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Letter to the Editor

Electron correlation and relativity of the 5*f* electrons in the U-Zr alloy system

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Abstract

We address a recently communicated conception that spin-orbit interaction and strong electron correlations are important for the metal fuel U-Zr system. Here, we show that (i) relativistic effects only marginally correct the uranium metal equation-of-state and (ii) addition of onsite Coulomb repulsion leads to an unphysical magnetic ground state of the body-centered cubic (γ) phase and a grossly overestimated equilibrium volume. Consequently, LSDA+U is deemed unsuitable for describing the electronic structure of the U-Zr system.

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Recently, Xiong et al. [1] reported on thermodynamic modeling of the U-Zr system motivated by its potential as a nuclear fuel for fast breeder reactors. This work [1] came on the heels of another report by Landa et al. [2] on the same system, but with very different results for the formation enthalpies and ultimate conclusion on the U-Zr phase diagram. The authors [1] argue that their calculated energetics are significantly more accurate than that by Landa et al. [2], and they further attribute the difference to strong electron correlations and the relativistic spin-orbit interaction.

In the present Letter we show that uranium metal, and thus the U-Zr metal nuclear fuel system, possess weakly correlated electrons that are adequately described within density-functional theory in the generalized gradient approximation, and that addition of onsite Coulomb repulsion using the LSDA+U formalism leads to finite magnetization of the γ phase in contradiction to experiments. Furthermore, we show that spin-orbit interaction is quite weak in uranium metal and that its inclusion will not significantly change the chemical bonding and formation enthalpies.

In order to illustrate our arguments, we perform comparative electronic-structure calculations using the full-potential linear augmented plane-wave (FPLAPW) method and the projector augmented plane-wave (PAW) method as implemented in the Wien2K [3] and VASP [4] codes. The Wien2K computations are set up with an APW + lo basis for the expansion of the wave functions within the muffin-tin spheres (with radius $R_{MT} = 2.5$ a.u.) in partial waves with angular momenta up to $l = 3$, and an LAPW basis for all higher angular momenta up to $l = 10$. The plane-wave cutoff (K_{max}) for the expansion of the wave functions in the interstitial region is chosen such that $R_{MT} \times K_{max} = 10$. We apply the LSDA+U scheme proposed by Anisimov et al. [5] (Wien2K) and Dudarev et al. [6] (VASP) to the uranium *f* orbitals, which approximately corrects for their electron self interaction. An effective $U_{eff} = U - J$ is chosen to be 2 eV ($J = 0$), which appears to be realistic for uranium systems [7]. The spin-orbit interaction is included using the second-variation method with scalar-relativistic orbitals as basis. This basis includes all eigenstates with energy less than 70 eV. In order to improve the description of the relativistic orbitals, the $p_{1/2}$ local orbitals are added to the basis set. For actinide metals, this technique for the spin-orbit coupling equals, with good approximation, that of the

complete four-spinor Dirac formalism [8-10]. All calculations use a 12×12×12 Monkhorst-Pack *k*-point grid and a plane-wave cutoff of 23 Ry.

In Table 1 we show our calculated equilibrium volumes (*V*) and bulk moduli (*B*) obtained with and without spin-orbit coupling (SOC) for bcc (γ) uranium metal using the Wien2K (VASP) codes. (The other component, Zr, is a light metal where relativistic effects are not important). The changes in *V* and *B* due to SOC are indeed quite small, consistent with results from previous publications [9, 11], and within the scatter of the experimental data. The reason why the volume expands slightly is that the separation of the $5f_{5/2}$ and $5f_{7/2}$ states, due to spin-orbit coupling, weakens the cohesion of the bonding electrons. The separation is very small, as seen in Figure 1 [11] where we plot the total electronic density-of-states (DOS) for α-U with and without SOC. Most of the difference occurs well above the Fermi level, and this also explains why SOC is more important in the heavier metals Pu and Am [12]. Because of the very small influence of SOC on *V* and *B* for γ-U, one may argue that also the formation enthalpies for the U-Zr system, that substantially depend on these properties, are insensitive to the SOC, contrary to the conclusion by Xiong et al. [1].

Next, we address the issue of strong electron correlation and the need for an LSDA+U type of approach for γ-uranium. Searching through the literature we could not find any publication where the LSDA+U methodology was applied to uranium metal, except that of [1], but for uranium oxides they are plentiful. However, we found that it has been considered for its nearest-neighbor metals Pa [13] and Np [14] (U lies between them in the Periodic Table). These publications suggest that LSDA+U is not necessary for the metals while for their oxides it is relevant, although the methodology itself is phenomenological. Focusing first on the uranium ground state, orthorhombic α-U, equilibrium and structural properties [11], elastic constants [11, 15], phonon spectra [16], various defects [17-19], and even subtle electronic-structure details related to the charge-density waves [20] are all satisfactorily described within conventional DFT. These results clearly imply that LSDA+U is not a relevant or necessary scheme for α-uranium. How about the high-temperature γ phase?

The γ phase is stable at temperatures above 1100 K and it has a significantly larger volume than α-U, see Table 1. One may suspect that this is due to *f*-electron

localization (strong *f*-electron correlation), but it actually stems from normal thermal volume expansion.

In Figure 2 we show the calculated α-U thermal volume expansion, using a parameter-free Debye-Grüneisen quasi-harmonic theory [21, 22]. Also included are experimental data points taken from Donohue [23]. The good agreement with experiment for the linear expansion coefficient (α_L) at room temperature gives us confidence that the quasi-harmonic model is reasonable. The thermal volume expansion shown in the figure further demonstrates (i) that at room temperature α-U has nearly identical volume to Mo-stabilized γ-U (extrapolated to zero Mo content) at the same temperature [23]; and (ii) at about 1100 K the calculated α-U volume is consistent with that measured [23] for the γ phase. Hence, the difference between the α and γ volumes is completely explained by thermal expansion with no need for additional *f*-electron localization. This conclusion is further underscored by a recent study [24] showing that the γ-phase mechanical stabilization is due to phonon-phonon interactions within a weakly correlated picture (DFT) of the electronic structure.

Nevertheless, we apply FPLAPW (PAW) calculations for γ-uranium using the Wien2K (VASP) codes in order to explicitly explore the effects of LSDA+U. The results from the two implementations are in qualitative agreement with each other and summarized in Table 1. They predict a metastable non-magnetic (non spin polarized, NSP) solution, that yield equilibrium *V* and *B* in better agreement with experiment than the spin polarized (SP) solution. The spin polarized LSDA+U ground-state solution (ferromagnetic, spin moment = 2.1 μ_B) has an unrealistically large equilibrium volume of 23 (23.6) $Å^3$/atom, and substantially underestimates the bulk modulus. The total energy difference between the SP and the NSP states, at their respective equilibrium volumes, is a significant 64 (110) meV/atom. The finding of magnetism is contrary to the observed non-magnetic state of uranium metal. We thus conclude that the LSDA+U treatment, while essential for some aspects (i.e., electronic spectra) of the strongly correlated insulating uranium oxide compounds, is detrimental and incorrect for weakly correlated metallic U-Zr alloys.

In conclusion we find that while the calculations by Landa et al. [2] can be mildly modified and improved by spin-orbit interaction, they do not suffer from fundamental

inaccuracies as proposed in [1] and their enthalpy of formation of the bcc structure shall remain realistic.

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Tables

Table 1.

Calculations of the equilibrium atomic volume (V) and bulk modulus (B) of γ-U obtained from the Wien2K and VASP packages. The VASP results are given in parenthesis. For the LSDA+U method both non spin polarized (NSP) and spin polarized (SP) treatments are considered with SP being the calculated ground state. All experimental atomic volumes and the bulk moduli are from Donohue [23] and Yoo et al. [25].

Method	V (Å^3/atom)	B (GPa)
Scalar relativistic	20.3 (20.1)	137 (134)
Spin-orbit interaction	20.6 (20.2)	150 (128)
LDA+U-NSP	21.1 (21.6)	130 (125)
LDA+U-SP	23.0 (23.6)	66 (92)
Experiment	21.2 – 22.1 (γ-U: 1100 K) 20.7 (α-U: 300 K)	113 (γ-U: 1100 K) 135 (α-U: 300 K)

Figures

Figure 1.

Calculated total electronic density of states for α-U with spin-orbit coupling ("SOC"; full line) and not ("scalar"; dashed line), taken from Ref. [11]. Notice essentially no difference between the results below the Fermi level that defines the zero energy.

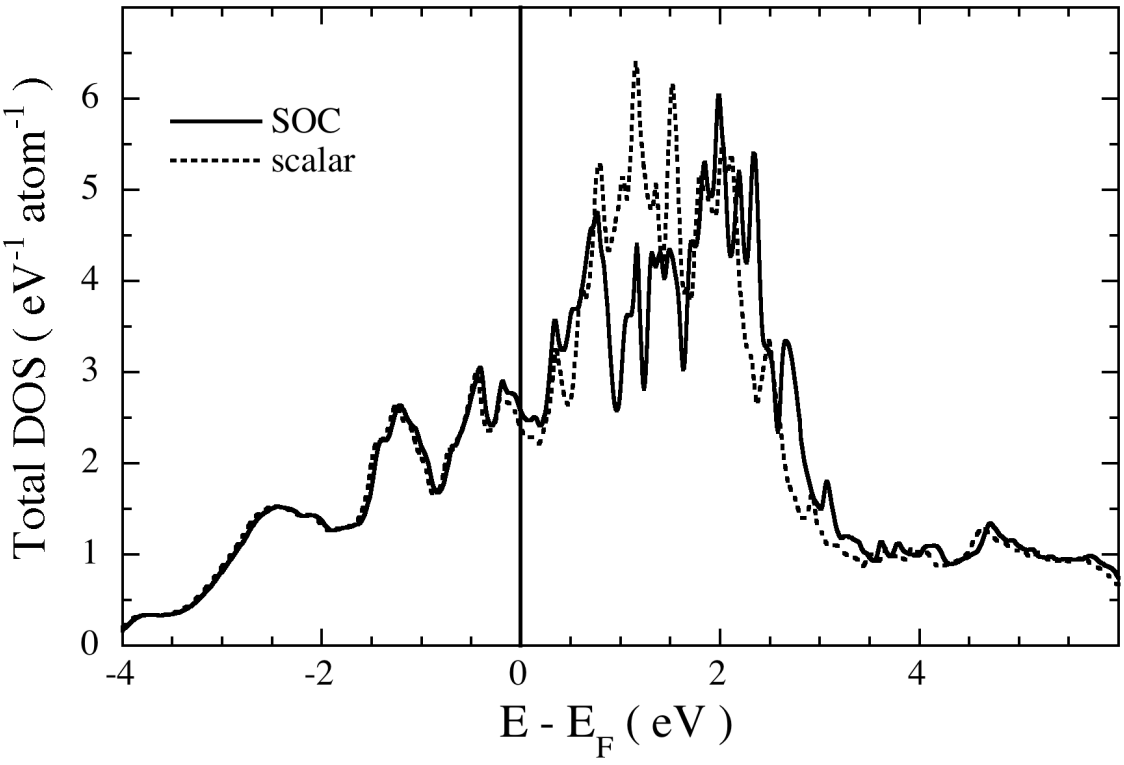

Figure 2.

The α-U atomic volume and linear thermal expansion coefficient (inset), as functions of temperature calculated from Debye-Grüneisen quasi-harmonic theory [21, 22]. Solid symbols show experimental data points. For the atomic volume, all data are for γ-U and from Donohue [23] where the room temperature value is obtained from extrapolation to zero content of Mo in Mo-stabilized γ-U. Room temperature linear coefficient of thermal expansion is for α-U and from Gschneidner [26].