PHYSICAL REVIEW B **66**, 085113 (2002)

First-principles elastic and structural properties of uranium metal

Per Söderlind
Department of Physics, Lawrence Livermore National Laboratory, Livermore, California 94550

(Received 22 April 2002; published 16 August 2002)

Density-functional electronic structure calculations have been used to investigate the ambient pressure and low-temperature structural and elastic properties of uranium metal. The equilibrium volume and bulk modulus have been calculated within the generalized gradient approximation (GGA). Also, the effect of the relativistic spin-orbit interaction on these properties has been investigated. Calculated structural properties of α-U compare very favorably with experimental data. The nine elastic constants of this ground-state orthorhombic phase have also been calculated, and compare reasonably well with experimental data, especially when experimental data are extrapolated to zero temperature. The results of the present investigation suggest that density-functional theory, in its GGA formulation, accurately describe the electronic structure of uranium, and possible correlation effects are well accounted for within this theory.

DOI: 10.1103/PhysRevB.66.085113 PACS number(s): 62.20.Dc, 71.20.−b, 71.15.Mb

I. INTRODUCTION

Uranium, being the heaviest naturally occurring element, has received a lot of attention for its nuclear properties and the nuclear energy that can be harvested. Less discussed are the properties of uranium metal which are largely determined by its electrons surrounding the nuclei in the solid. Interesting properties of uranium include low temperature charge-density waves (CDW) transitions,[1] anisotropic thermal expansion,[2] and a relatively complex crystal structure (orthorhombic).[3] The behavior of U at elevated pressure and temperature was recently studied experimentally,[4,5] and it was shown that the α phase is stable up to at least 1 Mbar at ambient temperature with a bcc phase developing[5] at higher temperatures. Modern reviews of the physical properties of uranium were given by Fisher[6] and Lander. *et al.*[7]

Theoretically, U is best treated with methods that are free from geometrical approximations (full potential) because of its open and distorted crystal structure. Density-functional and full-potential calculations a decade ago were able to reproduce the correct ground-state structure of U, using the local density approximation (LDA), but the equilibrium volume was not very well described.[8] A few years later the LDA was replaced by a generalized gradient approximation (GGA) treatment of the electron exchange/correlation, and now the equilibrium volume was in much better agreement with experiment.[9] Since then, several theoretical investigations of the equilibrium volumes in the actinides have been published, and a summary was given in the paper by Jones *et al.*[10]

As regards details of the crystal structure, Akella *et al.*[4] measured the axial ratios of α-U as a function of pressure and compared with first-principles theory. Of the two axial ratios, the c/a ratio was more sensitive to pressure and the theory accurately reproduced the experimental finding of a pressure induced increase of the c/a axial ratio. Later, the same theoretical technique was used to study the CDW in uranium,[1] which was shown to be driven by nesting features of the Fermi surface. The above theoretical results were all obtained from all electron full-potential methods, but more recently the structure of U was investigated by a plane-wave pseudopotential technique.[11] This latter theory, however, was neither successful in reproducing details of the experimental crystal structure nor equilibrium properties of U.

The electronic structure of uranium is dominated by $5f$ electron states which form bands that are very narrow and tend to bond the atoms in complex and distorted ways.[12] The combination of narrow $5f$ states and an open and distorted crystal structure make a theoretical treatment nontrivial. The problem is further made difficult by the increased importance of relativistic effects that arise for such a heavy material. In the following we apply an accurate electronic structure method, previously shown to be able to treat ground-state properties of the light actinides,[13] to carefully study the crystal structure of uranium. Moreover, we will calculate the nine independent elastic constants of α-U with this technique. With the exception of Th,[14] which has a simple face-centered-cubic (fcc) structure, elastic constants for an actinide metal have never been calculated from first principles, to our knowledge. The determination of elastic constants is important because these contain detailed information about the chemical bond and provide a very sensitive test of the theory.

In Sec. II we describe technical details of our method, including typical setup parameters for the calculations. This is followed by Sec. III, which deals with optimizing the structure of uranium. In Sec. IV we report our elastic constants for α-U and compare with experimental data. Finally, in Sec. V, a comparison with previous theories is made, and sources of errors in the computational approach and future prospects will be discussed. A detailed description of the elastic-constant calculation is provided in the Appendix.

II. COMPUTATIONAL DETAILS

The total energy is calculated for uranium with the crystal structure, lattice constant, and the atomic number as the only inputs. By varying the internal parameters (b/a, c/a, and y) as well as the lattice constant a, we can fully relax the crystal structure. For this relaxed geometry very small strains ($<1\%$) were applied so that the elastic constants could be extracted using relevant equations that, for completeness, are included in the Appendix. About 4–6 magnitudes of strains were used for every elastic constant, and a third degree polynomial was fitted to the corresponding energies so that the harmonic coefficient could be obtained. In most cases no geometrical relaxations during the deformations were allowed, but test calculations suggested that this effect on the elastic constants is rather small.

For these calculations we used the full potential version of the linear muffin-tin orbital (FP-LMTO) method.[15] This electronic structure method is an implementation of density-functional theory as applied for a bulk material. It is a first-principle method, no experimental numbers are used in the calculations except for the nuclear charge which is 92 for U. The errors in this approach are limited to the approximation of the exchange/correlation energy functional, cut offs in the expansion of basis functions, *k*-point sampling in integrations over the Brillouin zone, and the Born-Oppenheimer approximation. For the exchange/correlation approximation we used the GGA,[16] which has proven to be better for *f*-electron metals[9] than the more commonly used LDA. Spin-orbit coupling was included and implemented in a first-order variational procedure[17] for the valence *d* and *f* states. For the core states a fully relativistic Dirac equation was solved.

The use of full nonsphericity of the charge density and one-electron potential is essential for accurate total energies and in particular when elastic constants are calculated. This is accomplished in our method by expanding the charge density and potential in cubic harmonics inside nonoverlapping muffin-tin spheres and in a Fourier series in the interstitial region. In all calculations we used two energy tails associated with each basis orbital and for $6s$ and $6p$ and the valence states ($7s$, $7p$, $6d$, and $5f$) these pairs were different. With this "double basis" approach we used a total of six energy tail parameters and a total of 12 basis functions per atom. Spherical harmonic expansions were carried out through $l_{max}=6$ for the bases, potential, and charge density. The sampling of the irreducible Brillouin zone was done using the special *k*-point method[18] and the number of *k* points used were about 200–600 for the elastic constants and 54–128 for the crystal-structure relaxations. To each energy eigenvalue a Gaussian was associated with 20 mRy width to speed up convergency. In some cases we used the LDA for comparisons, and the chosen parametrization was that of von Barth and Hedin.[19]

III. CRYSTAL STRUCTURE

Uranium at low temperature up to at least 1 Mbar[4] is stable in a face-centered-orthorhombic ($Cmcm$) structure (see Fig. 1) that can be described with two atoms per cell. This α-U structure is a fingerprint of *f*-band involvement in the chemical bond,[20] and has also been seen experimentally in the phase diagram of the $4f$ metals Ce, Pr, and Nd, and theoretically in the $5f$ metal Pa.[21] This structure can be related to both the body-centered-cubic (bcc) and the hexagonally close-packed (hcp) structures through a Burgers-like transformation.[22]

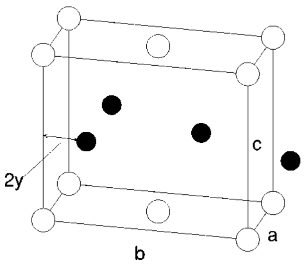

FIG. 1. The α-U crystal structure (Ref. 3). This is a face-centered orthorhombic unit cell ($Cmcm$) with nonequal *a*, *b*, and *c*.

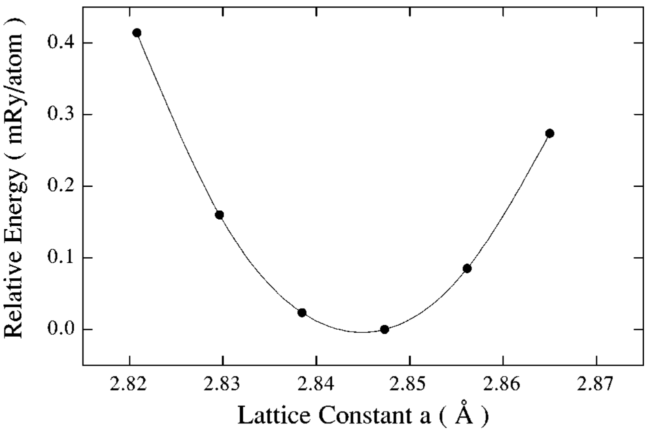

FIG. 2. Calculated energy dependence of the lattice constant *a* of α-U. Here the solid line is only to guide the eye. For this variation, b/a and c/a are kept constant and equal to 2.045 and 1.756, respectively.

Before calculating the elastic constants of α-U, which is the main purpose of this paper, we try and determine the fully relaxed structure and density of the metal. The total energy was calculated while varying a, b/a, c/a, and y in search for the absolute ground-state energy minimum. With the experimental room temperature data as a starting point, these four parameters were varied independently one at a time. When all four were optimized in a first iteration we repeated the procedure iteratively until a convergence criteria of about 10^{-3} was fulfilled. Figures 2, 3, and 4 show the energy as a function of a, b/a, and c/a, close to their respective equilibrium values (2.845 Å, 2.045, and 1.756). Note that the energies vary smoothly even for very small changes

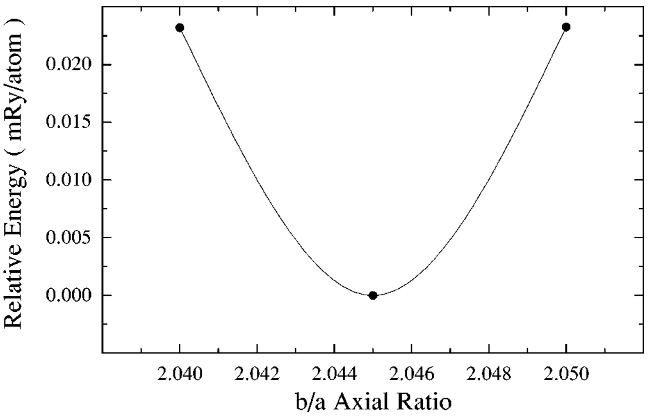

FIG. 3. Calculated energy dependence of the b/a axial ratio of α-U. Here the solid line is to guide the eye. For this variation, c/a (1.756) and the atomic volume (20.67 Å^3) are kept constant.

in the lattice parameters which is essential when determining their equilibrium values to the third decimal. It should be noted here that variations of b/a and c/a (Figs. 3 and 4) were performed for a constant atomic volume (20.67 Å^3). The data from these figures are comprised in Table I together with those from experiment. The experimental[23] axial ratios, and also y, show a linear decrease with decreasing temperature over a wide range from at least 180 K down to the first CDW transition in the vicinity of 40 K. To best compare with our zero temperature calculations, the experimental a, b, c, and y in Table I are measured[23] at a temperature just above the CDW transition (an extrapolation to 0 K yields essentially the same results). The bulk modulus (B) and its pressure derivative (B'), however, are measured at room temperature.[5]

The agreement with experiment for all calculated properties in Table I is impressive. With the exception of B', which is very dependent upon the equation-of-state fitting procedure, theory, and experiment are within about 1% of each other. For a comparison, full-potential scalar relativistic GGA calculations of the $4d$ and $5d$ transition metals yield atomic equilibrium volumes that are in about 2% root-mean-square error compared to room temperature experiment.[24]

IV. ELASTIC CONSTANTS

About a decade ago, accurate calculations of elastic constants of metals were reported,[8] which were done for nonmagnetic and cubic transition metals. Later, these studies were extended to include hexagonal transition metals[25] and more recently, elastic constants of complex orthorhombic systems were reported.[26,27] To date, no theoretical elastic constants of an actinide metal, with the exception of fcc Th (Ref. 14) and fcc (δ) Pu,[28] can be found in the literature. Here we present calculations for nine independent elastic constants for α-U. The calculations were performed for the relaxed phase as described in Sec. III. In general, no further relaxation was allowed in conjunction with the distortions used in calculating the elastic constants and the procedure follows closely that of Ravindran *et al.*,[26] but for completeness the relevant equations are included in the Appendix.

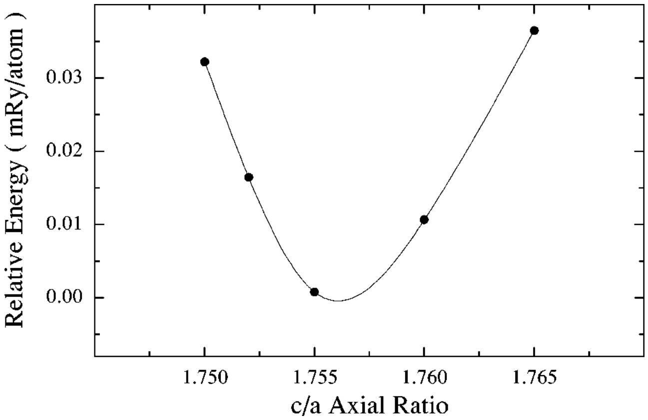

FIG. 4. Calculated energy dependence of the c/a axial ratio of α-U. Here the solid line is to guide the eye. For this variation, b/a (2.045) and the atomic volume (20.67 Å^3) are kept constant.

TABLE I. Ground-state properties of α-U from FP-LMTO. Volume and lattice constants are in units of Å and the bulk modulus in kbar. Experimental lattice constants (Ref. 23) measured at about 40 K, and B and B' are measured (Ref. 5) at room temperature.

	Atomic volume	a	b	c	y	B	B'
Theory	20.67	2.845	5.818	4.996	0.1025	1330	5.4
Experiment	20.52	2.836	5.866	4.935	0.1017	1355	3.8

In Table II we summarize our theoretical elastic constants and compare with experimental data. In this table, D_i are the deformations corresponding to the same column elastic constant (or linear combination thereof) which are described explicitly in the Appendix. The experimental data denoted "Experiment" in the table are room temperature data from Fisher and McSkimin.[29] These same authors studied the temperature dependence of c_{ii} a few years later,[30] and these data were also reviewed by Lander *et al.*[7] The temperature dependence of the elastic constants of uranium is rather strong, and with the exception of c_{11} which is nearly constant, c_{ii} increases linearly with decreasing temperature from about 100 K approaching the CDW transitions at about 50 K. To best compare our theoretical zero-temperature data with experiment we can easily do a linear extrapolation of c_{ii} from 100 K to zero, and the data obtained are denoted "Expt: $T=0$" in Table II. For the c_{ij} no such temperature variation has been measured and no extrapolation was therefore attempted. Focusing first on the c_{ii}, theoretical data overestimate the room temperature experimental data with an average amount of about 27% with the worst case being c_{11} that is almost 43% too large in the calculations. When extrapolating experimental data to zero K the average 27% error is decreased to about 15%. To give a perspective to this result, calculations for fcc Th (with three elastic constants c_{11}, c_{12}, and c_{44}) resulted in an average error of about 20% compared to experiment.[14] c_{ij} are extracted from linear combinations of elastic constants, and their relative error could be much larger because small relative errors of these linear combinations could propagate to large relative errors for the c_{ij}. This is clearly the case for the small shear constant c_{13}, see Table II. c_{12} and c_{23}, however, are in surprisingly good agreement with experimental room-temperature data.

The bulk modulus is of course also an elastic constant, and corresponds to an isotropic change in volume and involve radial but no angular distortions. Hence the energy versus volume relation can be used to directly calculate B. This was done in Sec. III by fitting the total energies of α-U versus volume to a Murnaghan form.[31] In practice, a very small volume interval was utilized for this purpose ($\pm 3\%$ of the equilibrium volume) and the obtained value is given in Table I as 1.33 Mbar. The bulk modulus could, however, also be expressed in terms of the elastic constants,[27] and in this case

$$B=\tfrac{1}{9}(c_{11}+c_{22}+c_{33}+2c_{12}+2c_{13}+2c_{23}). \qquad (1)$$

TABLE II. Elastic constants (Mbar) for α-U. No relaxation effects were accounted for in the theory, except for the D_8 deformation (see main text). D_7, D_8, and D_9 correspond to linear combinations of elastic constants; see Eqs. (A13), (A14), and (A15). Experimental data (Ref. 29) are measured at room temperature and "Expt: $T=0$" refers to data obtained from a linear extrapolation of experimental (Ref. 30) elastic constants to $T=0$ K (see the main text).

	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9			
	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}				c_{12}	c_{13}	c_{23}
Theory	3.0	2.2	3.2	1.5	0.93	1.2	4.2	6.1	3.1	0.50	0.05	1.1
Experiment	2.15	1.99	2.67	1.24	0.734	0.743	3.20	4.38	2.51	0.465	0.218	1.08
Expt: $T=0$	2.10	2.15	2.97	1.45	0.945	0.871						

Using the theoretical data of Table II the calculated B is equal to 1.3 Mbar, which is clearly consistent with the 1.33 Mbar obtained from the Murnaghan fit. Experimentally, the room temperature bulk modulus evaluated from Eq. (1) is equal to 1.15 Mbar, which is about 15% smaller than that reported by Yoo *et al.*[5] (1.355 Mbar). This discrepancy between the experimental reports of B is large and the reason is not known, but it could indicate that the older measurements underestimate elastic constants somewhat and this could possibly explain some of the difference between the present theory and experiment.[29,30]

V. DISCUSSION

As mentioned in Sec. I α-U is expected to be difficult to treat accurately in any first-principles theory. Here, we have used a full-potential technique to be able to study the relatively open and distorted structure of α-U and also converge total energies sensitive to small distortions in evaluating the elastic constants. All relativistic terms are accounted for, and the GGA is utilized for the exchange/correlation effects of the electrons. In order to give some guidance to other, less accurate, numerical treatments of α-U we perform calculations with the spin-orbit coupling switched off. Furthermore, the effect of gradient corrections to the electron exchange/correlation is tested on some key properties of α-U.

In Fig. 5 the calculated total electronic density of states (DOS) is plotted, with and without spin-orbit interaction (SO) for α-U. The dotted line represent the more approximate scalar relativistic calculation (scalar) that exclude spin-orbit effects. Note that above the Fermi level, showing the unoccupied states, there is a substantial difference between the two calculations whereas at or below the Fermi level the DOS's are very similar. Hence the effect of spin-orbit coupling on the total energy should be small for α-U. Figure 5 seems to suggest, however, that for a larger $5f$ band occupation, such as in Np or Pu, the SO effect could be of greater importance. The SO effect on the equilibrium volume and bulk modulus of α-U is very small. In Fig. 6 the total energy versus volume is plotted for α-U and bcc U with (SO) and without (scalar) spin-orbit coupling. For both structures, the SO expands the atomic equilibrium volume but no more than 2%. The calculated bulk modulus is correspondingly lower but not by much (4% for bcc U and 8% for α-U). The SO energy difference between α-U and bcc U is about 16.4 mRy/atom, which increases to about 17.3 mRy/atom for the scalar relativistic calculation. For reference, we also calculated fcc, hcp (ideal c/a), and bct ($c/a=0.825$) uranium total energies, and their difference relative to α-U are summarized in Table III. The bcc and the bct energies are of

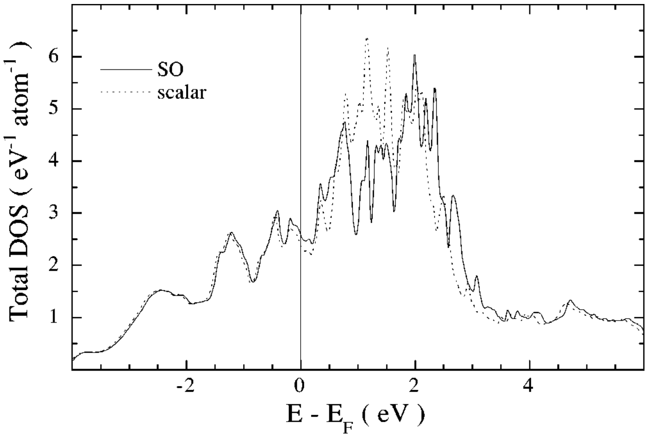

FIG. 5. Total electronic density of states for α-U at the theoretical equilibrium atomic volume 20.67 Å^3. The full line represents a calculation that includes spin-orbit coupling (SO), and the dashed line a calculation without spin-orbit coupling (scalar). The energies are shifted so that the Fermi level is equal to zero.

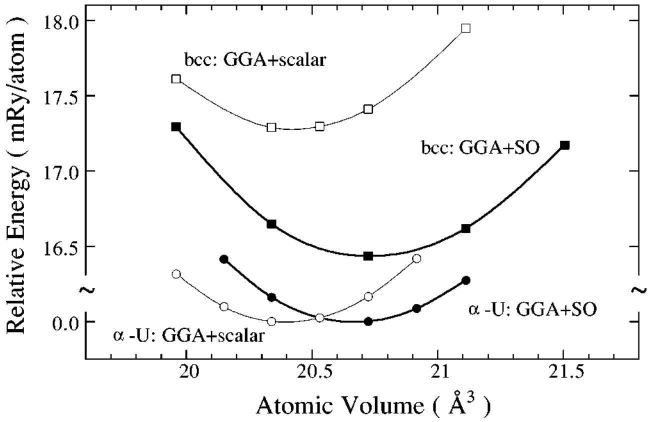

FIG. 6. Relative energies for α-U and bcc U, from calculations including spin-orbit coupling (SO) and without spin-orbit (scalar). The α-U energies are shifted so that the minium energy is equal to zero for both the SO and scalar calculation.

TABLE III. Total-energy differences (mRy/atom) for bcc, fcc, hcp (ideal c/a), and bct ($c/a=0.825$) uranium, relative to α-U. Present results are obtained from FP-LMTO within the GGA, with (SO) and without (scalar) spin-orbit coupling included. PP results (Ref. 11) were calculated within the LDA and no spin-orbit coupling.

Theory	E_{bcc}-E_α	E_{fcc}-E_α	E_{hcp}-E_α	E_{bct}-E_α
FP-LMTO SO	16.4	19.1	17.7	6.8
FP-LMTO scalar	17.3	24.7	21.1	7.8
PP	11.5	15.9		

particular interest because these phases have been predicted at high compression of uranium.[13]

Recently a pseudopotential (PP) approach was used[11] to study point defects in uranium dioxide. The obvious drawback with this treatment is the uncertainty in accuracy of the pseudopotential itself. Their[11] calculations also suffered from neglecting spin-orbit coupling and more importantly gradient corrections to the electron exchange/correlation functional. It is well known that for transition metals, and *f*-electron metals in particular, the LDA severely overestimates the chemical bond, and consequently the PP calculation gave an atomic volume for α-U that was about 8% smaller (18.98 Å^3) and a bulk modulus about 39% larger (1.88 Mbar) than the experimental data. These discrepancies are consistent with the use of the LDA and could most likely be improved by replacing the LDA with the GGA. In the PP study[11] the lattice parameters of α-U were optimized as well, and were $b/a=1.939$, $c/a=1.767$, and $y=0.107$. These data should be compared to the experimental data and the present theory in Table I. The PP calculations of c/a and y are consistent with experiment (1.74 and 0.1017) and present theory (1.756 and 0.1025). b/a, however, is in remarkable disagreement with experiment (2.068) and our FP-LMTO result (2.045). The cause for this could be the use of the LDA, or the neglect of spin-orbit coupling, or possibly a less than accurate pseudopotential. The two former approximations can easily be tested with our FP-LMTO code, and the result of this test is given in Fig. 7. Here the total energy of α-U was calculated as a function of b/a for the four permutations of GGA, LDA, SO, and scalar. For this test calculation, c/a, y, and the volume were kept fixed to their experimental values. As is clear from this figure, b/a is rather insensitive to the approximations with all values within less than 1%. To further test the results of the PP calculations, we calculated the b/a with the volume, c/a, and y given by the PP treatment. Our FP-LMTO approach then produced a b/a value equal to 2.05 which should be compared to the 1.939 PP result. Here we made an effort to make our all electron computation as similar as possible to the PP calculation, i.e., the LDA was used and no spin-orbit coupling. Still, the difference in b/a is almost 6% between FP-LMTO and PP methods, and our conclusion must be that the pseudopotential used[11] is not accurate enough to correctly reproduce the all-electron (FP-LMTO) results or experiment for the crystal structure of uranium. Also, the PP energy difference between α-U and bcc U is about 11.5 mRy/atom,[11] which is in poor agreement with our result of about 17 mRy/atom; see Table III.

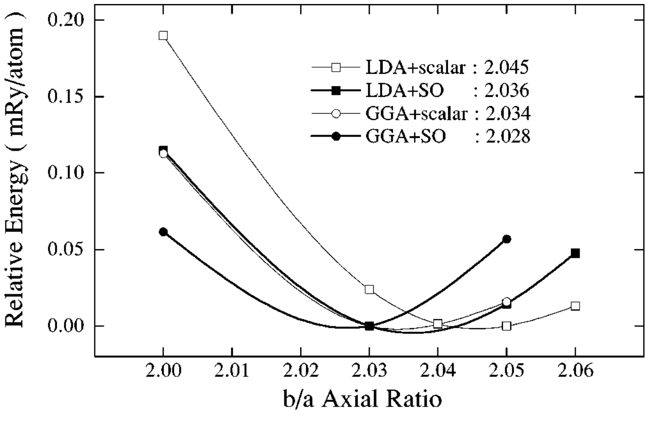

FIG. 7. Relative energies as a function of b/a axial ratio for four sets of calculations as marked in the figure. The optimized b/a value is given next to the legend.

The main purpose of the paper by Crocombette *et al.*[11] was to study point defects in uranium dioxide, and therefore it could be of interest also to compare the present technique with theirs for UO_2. This is a traditional Mott insulator which is antiferromagnetic with a bandgap at the Fermi level. The present GGA calculations do not reproduce either of these properties but predict UO_2 to be a ferromagnetic metal, a finding that is consistent with previous density-functional studies as well as that of Crocombette *et al.* The present theory predicts a lattice constant $a=5.46$ Å which should be compared to $a=5.24$ Å from Crocombette *et al.* and the experimental value $a=5.47$ Å. The present bulk modulus (1.7 Mbar) is somewhat soft compared to experiment (2.07 Mbar), whereas the bulk modulus of Crocombette *et al.* (2.52 Mbar) is too stiff.

Next we discuss the elastic-constant calculation. Overall, the agreement with experiment is good in light of the expected density-functional error for elastic constants of metals. This is especially true when the experimental data are extrapolated to zero temperature. Upon closer inspection, c_{13} is very small, and in relative terms in poor agreement with room-temperature data. Some of this error could likely be decreased if temperature effects could be accounted for, but the main problem with c_{13} is an unfavorable error propagation in the evaluation of this elastic constant. The distortion used to extract c_{13} is D_8 (see the Appendix), which involves a linear combination of elastic constants that is about 20 times larger than c_{13} itself. Consequently, a relative error associated with D_8 is increased by 20 times for c_{13} due to the way the error propagates. For c_{ii} this is not a problem because they are directly evaluated from the deformations D_i.

Note in Table II that all distortions (D_i) give rise to theoretical elastic constants (or linear combinations thereof) that are *larger* than experimental data. This is actually expected because no relaxations of the structure have been allowed during the distortions. Relaxation effects could only cause the distorted system to lower its energy and therefore lower the elastic constant. Unfortunately, with the present technique, it is very difficult to allow for such relaxation when calculating elastic constants. We did, however, try to calculate the effect of relaxation for the D_8 distortion by optimizing the geometry during this deformation, in which we also increased δ from less than 1% to about 2%. The increase to 2% distortion made the evaluation of the elastic constant less sensitive to errors made in the relaxation process. The D_8 distortion increases *a* and decreases *c* with an equal amount, while *b* is unchanged. Hence, in the relaxations b/a and y and the volume were optimized one at a time, while c/a was determined by the deformation. This decreased the energy associated with the distortion about 5% and most of this was due to the relaxation of the b/a axial ratio. The relaxation effects upon the other elastic constants could be more or less than 5%, but because of the extremely small distortions used for these (δ less than 1%) we will assume that the relaxation error in the calculations is not substantially more than 5%. The calculation of the bulk modulus supports the notion that relaxation effects on the elastic constants are rather small. When determining *B* from the Murnaghan fit as described in Sec. III, the total energy was calculated as a function of volume. The volume was varied for the fully relaxed equilibrium configuration of α-U by scaling the lattice constant *a*. In principal, the geometry should have been relaxed as a function of volume and the corresponding total energies used for the Murnaghan fit. Test calculations, that allowed for a structural relaxation at the smallest (20 Å^3) and largest (21.7 Å^3) volumes used for the fit of the bulk modulus, lowered the total energy (with respect to the energy minimum) by about 2%. It is therefore safe to assume that relaxation effects on the bulk modulus will not be greater than about 2%. The bulk modulus is also a linear combination of elastic constants [Eq. (1)], and it therefore seems plausible that relaxation effects are also limited for a calculation of these constants.

To summarize, we have studied the crystal structure of α-U in detail, and calculated the elastic constants for this phase. To our knowledge, elastic constants have never been calculated for such a complex *f*-electron system, although the crystal structure has been investigated theoretically before. For the most part elastic constants agree well with experiment and, for the crystal structure, the present theory is much better than other recently published theories. We believe that the present report provides evidence that carefully performed density-functional theory (DFT) can accurately describe uranium at low temperatures. This gives us confidence that DFT has predictive power for this material and could be used, for example, to aid in developing interatomic potentials that ultimately could be utilized to study mechanical properties of uranium.

ACKNOWLEDGMENTS

Valuable remarks from J. E. Klepeis are acknowledged. This work was performed under the auspices of the U.S. Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

APPENDIX

In this appendix, we describe the strains of the orthorhombic (α-U) structure used to calculate the nine independent elastic constants of this phase. The internal energy of a crystal under strain, δ, can be Taylor expanded in powers of the strain tensor with respect to initial energy of the unstrained crystal in the following way:

$$E(V,\delta)=E(V_0,0)+V_0\left(\sum_i \tau_i\xi_i\delta_i+\frac{1}{2}\sum_{i,j} c_{ij}\delta_i\xi_i\delta_j\xi_j\right)+O(\delta^3). \tag{A1}$$

The volume of the unstrained system is denoted V_0, and $E(V_0,0)$ is this system's internal energy. The Voight notation has been used in the equation above, i.e., xx, yy, zz, yz, xz, and xy are replaced with 1–6. Of course, yz, xz, and xy are equal to zy, zx, and yx, and for this reason ξ_i is equal to 1 for $i=1$, 2, and 3 and 2 for $i=4$, 5, and 6. τ_i above is a component of the stress tensor.

The three first elastic constants c_{11}, c_{22}, and c_{33} are obtained from the following distortions:

$$D_1=\begin{pmatrix}1+\delta & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{A2}$$

$$D_2=\begin{pmatrix}1 & 0 & 0\\ 0 & 1+\delta & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{A3}$$

and

$$D_3=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1+\delta\end{pmatrix}. \tag{A4}$$

The internal energies for these three distortions can be obtained from

$$E(V,\delta)=E(V_0,0)+V_0\left(\tau_i\delta+\frac{c_{ii}}{2}\delta^2\right). \tag{A5}$$

Next c_{44}, c_{55}, and c_{66}, are related to the distortion equations:

$$(1-\delta^2)D_4=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & \delta\\ 0 & \delta & 1\end{pmatrix}, \tag{A6}$$

$$(1-\delta^2)D_5=\begin{pmatrix}1 & 0 & \delta\\ 0 & 1 & 0\\ \delta & 0 & 1\end{pmatrix}, \tag{A7}$$

and

$$(1-\delta^2)D_6=\begin{pmatrix}1 & \delta & 0\\ \delta & 1 & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{A8}$$

These three elastic constants can then be extracted from the corresponding internal energy:

$$E(V,\delta)=E(V_0,0)+2V_0(\tau_i\delta+c_{ii}\delta^2). \tag{A9}$$

Finally, we introduce the following three distortions:

$$(1-\delta^2)D_7=\begin{pmatrix}1+\delta & 0 & 0\\ 0 & 1-\delta & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{A10}$$

$$(1-\delta^2)D_8=\begin{pmatrix}1+\delta & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1-\delta\end{pmatrix}, \tag{A11}$$

and

$$(1-\delta^2)D_9=\begin{pmatrix}1 & 0 & 0\\ 0 & 1+\delta & 0\\ 0 & 0 & 1-\delta\end{pmatrix}. \tag{A12}$$

The internal energies associated with these three distortions are given by the equations

$$E(V,\delta)=E(V_0,0)+V_0[(\tau_1-\tau_2)\delta+\tfrac{1}{2}(c_{11}+c_{22}-2c_{12})\delta^2], \tag{A13}$$

$$E(V,\delta)=E(V_0,0)+V_0[(\tau_1-\tau_3)\delta+\tfrac{1}{2}(c_{11}+c_{33}-2c_{13})\delta^2], \tag{A14}$$

and

$$E(V,\delta)=E(V_0,0)+V_0[(\tau_2-\tau_3)\delta+\tfrac{1}{2}(c_{22}+c_{33}-2c_{23})\delta^2], \tag{A15}$$

which can be solved for the three remaining elastic constants, c_{12}, c_{13}, and c_{23}.

---

[1] L. Fast, O. Eriksson, B. Johansson, J.M. Wills, G. Straub, H. Roeder, and L. Nordström, Phys. Rev. Lett. **81**, 2978 (1998).

[2] A.C. Lawson, C.E. Olsen, J.W. Richardson, Jr., M.H. Mueller, G.H. Lander, Acta Crystallogr., Sect. B: Struct. Sci. **44**, 89 (1988).

[3] J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974).

[4] J. Akella, S. Weir, J.M. Wills, and P. Söderlind, J. Phys.: Condens. Matter **9**, L549 (1997).

[5] C.-S. Yoo, H. Cynn, and P. Söderlind, Phys. Rev. B **57**, 10 359 (1998).

[6] E.S. Fisher, J. Alloys Compd. **213/214**, 254 (1994).

[7] G.H. Lander, E.S. Fisher, and S.D. Bader, Adv. Phys. **43**, 1 (1994).

[8] J.M. Wills and O. Eriksson, Phys. Rev. B **45**, 13 879 (1992).

[9] P. Söderlind, O. Eriksson, J.M. Wills, and B. Johansson, Phys. Rev. B **50**, 7291 (1994).

[10] M.D. Jones, J.C. Boettger, R.C. Albers, and D.J. Singh, Phys. Rev. B **61**, 4644 (2000).

[11] J.P. Crocombette, F. Jollet, L. Thien Nga, and T. Petit, Phys. Rev. B **64**, 104107 (2001).

[12] P. Söderlind, O. Eriksson, B. Johansson, J.M. Wills, and A.M. Boring, Nature (London) **374**, 524 (1995).

[13] P. Söderlind, Adv. Phys. **47**, 959 (1998).

[14] P. Söderlind, O. Eriksson, J.M. Wills, and A.M. Boring, Phys. Rev. B **48**, 9309 (1993).

[15] J.M. Wills (unpublished); J.M. Wills and B.R. Cooper, Phys. Rev. B **36**, 3809 (1987); D.L. Price and B.R. Cooper, *ibid.* **39**, 4945 (1989).

[16] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, and D.J. Singh, Phys. Rev. B **46**, 6671 (1992).

[17] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[18] D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973); S. Froyen, *ibid.* **39**, 3168 (1989).

[19] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[20] P. Söderlind, J.M. Wills, and O. Eriksson, Phys. Rev. B **57**, 1320 (1998).

[21] P. Söderlind and O. Eriksson, Phys. Rev. B **56**, 10 719 (1997).

[22] J.D. Axe, G. Grübel, and G.H. Lander, J. Alloys Compd. **213/214**, 262 (1994).

[23] C.S. Barett, M.H. Mueller, and R.L. Hittermann, Phys. Rev. **129**, 625 (1963).

[24] V. Ozolins and M. Körling, Phys. Rev. B **48**, 18 304 (1993).

[25] L. Fast, J.M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **51**, 17 431 (1995).

[26] P. Ravindran, L. Fast, P.A. Korzhavyi, B. Johansson, J.M. Wills, and O. Eriksson, J. Appl. Phys. **84**, 4891 (1998).

[27] O. Beckstein, J.E. Klepeis, G.L.W. Hart, and O. Pankratov, Phys. Rev. B **63**, 134112 (2001); J.E. Klepeis, O. Beckstein, O. Pankratov, and G.L.W. Hart, *ibid.* **64**, 155110 (2001).

[28] J. Bouchet, B. Siberchicot, F. Jollet, and A. Pasturel, J. Phys.: Condens. Matter **12**, 17 230 (2000); P. Söderlind, Europhys. Lett. **55**, 525 (2001).

[29] E.S. Fisher and H.J. McSkimin, J. Appl. Phys. **29**, 1473 (1958).

[30] E.S. Fisher and H.J. McSkimin, Phys. Rev. **124**, 67 (1961).

[31] F.D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).