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1997 J. Phys.: Condens. Matter 9 L549

(http://iopscience.iop.org/0953-8984/9/39/003)

J. Phys.: Condens. Matter **9** (1997) L549–L555. Printed in the UK PII: S0953-8984(97)86771-9

LETTER TO THE EDITOR

Structural stability in uranium

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Received 7 August 1997

Abstract. Diamond-anvil cell experiments and first-principles theory have been used to investigate the structural stability of uranium up to 1 Mbar in pressure. Experiments and theory agree; there is no phase transition in uranium below 1 Mbar. Previous speculations about a crystallographic phase transition in uranium below this pressure are thus shown to be incorrect. In this regard, uranium is exceptional in the series of light actinides, where pressure-induced phase transitions typically occur at pressure below 1 Mbar. The ground-state crystal structure of uranium is orthorhombic with three structural parameters: the axial ratios b/a and c/a, and an internal parameter y measuring the displacement, along the b-axis, of alternate planes. The experimental and theoretical results reported here indicate that one of these parameters, c/a, is substantially more sensitive to pressure than the other two, changing by as much as 5%, while b/a and y are constant within 1% within the pressure range studied. This flexibility in the α-U structure facilitates this structure over a wide pressure range. Theory suggests that electrostatic contributions to the total energy drive the variation in the c/a ratio as a function of pressure, and a simple model is utilized to show this.

A great variety of interesting and complex phenomena are to be found among the actinide elements and compounds, and for uranium metal in particular [1]. Uranium, the heaviest element found in nature, has received much attention over the years, primarily due to its reactor fuel applications. Interesting properties of this element include highly temperature-dependent elastic constants, the occurrence of a charge-density wave (CDW), anisotropic thermal expansion, and, like for the other light actinides, a unique crystal structure [1, 2]. Although the CDW gives rise to lattice distortions at equilibrium pressure and low temperatures, we have chosen to focus on the high-pressure behaviour of uranium in this letter.

The occurrence of complex crystal structures in the light actinide series and uranium was shown to be related to the itinerant 5f electrons that form very narrow bands close to the Fermi level [3]. The reason for this is a symmetry-breaking mechanism that lowers the total energy for a distorted (low-symmetry) crystal structure. The mechanism, which is similar to a Peierls or Jahn–Teller distortion, is effective in lowering the energy due to the appearance of narrow bands close to the Fermi level [3]. Hence, as the band broadens under compression, other interactions become increasingly important, and at high enough pressure electrostatic interactions will drive the metal into a high-symmetry structure. Recent studies of the structure behaviour of the actinides under compression, theoretical and experimental, have shown that this general picture is accurate. Thorium, the first actinide metal with non-negligible 5f occupation, was shown to undergo a phase transition from the fcc ground state to a bct phase at about 0.63 Mbar [4]. This phase transformation was later confirmed

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0953-8984/97/390549+07$19.50

by theoretical calculations [5] which also showed a transition at ultra-high pressure to a hcp phase. It was no surprise that the next element in the actinide series, Pa, showed a similar behaviour; several phase transitions were predicted by Söderlind and Eriksson [6] who used theoretical calculations to determine the structural sequence bct $\rightarrow$ α-U $\rightarrow$ bct $\rightarrow$ hcp. The first transition was calculated to take place at about 0.25 Mbar. Hence, both Th and Pa, the two actinides preceding U, undergo crystallographic phase transitions at moderate pressures. For the two subsequent elements, Np and Pu, the same behaviour is found; Np shows a phase transition from the α- to the β-phase at 0.14 Mbar [7] or possibly a bct phase [8], and in plutonium a low-pressure phase transition from monoclinic to hexagonal [9, 10] or orthorhombic [11]. Thus, for all of the light actinides there are one or more phase transitions occurring well below 1 Mbar, except for uranium. This clearly makes U different to the other light actinide metals in this regard. Not only has U a complex crystal structure, but also it is very stable in this structure over a very wide pressure range.

The fact that α-U is exceptionally stable, compared to the other light actinides, was not immediately recognized, and at first there were reports indicating a phase transition below 1 Mbar. Akella *et al* [12], already more than a decade ago, reported the appearance of two new reflections in their x-ray spectra occurring at a pressure of approximately 0.7 Mbar, suggesting the possibility of a phase transition occurring at this pressure. A more recent diamond-anvil cell study [13] concluded, however, that the reflections observed in the earlier study originated from anisotropic compression of the crystal axes rather than from a crystallographic phase transition. The subject became controversial when subsequent total energy calculations [3] for uranium indicated an α-U $\rightarrow$ bct phase transition at 0.8 Mbar. Hence, new studies, both experimental and theoretical, were needed to resolve the controversy regarding the high-pressure behaviour of uranium.

Using Mao–Bell-type diamond-anvil cells [14] the high-pressure study of uranium was extended to the multi-megabar range [15]. X-ray diffraction work was done at the National synchrotron light source, and the crystal structure of uranium at room temperature was investigated to multi-megabar pressures by the energy-dispersive technique. Diamond anvils with 300 μm cultes with a 50 μm central flat and a 7.5° bevel angle were used. Special attention was focused on the study of the anisotropic compression of the *a*-, *b*-, and *c*-axes under pressure. Such an anisotropy was clearly found, and could be characterized in the following way: as pressure increased, compression of the *c*-axial direction is less than that of the *a*- and *b*-directions, i.e. the c/a ratio is *increasing* with pressure whereas the b/a axis is relatively constant with pressure.

The results of this experiment were used as a basis for a new set of calculations, differing in two aspects from the previous calculations. The theoretical calculations which suggested the α-U $\rightarrow$ bct phase transition were performed without optimization of all of the structural parameters. Specifically, the energies of two structures, α-U with experimental axial ratios and bct with a c/a ratio equal to the experimental value for Pa, were compared. The new and detailed information obtained from the diamond-anvil cell discussed above was used here as a guide in conducting theoretical calculations of the structural stability, which are here performed allowing the crystal structure to relax with respect to the c/a ratio as a function of pressure. The b/a ratio and the internal parameter y were optimized at the zero-pressure experimental equilibrium volume and assumed to be constant as a function of the volume. This assumption was checked by optimizing b/a and y at one compressed volume; b/a was somewhat smaller at this volume, and y was somewhat larger, but the change in these parameters and the effect of this change on the total energy were much less than the effect of optimizing c/a. This optimization obviously increases the relative stability of the α-U structure compared to the bct structure in these new calculations.

In the present calculations we also adopted a more modern and accurate approximation for the exchange/correlation functional than was the case in the previous calculations [3], which allowed for a more accurate equation of state for uranium. Here we have used the recently presented generalized gradient approximation [16] in combination with a full-potential linear muffin-tin orbital technique (FP-LMTO) [17].

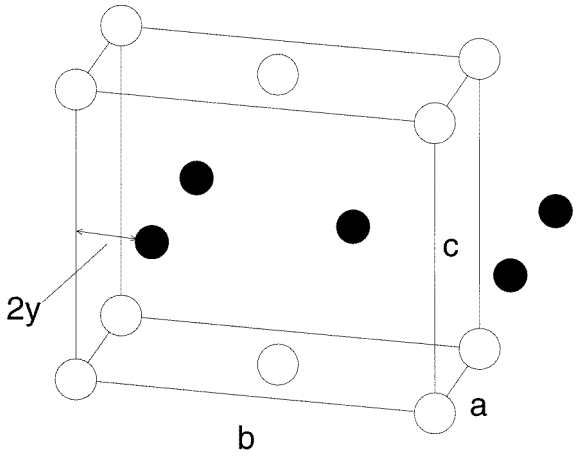

Figure 1. A schematic drawing of the ground-state structure of uranium. It is an orthorhombic structure with two different types of atom/unit cell. This is usually referred to as the α-U structure.

In figure 1 we show a schematic drawing of the α-U structure. This structure is face-centred orthorhombic, space group 63, with U atoms at Wyckoff positions 4(c): $(0, \pm y, \pm\frac{1}{4})$. The equilibrium (experimental) lattice parameters are $a = 2.858$ Å, $b = 5.876$ Å, $c = 4.955$ Å and $y = 0.105$. This structure may be visualized as an fcc lattice, subject to an orthorhombic distortion, followed by the displacement (along the z-axis) of alternate x–z planes. It can also be related to both the bcc and the hcp crystal structures [18, 19].

Our experimental and theoretical data for the c/a axial ratio as a function of volume are shown in figure 2. At the zero-pressure experimental equilibrium volume $V = V_0$, the c/a ratio is about 1.76 according to experiment and about 1% larger theoretically. With compression, the c/a ratio steadily increases to approximately 1.82 at a volume $V/V_0 \approx 0.70$. Over this range in volume, we estimate the change in the axial ratio b/a to be less than 2% and the change in the internal structural parameter y to be less than 5% by optimizing these parameters at a single compressed volume as described above.

The agreement between experiment and theory in figure 2 is most impressive, and the substantial increase of the c/a axial ratio with pressure stabilizes the α-U structure over the bct structure, so no transition between those phases occurs within the pressure range studied. Our calculated total energies for uranium are shown in figure 3. Clearly, the α-U phase is stable throughout the pressure interval studied. The change of the c/a ratio with pressure maintains uranium in its orthorhombic ground-state structure, but at higher pressures, it is expected to undergo a transition to the bcc structure [3], because the 5f bands broaden as the volume decreases, and the electrostatic energy, which favours close-packed and high-symmetry structures, dominates the structural energetics. Of these, the 5f-band filling favours the bcc structure [5]. Notice in figure 3 that the β-Np structure, compared to the bcc structure, is lower in energy at lower pressures but becomes increasingly unfavourable

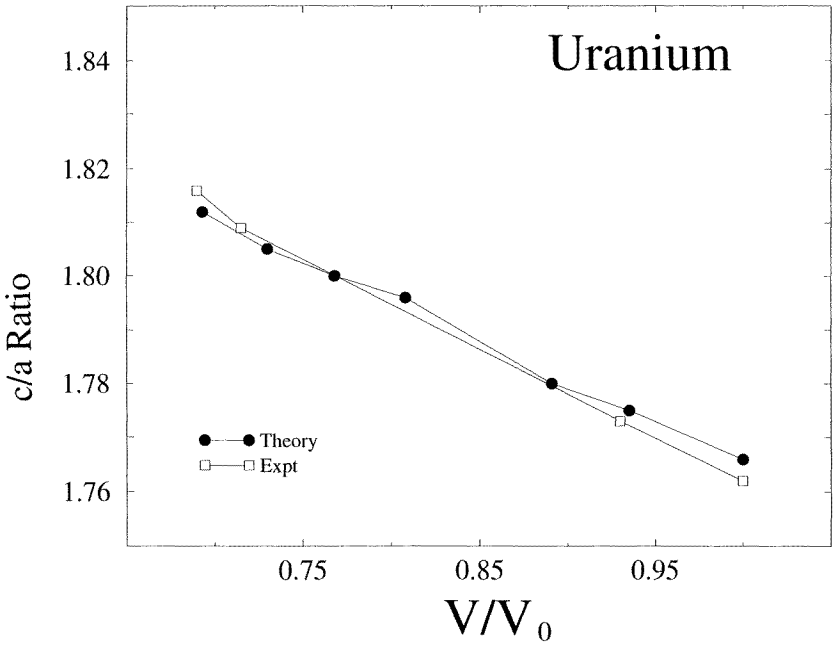

Figure 2. The experimental and theoretical volume dependences of the c/a axial ratio in α-U.

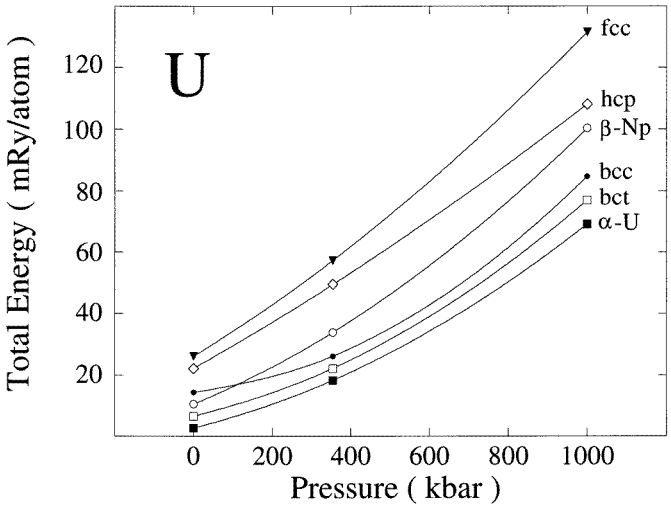

Figure 3. Total energies (FP-LMTO) for six different crystal structures: bcc, fcc, hcp, bct, β-Np, and α-U, plotted versus the calculated pressure. Lines connecting the data points are guides to the eye only. The bcc and bct structure have almost the same total energy at 1 Mbar; the bcc structure is denoted with solid circles.

at higher pressures. This behaviour was found also for Np [5], leading to a phase transition from the β-phase to bcc structure at about 0.57 Mbar in Np.

Let us return to the variation of the c/a value with pressure in the α-phase—figure 2.

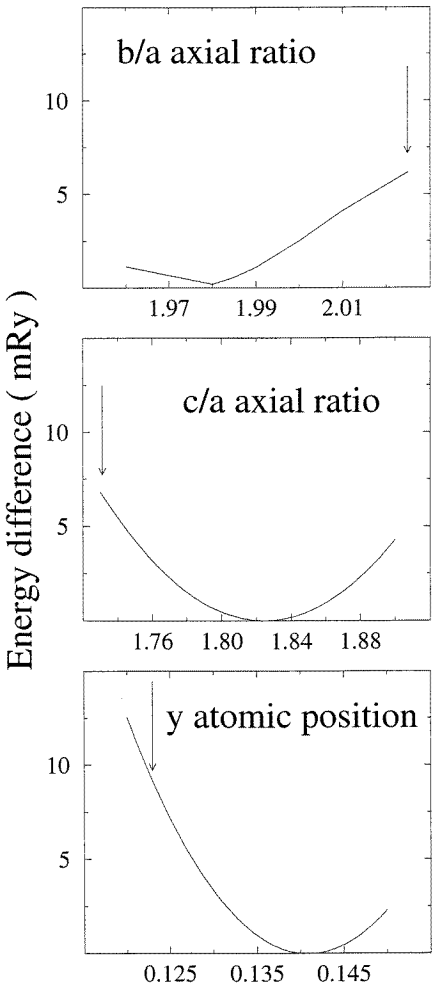

Figure 4. The Madelung (or Ewald) energy, shifted to have zero as the minimum value, of the α-U structure for independently varied b/a, c/a axial ratios and atomic position parameter, y. As a good approximation the volume was kept constant for all values of b/a and c/a. The arrows show the values of b/a, c/a, and y measured under ambient conditions.

This variation does not involve any symmetry change of the structure, and a Peierls distortion therefore cannot be the reason for this behaviour. We will show that instead the trend in the structural parameters is driven by the electrostatic energy of the lattice. The structure-dependent electrostatic contribution can be estimated using a simple model. The electrostatic energy [20] of a lattice of identical ions with charge $q|e|$ can be written in the form

$$E_{electro} = -\frac{1}{2}\,(q|e|)^2\frac{\alpha}{S} \tag{1}$$

where α is the lattice Ewald (or Madelung) constant and S the atomic Wigner–Seitz radius. The Ewald constant is dimensionless, of the order of one, and depends only upon the configuration of the ions, not the magnitude of the charge or the absolute spacing, both of which have been extracted in the equation above. By subtracting the electrostatic energy

for an ion and its share of the background as a uniform sphere of radius S, for which $\alpha = 9/5 = 1.8$, we get an estimate of the structure-dependent contribution:

$$\Delta E_{electro} = \frac{1}{2}\,(q|e|)^2 \frac{(1.8-\alpha)}{S}. \tag{2}$$

This description is of course a simplification. The complete electrostatic energy contribution is described as a sum over multipoles, rather than a simple monopole sum; the relatively low symmetry of the α-U structure might have required a model based on such a description. The success of the monopole model, however, suggests that the essential physics is contained in this simplified model. In figure 4 we show $\Delta E_{electro}$ as a function of b/a (upper panel), c/a (middle panel) and y (lower panel), shifted so that the lowest energy is zero. The effective charge is not unambiguously determined; in this model the effective charge $q|e|$ was calculated as in reference [21], and we kept the radius S and the charge $q|e|$ fixed to their equilibrium values while optimizing b/a, c/a, and y. Figure 4 suggests that the b/a ratio should decrease towards 1.98, the c/a ratio should increase to about 1.82, and y should increase to about 0.14 with increasing compression of uranium. This behaviour is in surprisingly good agreement with our FP-LMTO calculations; for the c/a value (figure 2), the agreement is excellent. The trend in the other two parameters (b/a and y) is in agreement with our experimental results and theoretical estimates, but the change is less than the simple model suggests. The relative success of our analytic model is a consequence of the fact that the electrostatic contribution to the total energy becomes more important with increasing pressure, whereas the symmetry-breaking distortion becomes less efficient. We would certainly expect this trend to continue, so at some higher pressure uranium would form in a high-symmetry structure which minimizes the $\Delta E_{electro}$ energy term. For high-symmetry structures such as bcc, fcc, and hcp this term is minimized and rather similar. This is clear since the Ewald constant (α) is essentially the same in these three crystal structures. The 5f-band filling determines which among the bcc, fcc, and hcp structures is favoured. For uranium, having about 3.5 5f electrons at high pressure, canonical band theory predicts the bcc structure to be more stable than either fcc or hcp structures [7].

On the basis of our diamond-anvil cell measurements we conclude that uranium remains in the α-U phase up to 1 Mbar. Theoretical calculations support this conclusion, but we argue that at higher pressures the bcc structure will become stable. We cannot exclude the possibility that uranium first transforms to an intermediate structure, and—if that is in fact the case—the bct structure is a good candidate for that intermediate phase.

We thank O Eriksson, B Johansson, and C Wu for valuable discussions. Part of this work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory, contract number W-7405-ENG-48. We thank M Anastasio and B Goodwin of LLNL/B-Div for supporting the experimental work. We acknowledge the help given by G S Smith in reducing the x-ray data.

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