the structural instability easily occurs by the deformation in the $ab$ plane, as indicated by the imaginary frequency branches along the high-symmetry N-P direction and the negative elastic constant ($C_{66}$). For instance, we adopted the strain deformation along the diagonal direction of the $ab$ plane of the $I4/mmm$ phase via the strain tensor as follows,

$$
\begin{pmatrix}
1.0 & \frac{1}{2}\sigma & 0 \\
\frac{1}{2}\sigma & 1.0 & 0 \\
0 & 0 & 1.0
\end{pmatrix}
$$

(3)

where $\sigma$ is the strain applied to the $a$ and $b$ axes. The deformation energies are compiled as a function of $\sigma$ in Fig. 4. It can be seen that, with increasing $\sigma$ from zero to around 8%, the deformation energies reduces dramatically. This fact directly reveals the structural instability of the $I4/mmm$ phase. Furthermore, for the energy-lowest $Pnmm$ phase the phonon dispersions shown in Fig. 3 shows no any imaginary frequencies, suggesting its dynamical stabilities. Because the atomic masses of Mo and U are highly different, the phonon densities of states can be clearly separated by Mo and U. As shown in Fig. 3, the low-frequency region (below 4 THz) is dominated by the U atom because the acoustical models are mainly originated from the heavy elements and above 5 THz it is obvious that the phonon modes are mainly from the Mo atoms. Finally, according to the phonon densities of states the zero-point vibrational energies for both $I4/mmm$ and $Pnmm$ phases can be derived to be 0.054 and 0.066 eV/f.u., respectively. It needs to be emphasized that the zero-point vibrational energy may not be accurate because of the existence of the imaginary frequencies.

3.4 Thermal volume expansion and specific heat of $U_2Mo$

As the metallic fuel, one would concern seriously the thermodynamic properties, in particular, the thermal expansion of volumes and the specific heats. In order to elucidate these properties, we have calculated the DFT static energies $U(V)$ and the phonon free energies $F_{phonon}(T;V)$ at seven different volumes around the the equilibrium state. The thermodynamic functions $G(T,p) = \min[U(V) + F_{phonon}(T;V)]$ were fitted to the integral form of the Vinet equation of state (EOS) at the pressure of $p = 0$. The Gibbs free energies at finite
temperatures were obtained at the minimum values of the thermodynamic functions, the corresponding equilibrium volumes and the isothermal bulk moduli were obtained also from the Vinet EOS. The corresponding results of the Pmmn phase of U₂Mo are compiled in Fig. 5. It can be seen that the thermal expansion of the volume is observed with the increasing equilibrium volume. Therefore, based on these data, we have derived the thermal expansion (including thermal expansion coefficients) of the ground-state Pmmn phase of U₂Mo. It needs to be emphasized that, because the I4/mmm phase at its equilibrium state exhibits negative phonon modes, hence there is no way to calculate its thermal expansion properties. As illustrated in Fig. 6 of the Pmmn phase, the thermal volume expansion, which was defined as \( \Delta L/L_0 \) (\( L_0 \) is \( L = V^{1/3} \) at 300 K and \( \Delta L = L - L_0 \)), is compiled as a function of temperatures. It can be seen that the thermal expansion of the volumes increase as the temperature increases. Surprisingly, above 400 K the theoretically derived values of the Pmmn phase agree well with the experimentally measured data of the I4/mmm phase. It has been noted that U₂Mo exhibits a high-temperature disordered \( \gamma(U,Mo) \) transformation above 853 K. But, in our current calculations no disordered transition has been considered. The thermal expansion coefficients of the Pmmn phase of U₂Mo have been further compiled in Fig. 7.

Furthermore, the heat capacities \( C_p \) at the constant pressure calculated by QHA and \( C_v \) at the constant volume of Pmmn U₂Mo have been derived as shown in Fig. 7, as well as the
The most typical feature of their DOSs is that the density at the Fermi level now occupies the nearly pseudogap in the case of $Pmmm$ phase. Moreover, for $I4/mmm$, the Mo-4$d$ electrons exhibit very low densities above the Fermi level, and thus would not be expected to play a major role in bonding, whereas for $Pmmm$, Mo-4$d$ and U-5$f$ electrons show a relatively stronger hybridization. Around the Fermi level that is mainly dominated by the $f$ orbital, the $f$ occupation exhibits significant variance upon these two structures, as shown in Figs. 8(a) and (b). It can be seen that the density of states at the Fermi level, $N(E_F) = 5$ states eV$^{-1}$ f.u.$^{-1}$, for the $Pmmm$ phase shows a significant decrease, as compared with the $N(E_F)$ of 7.5 states eV$^{-1}$ f.u.$^{-1}$ for the $I4/mmm$ phase. This fact reveals the electronic stability of $Pmmm$ phase, in agreement with the comparisons of the total energies, elastic constants and phonon spectra. Importantly, this large change becomes more apparent within the HSE framework due to the fact that the nonlocal exchange interaction heavily separates the Mo-$d$ and U-$f$ states around the Fermi level. As illustrated in Fig. 8(d) the Fermi level now lies in the deep valley, with a density of only about 1.5 states eV$^{-1}$ f.u.$^{-1}$, which is only 30% of the DFT-PBE derived density, as shown in Fig. 8(b). In particular, the consistent fact for both DFT-PBE and HSE-derived DOSs is that, when comparing with the $I4/mmm$ phase, the decrease of the density at the Fermi level for the $Pmmm$ phase is mainly due to the separations of the occupied bonding and unoccupied antibonding states, implying the electronic stability in the $Pmmm$ phase.

4 Conclusions

In summary, we have systematically explored the ground-state properties of U$_2$Mo from first-principles calculations. In combination with the evolutionary structural searches, we have proposed a new ground-state $Pmmm$ phase, which is theoretically confirmed to be stable within standard DFT, HSE and DFT+D framework. The $Pmmm$ ground-state phase is indeed closely correlated with the previously characterized $I4/mmm$ phase. As comparison with available experimental data of the $I4/mmm$ phase, the standard DFT calculations accurately yielded the lattice constants. The DFT calculation underestimates the enthalpy of formation when comparing with the early reported FP-LMTO results for which an agreement has been, however, achieved by the HSE calculations. However, the addition of dispersion corrections destroys the perfect agreement of lattice parameters of Im$\bar{3}$m-$U$ and Im$\bar{3}$m-Mo with experimental achieved at the DFT level. The elastic and vibrational properties of $I4/mmm$ and $Pmmm$ phases have been derived within the standard DFT and DFT+D framework. The detailed analysis demonstrated that the mechanical insta-
bility of 14I4mmm stems from the deformation in the ab plane, whereas the ground-state Pmmn phase is both dynamically and thermodynamically stable, without any imaginary frequencies in its phonon dispersions. The DFT+D method increases the elastic constants but does not change the mechanical and vibrational instabilities of 14I4mmm. These results reveal that the van der Waals interactions is very weak in pure U and Mo solids and U2Mo alloys. The analyses of the derived DOSs demonstrated the electronic instability of the 14I4mmm as compared with the Pmmn: the total electronic density at the Fermi level of Pmmn is significantly reduced with respect to that of 14I4mmm. Finally, we have derived the temperature-dependent, elastic, and thermal expansion of volume as well as specific heats of U2Mo at its ground state. We hope that these theoretical results will further stimulate the experimental investigation of the ground-state properties of U2Mo.

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References
Table 1 The optimized structural parameters (lattice constant in Å, the atomic positions) and enthalpy of formation ($\Delta H_f$ in eV/atom) for both $I4/mmm$ and $Pmmm$ phases of $U_2Mo$ within standard DFT and DFT+D, as compared with available experimental data.

<table>
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<th>$\Delta H_f$</th>
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Table 2 Calculated elastic constants (in GPa), Possion’s ratio ($\nu$), sound velocity ($V_s$, $V_L$, and $V_M$ in m/s), Debye Temperature ($\Theta_D$ in K), theoretical density ($\rho$ in g/cm$^3$) at 0 K within standard DFT and DFT+D. BC and MP represent Bloch corrections method and Methfessel-Paxton method for how the partial occupancies were set for each orbital, respectively.

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Table 3 Calculated elastic constants (in GPa) and Debye Temperature ($\Theta_D$ in K) of $Pmmm$ $U_2Mo$ as a function of temperature (in K) within standard DFT.

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