Comment on "Correlation and relativistic effects in U metal and U-Zr alloy: Validation of *ab initio* approaches"

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In a recent paper, Xie *et al.* [Phys. Rev. B **88**, 235128 (2013)], report that the density-functional theory (DFT) with the so-called DFT plus Hubbard U (DFT + U) modification improves energetics, volumes, and formation enthalpies over the standard form of DFT for uranium metal and U-Zr alloys. Also, spin-orbit coupling (SOC) was argued to advance the aforementioned properties in these systems. We demonstrate, contrarily, that neither the Hubbard U approach nor SOC is necessary for a correct description of uranium metal and U-Zr alloys. We further illustrate that the combination of DFT + U and SOC in the projector augmented-wave calculations by Xie *et al.* results in unrealistically large volume expansions, particularly for γ-U, in stark contrast to all previous calculations for elemental uranium. This in turn may also explain why the DFT + U with SOC model predicts negative enthalpy of mixing in the U-Zr alloy system contradicting conventional DFT as well as one of the main features of the experimental U-Zr phase diagram. The assertion by Xie *et al.* that DFT + U is an improvement over DFT for these systems is illustrated to be incorrect.

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Xie *et al.* [1] carried out a study of the electronic structure, equilibrium properties, and energetics for U metal and U-Zr alloys, with the Vienna *ab initio* simulation package (VASP) [2] in the framework of density-functional theory (DFT) using electron-ion interaction described with the projector augmented-wave (PAW) method. The chemical disorder in the U-Zr alloys was treated within the quasirandom structure technique [3] while electron correlation was considered beyond standard DFT in the so-called DFT + U approach. In addition, the influence of spin-orbit coupling (SOC) was investigated.

The authors conclude that a *single* "optimal" Hubbard $U_{\text{eff}} = U - J$ of 1.24 eV, combined with SOC, for both elemental U and U-Zr alloys, provides the best statistical agreement with experiments thus motivating the necessity of these interactions. However, there is a wealth of studies implying the opposite [4–15], namely, that neither DFT + U nor SOC are necessary for an accurate description of uranium metal or its alloys with zirconium. We argue that the DFT + U approach for these systems leads to inconsistencies and inaccurate results for formation enthalpies, atomic volumes, and magnetic properties and should best be avoided, contrary to the conclusion of [1] where it is argued to be an improvement over conventional DFT.

Let us briefly focus first on the atomic volume of α-U as an example and only use data taken from Table IV in Ref. [1]. Here we find that the DFT + U + SOC ("optimal" $U_{\text{eff}} = 1.24$ eV) treatment gives an atomic volume of 20.94 Å^3, while a carefully performed all-electron calculation [4], within standard DFT, gives 20.40 Å^3. The all-electron result is thus in significantly better agreement with experimental data at 45 K (20.53 Å^3) with no deterioration due to SOC [4] (20.67 Å^3), suggesting that the DFT + U + SOC exacerbates the comparison to low-temperature measurements. On the other hand, the DFT + U + SOC may cause a fortuitous improvement in the VASP-PAW calculations [1] due to cancellation of errors. Namely, from Table IV in Ref. [1] we find that VASP-PAW seriously underestimates the atomic volume of α-U (20.06 Å^3). It thus seems rather clear that the deficiency in the VASP-PAW calculation for uranium is counterbalanced to some extent by the addition of DFT + U + SOC while still not giving the accuracy of the all-electron standard DFT.

Next, we consider the γ (body-centered-cubic) phase of uranium metal and the U-Zr alloy system. Again, we find large volume expansions associated with the DFT + U + SOC model (Table IV in Ref. [1]). In Fig. 1 we plot the tabulated VASP-PAW volumes [1] versus molar fraction of Zr. As is immediately apparent, the positive deviation from the straight line (often referred to as Zen's law) appears unusual and to our knowledge unprecedented. In trying to understand the reason to this puzzling behavior we discover that SOC, when combined with DFT + U, has an anomalous influence on the atomic volumes. We illustrated this in Fig. 2 where we display the relative volume expansion due to SOC for the U-Zr alloy system. Once more we find a surprising behavior with a 7% expansion for γ-U that drops to 3.5% with only 6 molar fraction of Zr, while the same property for the standard DFT (VASP-PAW) calculations is always less than 1%. In addition, we compare with our own all-electron results, performed similarly to that in [4], that also suggest that SOC has a very small influence on the volumes. It should be noted that the volume effect of SOC on uranium was found to be very small (1%–2%) 3 decades ago [14] and that this conclusion has never been questioned in the many calculations performed for uranium, until now [1].

Let us now turn our attention to the calculated [1] enthalpy of mixing of the U-Zr alloy system. In Fig. 3 we display the DFT + U ("optimal" $U_{\text{eff}} = 1.24$ eV) with and without SOC together with corresponding standard DFT calculations by Landa *et al.* [16] and three CALPHAD assessments [17–19], all taken from Fig. 5 in Ref. [1]. Notice that the standard DFT calculations [16] agree much better with two of them [17,18]. The third assessment by Xiong *et al.* [19] is numerically closer to the DFT + U than to the DFT [16], but more important, it is always significantly positive in agreement with conventional DFT and DFT + U (no SOC) but in fundamental

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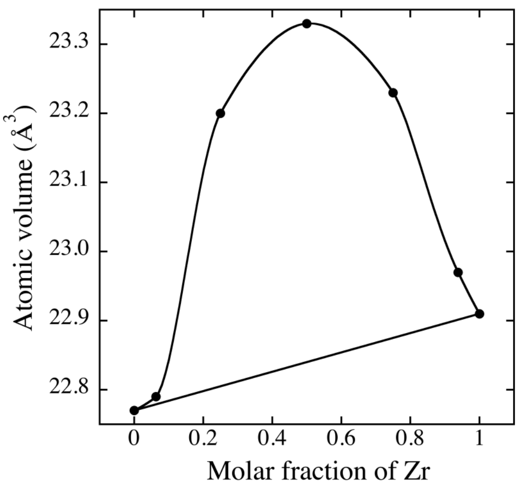

FIG. 1. VASP-PAW results taken from Table IV in Ref. [1] showing the volume dependence on Zr content for the DFT + U + SOC ($U_{\mathrm{eff}} = 1.24$ eV) calculations.

disagreement with DFT + U + SOC theory. The latter model gives *negative* enthalpies for a majority of the mixing which is *inconsistent with the known miscibility gap* for the γ phase in the experimental phase diagram. From Fig. 3 it is clear that this gap could not extend beyond an alloy composition of about 70 at.% Zr, in contradiction to the experimental evidence. We speculate that this discrepancy is the reason that another (much smaller) Hubbard U was applied in a related paper by some of the same authors [19]. It appears [1] that either $U_{\mathrm{eff}} = 0.99$ eV (no SOC) or $U_{\mathrm{eff}} = 0.49$ eV (SOC) was applied for the energetics of the thermodynamics (the value of a U_{eff} was not quoted in [19]) leading to a miscibility gap in the entire composition range as expected from the known phase diagram (Fig. 7 in Ref. [19]). In the case of DFT + U + SOC, the low value, $U_{\mathrm{eff}} = 0.49$ eV, is in stark contrast to the "optimal" $U_{\mathrm{eff}} = 1.24$ eV preferred in Ref. [1].

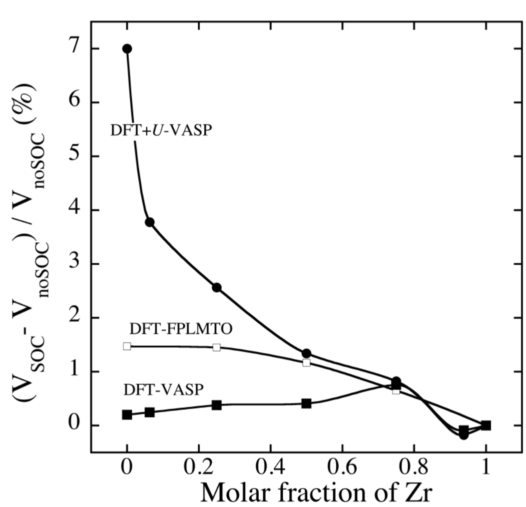

FIG. 2. VASP-PAW results taken from Table IV in Ref. [1] showing the relative volume expansion due to SOC for the DFT + U + SOC ($U_{\mathrm{eff}} = 1.24$ eV) calculations. Results from full-potential linear muffin-tin orbitals (FPLMTO) method all-electron calculations are also shown.

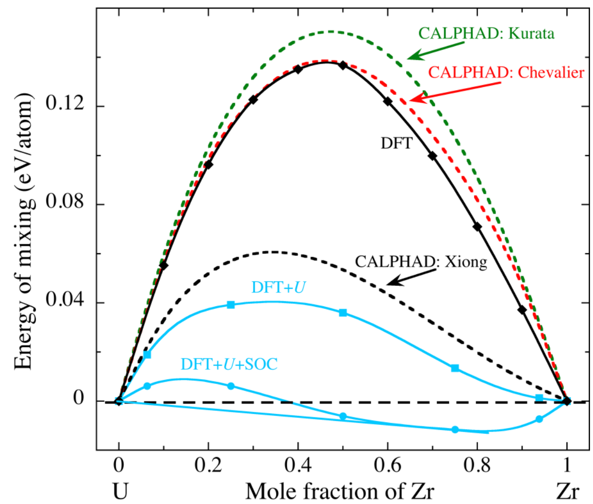

FIG. 3. (Color online) Enthalpy of mixing for three CALPHAD assessments: Chevalier *et al.* [17], Kurata [18], and Xiong *et al.* [19]. The DFT results (solid diamonds) refer to calculations by Landa *et al.* [16]. The DFT + U + SOC and DFT + U ($U_{\mathrm{eff}} = 1.24$ eV) results (solid circles and squares, respectively) are from Xie *et al.* [1]. The straight line attached to the DFT + U + SOC results indicates the bound of the miscibility gap.

The use of greatly different values for U_{eff}, depending on the studied property, implies a parameter-fitting procedure with a model that is incomplete or inappropriate. It should be noted that for the calculation of enthalpy of mixing one has to keep U_{eff} constant over the entire concentration range to maintain a well-defined quantity.

Another provocative aspect of the DFT + U model for uranium metal is that it predicts significant spin and orbital magnetic moments for most phases of uranium and all γ-U-Zr alloys (see Fig. 7 in Ref. [1]). The authors [1] claim that antiparallel spin and orbital contributions nearly cancel and that this is consistent with the known nonmagnetic state of uranium metal. Actually, this type of magnetic cancellation has been discovered in UFe_2 [20] where polarized-neutron measurements decouple the spin and orbital contributions (both are about 0.23 μ_B). If this cancellation phenomenon indeed exists in uranium metal, it would have been known from polarized-neutron experiments.

In summary, we have independently analyzed the results presented in the paper by Xiong *et al.* [1] and come to the conclusion, contrary to its authors, that the DFT + U + SOC model for uranium metal and the U-Zr alloy system is not better but worse than careful all-electron calculations performed within conventional DFT. The DFT + U + SOC theory appears to rather significantly overestimate atomic volumes resulting in a strong deviation from Zen's law that is anomalous. One reason may be that the influence of SOC is greatly exaggerated leading to extreme volume expansions (7% for γ-U, Fig. 1). Another unsettling realization is that not a distinct Hubbard U can be utilized in the DFT + U + SOC scheme for optimal results in terms of energetics of thermodynamics ($U_{\mathrm{eff}} = 0.49$ eV) and atomic volumes ($U_{\mathrm{eff}} = 1.24$ eV). Lastly, the fact that the DFT + U treatment gives rise to magnetism in a nonmagnetic metal (uranium), cast doubts on the appropriateness of this methodology for uranium and the U-Zr alloys. We furthermore expect that similar problems and inconsistencies will occur if the DFT + U technique is applied more generally to other metallic actinide fuel systems.

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