First-principles study of ground-state properties of U\textsubscript{2}Mo†

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By means of first-principles calculations, we have systematically investigated the structural, elastic, vibrational, thermal and electronic properties of the ground-state phase for the intermetallic compound U\textsubscript{2}Mo. Our results reveal that the previously synthesized \textit{I\textsubscript{4}/mmm} structure of U\textsubscript{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 \textit{Pmmn} phase, which has been confirmed theoretically to be stable, both thermodynamically and vibrationally. Moreover, through the DFT + \textit{D} technique we have discussed the influence of van der Waals interactions on the structural, elastic and vibrational properties, revealing a weak effect in pure U and Mo solids and U\textsubscript{2}Mo alloy. The analysis of the electronic band structures evidences its electronic stabilities with the appearance of a deep valley in the density of states at the Fermi level. Moreover, we have investigated further the temperature-dependent structural, thermal expansion and elastic properties of our proposed \textit{Pmmn} ground-state phase. These results are expected to stimulate further experimental investigations of the ground-state phase of U\textsubscript{2}Mo.

1 Introduction

In comparison with mixed-oxide (MOX) fuels, metallic fuels exhibit significant potential advantages for fast reactors due to their superior properties. They have been applied over a rather long history.\textsuperscript{1} For instance, the first prototype fast breeder reactor, Clementine, became operational in 1949 at the Los Alamos National Laboratory using metallic fuel (\textit{i.e.}, \textdelta-stabilized plutonium). The main concern regarding metallic nuclear fuels is their irradiation performance and compatibility with cladding materials. However, the early metallic fuels (\textit{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 with higher burn-up. In the 1990s, a variety of U–Pu–X ternary alloys (X = Mo, Nb, Ti and Zr) were 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 systems (ADS) call for a 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.\textsuperscript{2–10} 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 (\textit{e.g.}, U\textsubscript{6}Si, U\textsubscript{6}Fe and U\textsubscript{6}Mn\textsuperscript{11}). Interestingly, Mo has a high solubility (\textit{ca.} 35 at\%) in \textgamma-U at high temperatures above 833 K. However, below this temperature, the Mo-soluted \textgamma-U alloy is decomposed into \textalpha-U and U\textsubscript{2}Mo. Experimental measurement already revealed that U\textsubscript{2}Mo crystallizes in the C\textit{11}_{\text{b}} (MoSi\textsubscript{2} prototype with the space group of \textit{I\textsubscript{4}/mmm}) structure. To date, there have been experimental investigations on the thermodynamic properties for various U–Mo alloys.\textsuperscript{9,12,13} In particular, for U\textsubscript{2}Mo some thermodynamic properties have been measured.\textsuperscript{14} Recently, using Mo doping combined with ultrafast cooling, Tkach \textit{et al.}\textsuperscript{15} have investigated fundamental electronic properties including the Sommerfeld coefficient and magnetic susceptibility of \textgamma-U. Their results have uncovered that the Mo-doped \textgamma-U exhibits a conventional BCS superconductivity with \textit{T}_{\text{c}} \textit{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\textsubscript{2}Mo, indicating a possible paramagnetic state.

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In fact, during the past few decades, many theoretical and computational results on U-based alloys have been published, despite several crucial challenges to 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 those challenges, some basic properties (such as, zero-pressure, zero-temperature equilibrium-volumes and bulk moduli) can be successfully derived for the light-actinide metals\(^{16}\) using the all-electron, full-potential, electronic-structure method: the full-potential linear augmented-plane-wave (FLAPW) and linear combinations of the Gaussian-type orbital-fitting functions (LCGTO-FF) methods. It has been recognized that for the ground-state orthorhombic \(\gamma\)-U phase, the equilibrium and structural properties, elastic constants,\(^{18}\) phonon spectra,\(^{19}\) various defects,\(^{20–22}\) and even subtle electronic-structure details related to charge-density waves\(^{23}\) have been all well described within conventional DFT.\(^{24}\) However, for strongly correlated uranium dioxide\(^{25,26}\) and uranium mononitride,\(^{27}\) the DFT + \(U\) treatment has been applied to reproduce well the experimental findings. Some investigations also demonstrated that the standard DFT methods are valid in describing the point defect properties of \(U\)\(^{28,29}\) and \(UN\)\(^{30}\).

As yet there have been few attempts to perform \(ab\) \(initio\) study of the formation enthalpy of Mo-soluted \(\gamma\)-\(U\) alloys. Through the cluster expansion technique\(^{31}\) 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, \(U\)\(_2\)\(Mo\) 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, \(ca.\) 2273 K for \(U\)\(_2\)\(Mo\), which is much higher than the experimental value of ca. 853 K.\(^{14}\) Using the exact muffin-tin orbital method (EMTO) and full-potential linear muffin-tin orbital method (FPLMTO), Landa \textit{et al.}\(^{32}\) have calculated the formation energy and electronic density of states (DOS) for the disordered Mo-soluted \(\gamma\)-\(U\) alloy in comparison with the ordered \(U\)\(_2\)\(Mo\). The results showed a significant reduction of the DOS in the vicinity of the Fermi level \(E_F\) in the case of the ordered phase, which causes a decrease of the band-structure contribution to the total energy. Recently, Jaroszewicz \textit{et al.}\(^{33}\) have derived the thermal properties of the \(U\)\(_2\)\(Mo\) by the full-potential LPAW method.

Here, through first-principles calculations within the framework of standard density functional theory (DFT), DFT + \(D\) and hybrid functional (HSE) by including the nonlocal exchange–interaction effect, we have calculated the thermodynamic, mechanical, elastic and vibrational properties of \(U\)\(_2\)\(Mo\). Our results demonstrated that the previously characterized tetragonal C11\(_b\) phase of \(U\)\(_2\)\(Mo\) is unstable, neither energetically nor vibrationally. Alternatively, by utilizing the evolutionary search of USPEX\(^{34–36}\) we have found a new ground-state phase of \(U\)\(_2\)\(Mo\), which crystallizes in the orthorhombic structure \((Pmmn)\). 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 + \(D\) 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 \(ab\) \(initio\) Simulation Package (VASP)\(^{37–39}\) by utilizing the projector augmented wave (PAW) method\(^{40,41}\) within the framework of density functional theory (DFT).\(^{32,42}\) The description of the exchange–correlation adopted the Perdew, Burke and Ernzerhof (PBE)\(^{43}\) generalized gradient approximation (GGA). The \(k\)-space integration with incompletely filled orbitals was performed with the tetrahedron method\(^{45}\) with Blöchl correction.\(^{46}\) Optimizations are achieved by minimizing forces and total energies. The convergence criteria of the total energy and the force were set to be 0.01 meV and 0.001 eV Å\(^{-1}\), respectively. The semicore 6s\(^2\)6p\(^5\)5f\(^3\)6d\(^7\)s\(^2\) of \(U\) and the valence state 4d\(^{10}\)5s\(^2\) of \(Mo\) were included in the PAW potentials. We used a plane wave cut-off energy of 400 eV, which has been found to be sufficient for the precise energetics of all the elements considered in the present work. For the calculation 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.\(^{47}\) The elastic tensor is calculated both for rigid ions as well as allowing for internal relaxation of the ionic Hessian matrix and multiplying by the internal strain tensor.\(^{48}\) 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 the polycrystalline elastic moduli, the Voigt–Reuss–Hill approximation\(^{49–51}\) is applied. The polycrystalline mechanical properties calculated here include shear modulus \((G)\), Young’s modulus \((E)\), Poisson’s ratio \((\nu)\), and the Debye temperature \((\Theta_D)\).\(^{18}\) For the bulk properties of the tetragonal and orthorhombic \(U\)\(_2\)\(Mo\), the \(7 \times 7 \times 7\) and \(13 \times 13 \times 15\) \(k\)-mesh sampling has been applied, respectively, in the Brillouin Zone (BZ) according to the Monkhorst–Pack scheme.\(^{52}\) During our calculations the spin-polarized calculation was considered, but \(U\)\(_2\)\(Mo\) was indeed nonmagnetic. Therefore, the nonspin-polarized calculations were adopted for all calculations. To determine the ground-state enthalpy of formation, we have also calculated the total energies of bcc \(U\) and \(Mo\) metals with the \(19 \times 19 \times 19\) \(k\)-mesh sampling and 500 eV cut-off energy.

It is well-known that \(U\) often exhibits localized f-electronic states, thus we have introduced a hybrid functional (HSE)\(^{53,54}\) to calculate the total energies and electronic structure of \(U\)\(_2\)\(Mo\). 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 ($\chi$) and correlation ($c$) functional as follows,

$$E_{xc}^{\text{HSE}} = \frac{1}{4}E_{xc}^{\text{HF},\text{sr} \mu} + \frac{3}{4}E_{xc}^{\text{PBE},\text{sr} \mu} + E_{xc}^{\text{PBE},\text{lr} \mu} + E_{xc}^{\text{PRE}},$$

(1)

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$^{-1}$. We have used $\mu = 0.2$ Å$^{-1}$. 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{55–59,74,75} In the case of HSE06 calculations, a $5 \times 5 \times 5$ and $4 \times 3 \times 7$ k-mesh sampling were used for $I4/mmm$ and $Pmnm$ phases of U$_2$Mo, respectively, and a $9 \times 9 \times 9$ k-mesh sampling for bcc phases of U and Mo.

It has recently been recognized that the van der Waals interactions are necessary for calculating accurately 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 of the parameters (i.e., cutoff energy, k-mesh sampling) for the structural relaxation, elastic, vibrational properties are set as the same as standard DFT. The obtained results are listed in Table 1, along with the available experimental data.

The phonon spectra and thermodynamic properties have been derived within the code of Phonopy\textsuperscript{64,65} by constructing a supercell approach within the conventional DFT framework. The real-space force constants of the supercell were calculated by the 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 $2 \times 2 \times 2$ supercells were 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$_2$Mo

We first performed a structural search for the ground-state phase of U$_2$Mo by USPEX in conjunction with VASP codes within the standard DFT framework, as what has been done for the W–B, Mn–B and Cr–B systems.\textsuperscript{56–58} Interestingly, the USPEX search found that the most stable ground-state phase is the orthorhombic $Pmnm$ structure for U$_2$Mo, as shown in Fig. 1 (right panel). In contrast, the experimentally synthesized $I4/mmm$ phase (in Fig. 1 (left panel)) is not the energetically lowest one. Structurally, the proposed ground state $Pmnm$ phase is indeed closely related to the metastable $I4/mmm$ phase. As illustrated in Fig. 1, by structural distortion of the $I4/mmm$ phase by elongating the $c$ axis but shortening both the $a$- and $b$-axes, the $Pmnm$ structure will appear. The optimized lattice parameters (lattice constants and atomic positions) are compiled in Table 1 and the relaxed structural parameters of the $I4/mmm$ phase derived by standard DFT calculations with the PBE functional are in nice agreement with available experimental findings.\textsuperscript{67} However, the DFT + $D$ schemes underestimate the lattice parameters of $I4/mmm$, $Im\bar{3}m$–U, $Im\bar{3}m$–Mo and $I4/mmm$–U$_2$Mo compared with the experimental findings.\textsuperscript{67–69}

In addition, their enthalpies of formation have been calculated according to the following expression,\textsuperscript{70}

$$\Delta H_f = \frac{E_{\text{total}}^{\text{U}_2\text{Mo}}}{3} - \frac{2E_{\text{solid}}^{\text{U}} + E_{\text{solid}}^{\text{Mo}}}{3}$$

(2)

where $E_{\text{total}}^{\text{U}_2\text{Mo}}$ is the total energy of the U$_2$Mo at the equilibrium state, and $E_{\text{solid}}^{\text{U}}$ and $E_{\text{solid}}^{\text{Mo}}$ 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 U₂Mo. Our calculated results within standard DFT-PBE calculations demonstrated that the Pnmm phase has an enthalpy of −0.145 eV per atom, which is more stable by about 0.042 eV per atom than that of the I4/mmm phase. Our calculated enthalpy of −0.103 eV per atom for the I4/mmm phase is lower than the earlier theoretical data of −0.064 eV per atom and −0.034 eV per atom calculated by cluster expansion in combination with the FLAPW method and the EMTO-FPLO method, respectively. Through the HSE calculations, the proposed Pnmm phase is still more stable by about 0.11 eV per atom than the I4/mmm phase, further evidencing that the Pnmm phase is the ground-state phase. Furthermore, the HSE-derived enthalpies of formation of both the Pnmm and I4/mmm phases are −0.144 eV per atom and −0.037 eV per atom, respectively. For the former, the HSE-derived value is nearly the same that derived from the DFT-PBE, whereas for the latter the HSE-derived value is only about one third of the DFT-PBE data. It also should be mentioned that the HSE-derived value is nearly the same that derived from the DFT-PBE, whereas for the latter the HSE-derived value is about one third of the DFT-PBE, demonstrated that the crystal of the 4/mmm phase is lower than the earlier theoretical data of C₀/Cₐ at 0 K within standard DFT and DFT + D. BC and MP represent the Bloch correction method and the Methfessel–Paxton method for how the partial occupancies were set for each orbital, respectively. The C₆₆ value is about 20 GPa, which is very soft. However, using the same method of Bloch correction (BC) as adopted by Jaroszewicz et al., we have obtained a negative C₆₆ of −12 GPa, as shown in Table 2. In particular, it has been noted that because the C₆₆ itself is too small its value is very sensitive to the choice partial occupation setting for each orbital during the calculations. If the Methfessel–Paxton method (MP) is used for the partial occupancies with a small enough smearing-parameter, the C₆₆ and C₄₄ values are both small (9 GPa and 8 GPa, respectively). This fact demonstrated that the crystal of the 4/mmm phase is very soft/unstable against the shear deformation along directions of the C₆₆ or C₄₄ elastic tensors. Moreover, the DFT + D scheme overestimates the elastic constants but does not change the instability of the 4/mmm phase, as shown in Table 2. Furthermore, we have also computed the elastic constants of the Pnma phase in Table 2, evidencing that both the BC and MP methods yield very consistent data. In addition, the elastic constants derived both by standard DFT and DFT + D schemes for the Pnma phase satisfy the mechanical stability criteria of the orthorhombic system: C₁₁ > 0, C₂₂ > 0, C₃₃ > 0, C₄₄ > 0, C₆₆ > 0, C₁₁ + C₂₂ + C₃₃ + 2(C₁₂ + C₁₃ + C₂₃) > 0, C₁₁ + C₂₂ − 2C₁₃ > 0, C₃₃ − 2C₁₃ > 0, and C₂₂ + C₃₃ − 2C₃₃ > 0. These facts demonstrate the elastic stability of the Pnma phase. Based on the derived elastic constants, we further calculated their Young’s moduli, shear moduli, Poisson’s ratios, sound speeds (transverse sound speed, Vₜ, longitudinal sound speed, Vₗ, average sound speed, vₐ), and Debye temperatures, as shown in Table 2. The Debye temperature (θ_D) is known as an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. The θ_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 θ_D is 265 K for Pnma, which is higher than the θ_D of 195 K for I4/mmm. Moreover, the θ_D for Pnma 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 Pnma phase of U₂Mo 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.

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

We have calculated further the elastic constants of the single crystalline I4/mmm and Pnma phases of U₂Mo in Table 2. We note that the elastic constants of the I4/mmm phase was also calculated by Jaroszewicz et al. Except for C₆₆, all other elastic constants are in good agreement with each other between our current data and the previous calculations. Interestingly, the C₆₆ value is about 20 GPa, which is very soft. However, using the same method of Bloch correction (BC) as adopted by...
phonon dispersions and the phonon densities of state of both the $I4/mmm$ and $Pmmn$ 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 very 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 $Pmmn$ phases do not change significantly (see Fig. S1†). These results reveal that the van der Waals interactions on a pure U solid and its alloy are very weak.

This detailed analysis demonstrates that the structural instability occurs easily by 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,

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

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 reduce dramatically. This fact directly reveals the structural instability of the $I4/mmm$ phase. Furthermore, for the lowest-energy $Pmmn$ phase, the phonon dispersions shown in Fig. 3 do not shows any imaginary frequencies, suggesting its dynamic stability. Because the atomic masses of Mo and U are very different, the phonon densities of state 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 acoustic modes originate mainly from 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 the $I4/mmm$ and $Pmmn$ phases can be derived to be 0.054 and 0.066 eV f.u. $^{-1}$, 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 $U_2Mo$

Regarding the metallic fuel, we are concerned specifically with the thermodynamic properties, in particular, the thermal expansions of volume and the specific heats. In order to elucidate these properties, we have calculated the DFT static...
energies $U(V)$ and the phonon free energies $F_{\text{phonon}}(T;V)$ at seven different volumes around the equilibrium state. The thermodynamic functions $G(T,p) = \min_V [U(V) + F_{\text{phonon}}(T;V)]$ were fitted to the integral form of the Vinet equation of state (EOS) at a 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 $U_2Mo$ are compiled in Fig. 5. It can be seen that the thermal expansion of the volume is observed with increasing equilibrium volume. Therefore, based on these data, we have derived the thermal volume expansion (including thermal expansion coefficients) of the ground-state $Pmmn$ phase of $U_2Mo$. It needs to be emphasized that, because the $I4/mmm$ phase at its equilibrium state exhibits negative phonon modes, there is no way to calculate its thermal expansion properties. As illustrated in Fig. 6, the $Pmmn$ phase, the thermal volume expansion, which was defined as $\Delta L/L_0$ ($L_0 = V^{1/3}$ at $300 \text{ K}$ and $\Delta L = L - L_0$), is compiled as a function of temperature. It can be seen that the thermal expansion of the volume increases as the temperature increases. Surprisingly, above $400 \text{ K}$ 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 $U_2Mo$ exhibits a high-temperature disordered $\gamma(U,Mo)$ transformation above $853 \text{ K}$, but in our current calculations no disordered transition has been considered. The thermal expansion coefficients of the $Pmmn$ phase of $U_2Mo$ have been further compiled in Fig. 7.

Furthermore, the heat capacities $C_p$ at constant pressure calculated by QHA and $C_v$ at a constant volume of $Pmmn$ $U_2Mo$ have been derived as shown in Fig. 7, as well as the experimental data of the $I4/mmm$ phase. As the temperature increases, it rises rapidly up to ca. $150 \text{ K}$ but is nearly constant at high temperatures above ca. $200 \text{ K}$. The discrepancies between $C_p$ and $C_v$ of the $Pmmn$ phase is very small at low temperature. This fact can be interpreted by the following well-known thermodynamic relationship between $C_p$ and $C_v$:

$$C_p = C_v + BVT^2,$$  \hspace{1cm} (4)

where $z$ is the coefficient of volumetric thermal expansion while $B$ is the bulk modulus. Based on a purely harmonic model, there is no thermal expansion and $C_v$ must be equal to $C_p$. The term $BVT^2$ can thus be viewed as the correction arising from the anharmonic effect. However, it has been noted that the $C_p$ of the $Pmmn$ phase of $U_2Mo$ agrees well with the experimental
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 DOS is that, when comparing with the $I4/mmm$ phase, the decrease of the density at the Fermi level for the $Pmnn$ phase is mainly due to the separation of the occupied bonding and unoccupied antibonding states, implying the electronic stability of the $Pmnn$ phase.

4 Conclusions

In summary, we have explored systematically 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 $Pmnn$ phase, which is theoretically confirmed to be stable within standard DFT, HSE and DFT + $D$ framework. The $Pmnn$ ground-state phase is indeed closely correlated with the previously characterized $I4/mmm$ phase. In comparison with available experimental data of the $I4/mmm$ phase, the standard DFT calculations yielded accurately the lattice constants. The DFT calculation underestimates the enthalpy of formation when compared with the earlier-reported FP-LMTO results, but these agree with the results of the HSE calculations. However, the addition of dispersion corrections destroys the perfect agreement of the lattice parameters of $Im\bar{3}m$-$U$ and $Im\bar{3}m$-$Mo$ with experiment, achieved at the DFT level. The elastic and vibrational properties of $I4/mmm$ and $Pmnn$ phases have been derived within the standard DFT and DFT + $D$ framework. This detailed analysis demonstrated that the mechanical instability of $I4/mmm$ stems from deformation in the $ab$ plane, whereas the ground-state $Pmnn$ 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 $I4/mmm$. These results reveal that the van der Waals interactions are very weak in pure U and Mo solids and U$_2$Mo alloys. The analyses of the derived DOS demonstrated the electronic instability of the $I4/mmm$ as compared with the $Pmnn$: the total electronic density at the Fermi level of $Pmnn$ is significantly reduced with respect to that of $I4/mmm$. Finally, we have derived the temperature-dependent structural, elastic, and thermal expansion of volume as well as specific heats of U$_2$Mo at its ground state. We hope that these theoretical results will further stimulate the experimental investigation of the ground-state properties of U$_2$Mo.

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Fig. 8 The calculated densities of state (DOS) of the $I4/mmm$ (panels: a and c) and the $Pmnn$ phases (panels: b and d) within standard DFT (panels: a and b) and the HSE (panels: c and d) frameworks. The black curves denote the total DOS. The U-5f and Mo-4d projected local DOS are depicted by magenta dashed and green dashed-dot curves, respectively.
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