Structural Properties of Lanthanide and Actinide Compounds within the Plane Wave Pseudopotential Approach

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We show that plane wave ultrasoft pseudopotential methods readily extend to the calculation of the structural properties of lanthanide and actinide containing compounds. This is demonstrated through a series of calculations performed on UO, UO_2, UO_3, U_3O_8, UC_2, α-CeC_2, CeB_6, CeSe, CeO_2, NdB_6, TmOI, LaBi, $LaTiO_3$, YbO, and elemental Lu.

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The plane wave pseudopotential approach has developed steadily in applicability. Initially, empirical pseudopotentials were constructed for the so-called "easy" elements such as silicon and aluminum. These potentials were used mainly in the prediction and understanding of electronic band structures and were found to be particularly accurate for semiconductors. With the subsequent development of *ab initio* pseudopotentials and expressions for the accurate calculation of forces and stresses, the plane wave pseudopotential approach has come into its own as the method of choice for the first principles prediction of structural parameters.

A combination of improved computing resources, algorithms, and pseudopotential formalisms has allowed the plane wave pseudopotential technique to be applied to ever "harder" elements, such as, initially, the first row elements (including carbon and oxygen), and later the transition metal elements. In this paper we will show that the pseudopotential formalism due to Vanderbilt [1], in which the norm-conserving constraint is removed in the pseudisation process, allows the steady march through the periodic table to be taken to completion, in that we can reliably calculate structural parameters of compounds containing f electrons. In support of our approach, recent benchmark calculations on atoms by Liu and Dolg [2] find that current density functionals work well for compact $4f$ shells, correcting opposite statements by other authors. A similar conclusion has been reached by Söderlind *et al.* who performed calculations on a series of f-electron metals [3,4] using gradient corrected functionals.

There have been numerous other all-electron, first principles studies of f-electron systems [5–11], but, while accurate and relevant results have been obtained, the vast majority of the structures investigated have been of a small size and high symmetry. Previous attempts to apply the pseudopotential approach [12,13], which is more suitable for large, low-symmetry structures, to the calculation of f-electron systems have lacked one or more of the ingredients described below, in particular this is the first time that ultrasoft pseudopotentials have been used.

The extension of the plane wave pseudopotential method to f-electron systems requires nothing more than a timely combination of already widely used techniques. The plane wave pseudopotential technique is reviewed in Ref. [14]. It is one of the density functional [15] based methods. In this paper we use both the local-density approximation (LDA) parametrization due to Perdew and Zunger [16] and the generalized gradient approximation (GGA) due to Perdew and Wang [17]. Many of the systems treated here are spin polarized, so we use the spin-polarized versions of these functionals unless otherwise stated. Some of the systems are also metallic, and so we use the density mixing scheme described by Kresse and Furthmüller [18] to efficiently reach self-consistency. Within the constraints of the imposed space group symmetry we automatically determine the occupancy and spin state of the ground state. To describe the electron-ion interaction we use the ultrasoft pseudopotentials developed by Vanderbilt and co-workers [2,19], extended so that nonlocal projectors were available up to $l = 3$ allowing f electrons to be accurately described. This requires charge augmentation terms

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up to and including $l = 6$. To obtain good pseudopotentials, so-called "shallow-core" electrons are included as valence electrons (for example, the $5s$ and $5p$ electrons for the lanthanides). In order to optimize the structures it is essential that we calculate the first derivatives of the total energy — the forces and stresses. The expressions required for the case of ultrasoft pseudopotentials have been summarized by Focher and Chiarotti [20]. The first Brillouin zone is sampled using the Monkhorst-Pack scheme [21] so that distances between sampling points are always less than 0.04 $Å^{-1}$ and the largest plane wave cutoff required is about 400 eV. The particular implementation used in this work is CASTEP [22], and the pseudopotentials were taken from the standard database distributed with this code. Its use in the first principles study of inorganic crystals has been recently reviewed by Milman *et al.* [23]. No attempt is made to model the spin-orbit terms that are thought to be large in these systems.

In order to build confidence in this approach we have chosen a spectrum of test compounds, ranging from uranium and cerium oxides to elemental lutetium metal. This includes examples of both metals and insulators, lanthanides and actinides, and open- and closed-shell systems.

By far the most economically important uranium-bearing mineral is uraninite [24], UO_2, which crystallizes in the fluorite-type structure with space group $Fm\bar{3}m$. It has a lattice constant of $a_{\text{exp}} \approx 5.458$ Å, depending on the degree of partial oxidation of U^{4+} to U^{6+} [25]. The calculated value for the ideal structure is $a_{\text{theo}} = 5.474$ Å, and is thus in good agreement with experiment. While this Letter focuses on structural properties it is interesting to note that density-functional theory (DFT) predicts UO_2 to be metallic, while it is in fact an insulator. This confirms the common view that the electronic properties of lanthanide- and actinide-containing compounds require a treatment beyond DFT.

A useful uranium pseudopotential must also be able to describe other oxidation states, such as U^{2+} and U^{6+}. For cubic UO, the experimental lattice parameter is 4.92(2) Å [25], while the calculated value is 4.961 Å, again in good agreement. Several polymorphs of UO_3 are known, and they are interesting from a crystallographic point of view. The experimentally determined and computed structural parameters of three structurally different polymorphs are given in Table I. With one exception, namely, the free oxygen coordinate in the hexagonal polymorph, all structural parameters are in good agreement with experimental values. We believe that our theoretical value for $O(z)$ in the hexagonal polymorph is likely to be more reliable than the experimentally determined value, as the latter has been derived from estimated film intensities [26].

A more subtle test is the modeling of a mixed-valence compound, such as U_3O_8. For a hexagonal polymorph with space group symmetry $P\bar{6}m2$ we obtain $a_{\text{theo}} = 6.829$ Å and $c_{\text{theo}} = 4.145$ Å, which agrees well with the corresponding experimental parameters of $a_{\text{exp}} = 6.817$ Å and $c_{\text{exp}} = 4.145$ Å [27]. This structure has three internal degrees of freedom, with experimental values $U(x) = 0.3526$, $O1(x) = 0.7453$, and $O2(x) = 0.3609$. The corresponding values of the relaxed structure are 0.35057, 0.74799, and 0.35893, respectively. In summary, the structures of the uranium oxides are very well reproduced, irrespective of the oxidation state of uranium. This implies that we might expect to be able to reliably model other uranium compounds. Indeed, this is found to be true for UC_2 (see Table III below).

To show that it is not just equilibrium properties which are reliably reproduced, the elastic constants of one of the uranium oxides, UO_2, were also calculated using the method of imposed strains. The results are given in Table II, and are consistent with those expected for the density-functional theory approach in general [28] and with previous all-electron studies [29,30].

TABLE I. Polymorphs of UO_3. A (–) indicates that the parameter is fixed by symmetry.

Space group	$Pm\bar{3}m$[a]			$P\bar{3}m1$[b]			$P2_12_12_1$[c]	
a [Å] expt.	4.165(8)			3.971			7.511(9)	
a [Å] theory	4.152			3.804			7.585	
b [Å] expt.	–			–			5.466(8)	
b [Å] theory	–			–			5.516	
c [Å] expt.	–			4.168			5.224(8)	
c [Å] theory	–			4.136			5.274	
$U(x,y,z)$ expt.	0	0	0	0	0	0	0.0699	0.1329	0.0350
$U(x,y,z)$ theory	–	–	–	–	–	–	0.0672	0.1167	0.0410
$O1(x,y,z)$ expt.	$\frac{1}{2}$	0	0	0	0	$\frac{1}{2}$	0.4947	0.1263	0.3284
$O1(x,y,z)$ theory	–	–	–	–	–	–	0.4945	0.1351	0.3203
$O2(x,y,z)$ expt.				$\frac{1}{3}$	$\frac{2}{3}$	0.17	0.1604	0.3872	0.2124
$O2(x,y,z)$ theory				–	–	0.1087	0.1530	0.3810	0.2220
$O3(x,y,z)$ expt.							0.6735	0.6176	0.6654
$O3(x,y,z)$ theory							0.6777	0.6267	0.6634

[a]Expt. data from [37].
[b]Expt. data from [26].
[c]Expt. data from [38].

TABLE II. The elastic constants (in GPa) of UO_2, where $C' = \frac{1}{2}(C_{11} - C_{12})$, $B = \frac{2}{3}(C_{11} + 2C_{12})$.

	C_{11}	C_{12}	C_{44}	C'	B
expt. [39]	389.3	118.7	59.7	135.3	208.9
calc.	318.2	96.0	43.1	111.1	170.1

We calculated the ground state structures of α-CeC_2, CeB_6, CeSe, and CeO_2. α-CeC_2 crystallizes in space group $I4/mmm$. The structure was determined by Atoji [31], and the experimental and theoretical data are compared in Table III. The structure of CeB_6 has space group $Pm\bar{3}m$ and one free internal structural parameter, determining the position of the boron atoms. A comparison of experimental and theoretical data is presented in Table IV. Svane *et al.* [11] found that within the SIC-LSD approach it is necessary to "localize" a single f electron per Ce atom to obtain good structural parameters for CeSe in the rock-salt structure. In contrast, our calculations using a spin-polarized GGA require no special treatment of individual electronic states. The experimental lattice parameter is 5.990 Å [32] while we calculated a value of 6.043 Å. In CeO_2 all atomic positions are fully constrained by the space group symmetry. The experimentally determined lattice parameter of this cubic structure with space group $Fm\bar{3}m$ is 5.411 Å [33], while the geometry-optimized structure had a lattice parameter of 5.421 Å. For all of these cerium compounds, the pseudopotential approach agrees closely with experiment.

The accuracy of this approach is sufficient to resolve the difference in the unit cell volumes for the $Fm\bar{3}m$ structures of CeO_2 and UO_2. Experimentally the lattice parameter of CeO_2 is about 1.1% smaller than that of UO_2, while a comparison of the theoretical values gives 1.0%. However, smaller differences are not resolved. For example, NdB_6 (Table IV) experimentally has a lattice parameter about 0.2-0.3% smaller than that of CeB_6, while our calculations indicate that it should be about 0.9% larger. This is the limit of reliability of the GGA-DFT structures, whether or not f electrons are present.

That equally accurate results can also be obtained for systems with many f electrons is demonstrated by our calculations on cubic YbO, which crystallizes in space group $Fm\bar{3}m$ with $a_{\text{exp}} = 4.86$ Å [34], while the pseudopotential calculations gives $a_{\text{theo}} = 4.8405$ Å. The structure of a thulium-containing compound, TmOI, given in Table V, is also well reproduced.

We performed calculations on the closed f-shell lutetium metal with similarly good results. The experimental [35] a/c ratio for the hexagonally close packed structure is 0.630 and the unit cell volume, V_0, is 59.80 Å^3. The corresponding LDA results are a/c = 0.640, $V_0 = 53.373$ Å^3 and the GGA ones are a/c = 0.638, $V_0 = 59.014$ Å^3. The gradient corrected functional is shown to be essential for close agreement to experiment.

For the sake of completeness, we have also checked some lanthanum-bearing compounds. Cubic LaBi has $a_{\text{exp}} = 6.57$ Å [34], the theoretical value is $a_{\text{theo}} = 6.648$ Å. For the orthorhombic low-temperature study of $LaTiO_3$ the calculated structure is in similarly good agreement with the experimental values (Table VI).

In this Letter we have shown that the structural properties of lanthanide- and actinide-containing systems can be investigated on the same footing as the rest of the periodic table using density-functional theory, ultrasoft pseudopotentials, and a modest number of plane waves. As a result of the inherent efficiency of the plane wave methods, the theoretical study of complex, low-symmetry lanthanide- and actinide-containing compounds becomes possible. This is a significant advance compared to previous all-electron approaches which, while accurate, are less efficient computationally. The ability to accurately calculate forces and stresses allows efficient structural optimization. We confirm that the LDA is not always sufficient to describe the exchange and correlation energies, but that the use of the GGA produces results as good as those found for

TABLE III. Comparison of the experimentally determined structural parameters of α-CeC_2 and UC_2 to the corresponding theoretical values.

	CeC_2[a]		UC_2[b]	
	Expt.	Theory	Expt.	Theory
a [Å]	3.875	3.906	3.509–3.522	3.524
c [Å]	6.477	6.486	5.980–5.988	5.946
C(x)	0.401	0.401	0.388–0.4	0.3860
d(C-C) [Å]	1.281	1.280	1.321	1.312
d[(Ce, U)-C] [Å]	2.598	2.603	2.334	2.317
d[(Ce, U)-C] [Å]	2.814	2.835	2.577	2.577

[a]Expt. data from [31].
[b]Expt. data from [25,40,41].

TABLE IV. Comparison of the experimentally determined structural parameters of CeB_6 and NdB_6 to the corresponding theoretical values. Ce and Nd are chosen to occupy the Wyckoff position 1(b), which implies that the carbon atoms are on position 6f.

	CeB_6[a]		NdB_6[b]	
	Expt.	Theory	Expt.	Theory
a [Å]	4.140	4.098	4.127	4.136
B(z)	0.1992	0.200	0.1989	0.2023
d(B-B) [Å]	1.76	1.737	1.755	1.741
d[(Ce, Nd)-B] [Å]	3.04	3.012	3.032	3.042

[a]Expt. data from [42,43].
[b]Expt. data from [44].

TABLE V. Comparison of the experimentally determined and calculated structure of TmOI.

	Expt.[a]	Theory
a [Å]	3.887	3.917
c [Å]	9.166	9.175
I(z)	0.68	0.6751
O(z)	0.125	0.1167

[a]Expt. data from [45].

TABLE VI. Comparison of the experimentally determined low temperature (10 K) and calculated structure of orthorhombic $LaTiO_3$.

	Expt.[a]	Theory
a [Å]	5.630	5.602
b [Å]	5.584	5.712
c [Å]	7.901	7.899
La(x)	0.99269	0.98626
La(y)	0.04705	0.04399
O1(x)	0.07902	0.07262
O1(y)	0.49339	0.48587
O2(x)	0.70941	0.71763
O2(y)	0.29237	0.28028
O2(z)	0.04204	0.03882

[a]Expt. data from [46].

the rest of the periodic table. In the systems that we studied, the spin-orbit interaction apparently had little influence on the structural properties, leading us to speculate that this term is strongly atomic in nature, and that changes with geometry are insignificant at the level of accuracy obtainable with current DFT based methods. However, Söderlind [36] suggests that relativistic effects must be included for accurate structural energies of the heavier actinides. In light of this study we expect that the pseudopotential approach will increasingly complement the computationally more costly approaches currently in use for the theoretical structural study of lanthanide- and actinide-containing compounds.

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