Theoretical Aspects of the Charge Density Wave in Uranium

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Using a first principles total energy method, we have reproduced the observed charge density wave (CDW) state of α-uranium (called α_1). This CDW is found to be a result of a Peierls-like transition, i.e., by opening of partial gaps at the Fermi level. The part of the Fermi surface affected by the distortion shows a strong nesting of fairly narrow f bands. In addition we suggest that the slightly modified α_1 CDW state, which is called α_2 and is observed by cooling the α_1 phase, is caused by a closely related mechanism, namely, by a nesting of the Fermi surface in the b direction. This is consistent with the observed CDW ordering. [S0031-9007(98)07255-X]

Today the charge density wave (CDW) [1–3] state has almost exclusively been observed in quasi-one-dimensional systems, as, for example, in NbSe$_3$ [4]. However, there is one important exception to this experimental fact, namely, uranium metal [5]. Indeed, uranium is also the only element in the periodic table which exhibits such a behavior. Thus it becomes particularly important to verify this unique property theoretically. In fact, it was only after several decades of thorough experimental work that it was experimentally established that uranium metal exhibits a sequence of low temperature states, which have been identified as charge density waves (the different phases are called α_1, α_2, and α_3). The first transition takes place at 43 K (α_1) and the last one stabilizes below 23 K (α_3). After the completion of the last CDW transition, uranium has in fact transformed to an element where the primitive cell has a volume of ~ 6000 Å^3 [5]. On the theoretical side there has not been a corresponding refinement of the theoretical treatment to cope with these fine details of the low temperature crystal structure of uranium.

Despite the fact that the conceptual possibility of CDW states was suggested many years ago for simple metals [6], uranium has remained a unique exception among the elements showing such behavior (the spin-density wave of chromium is accompanied by a weak CDW [7,8], but the latter is simply induced by the former). One may wonder why a CDW state has not been observed in other elements since in compounds (especially compounds with "one-dimensional" character) the CDW state is more frequently observed [6,3]. An "ideal" one-dimensional CDW system has a periodic charge density given by [3]

$$\rho = \rho_0 + \Delta\rho \cos(2k_F r + \phi), \tag{1}$$

where ρ_0 is the density of the normal state and $\Delta\rho$ is the magnitude of the charge density wave, whereas k_F is the Fermi wave vector of the undistorted lattice and ϕ is a phase factor. As a consequence of this added periodicity in the system, a so called "Peierls gap" opens up in the energy level distribution at the Fermi level, E_F. This modified electron density is then normally accompanied by a movement of atomic positions (dimerization) and the CDW may be identified from this structural distortion. The origin of the CDW in one-dimensional compounds has been discussed in terms of Peierls distortions [2] and Kohn anomalies [9]. The superconducting properties of the CDW condensate, suggested by Fröhlich [1], has until this date not been discovered, presumably due to the pinning of the CDW [3]. Instead, normally the resistivity behavior is characteristic of a gaped system, and in addition there is the complication of the sometimes observed nonlinear current-voltage (I-V) relationship [3].

The most characteristic identification of a CDW in uranium has been found from the observation of the structural transition [5]. Neutron experiments indicate that the CDW at 43 K is associated with a significant phonon softening, a fact which may help understanding this martensitic transition [10]. From a materials science point of view, the CDW state in uranium manifests itself by a small but still drastic change in many physical properties: lattice parameter, resistivity, elastic response, and thermal expansion [5].

The transition at 43 K (α_1) is much simpler than the other two transitions at lower temperatures. It involves only a doubling of the conventional unit cell along the a direction. The corresponding atomic displacements are larger, by an order of magnitude, than the displacements occurring at the other two transitions. Furthermore the survival of this state to higher temperatures (compared to the others) signals that this transition to the α_1 phase is energetically also the most important one. For these reasons we will here focus our attention on the α_1 CDW state. The structural arrangement of this distortion is shown in Fig. 1. Notice that the α_1 CDW state is characterized by one parameter, labeled u in Fig. 1. The doubled unit cell volume associated with α_1-U is built up from two atomic layers, distinguished by open and closed circles in the figure. A possible primitive cell is indicated by the box in the figure (thin line). When

$u = 0$ the 8 atom cell of the α_1 state can be reduced to the ordinary undistorted 2 atom α-uranium structure. The atom displacement u illustrated in Fig. 1 corresponds to an optical phonon mode in the undistorted α-uranium structure, usually referred to as Σ_3 in the literature [5].

There are a number of unanswered questions concerning the CDW in α-U. The most important one is the following: Which mechanism drives the transition? Since f-electron elements are known to have structural properties which deviate from the rest of the elements [11] in the periodic table it is natural to ask if it is the presence of f electrons in the chemical bonding which causes the CDW state. Answering these questions will contribute to our understanding of chemical bonding in general, especially that of f electron systems. At this stage one may also speculate if there are other elements (in addition to U) that will undergo a CDW or CDW-like transition. The observation of such a state, however, might require that a sufficiently accurate experimental probe is available. In order to shed light on these issues we have undertaken a total energy study on the CDW state in uranium and we have analyzed its origin. Given that extremely small distortions are involved, it is from a computational viewpoint a most challenging problem. It poses very hard requirements of the theoretical treatment, not the least on the representation of the electron density distribution of the undistorted α-uranium crystal structure. This is of particular interest since we are dealing with an f-electron element, something often associated with difficult questions concerning the influence of electron correlation. A strong correlation picture has for instance been used to explain some photoelectron-spectroscopy experiments on uranium metal [12]. In the present paper we apply the standard local density theory in combination with a full potential scheme, the same theory and technique that
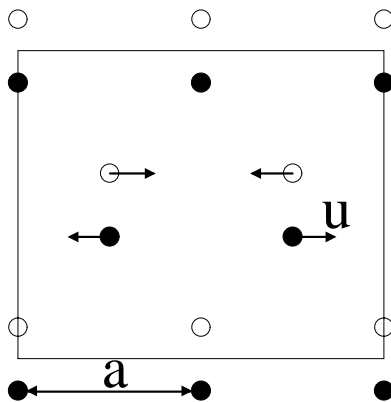
is used to treat the electronic structure of, for instance, copper. This type of theoretical treatment has had a documented success in reproducing various low symmetry crystal structures within the actinide series [11,13].

We have calculated the total energy of the CDW state in uranium as a function of the magnitude of an appropriate atomic distortion. The total energy calculations were based on the relativistic full-potential method developed by Wills [14], which employs linear muffin-tin orbitals as basis functions [15]. The calculations have been done at the experimental lattice data [5], except for the volume dependent calculations, where the parameters $\frac{b}{a}$, $\frac{c}{a}$, and y were kept constant. This is justified in the studies by Akella *et al.* [13], where the volume dependence of these parameters was found to be weak in the relevant volume range.

In Fig. 2a we show the calculated total energy as a function of the CDW lattice distortion, u. The α-U structure corresponds to $u = 0$. Figure 2a clearly shows that the undistorted α-U is unstable towards the α_1 CDW state. The magnitude of the lattice distortion which minimizes the total energy is ~ 0.028 Å, which compares extremely well with the experimental value of ~ 0.027 Å. In Fig. 2a we also present our results for two different k-point samplings, namely, using 80 and 252 k points in the total Brillouin zone (BZ), respectively. Clearly there is no significant difference in the behavior of the total energy as a function of distortion for the two different
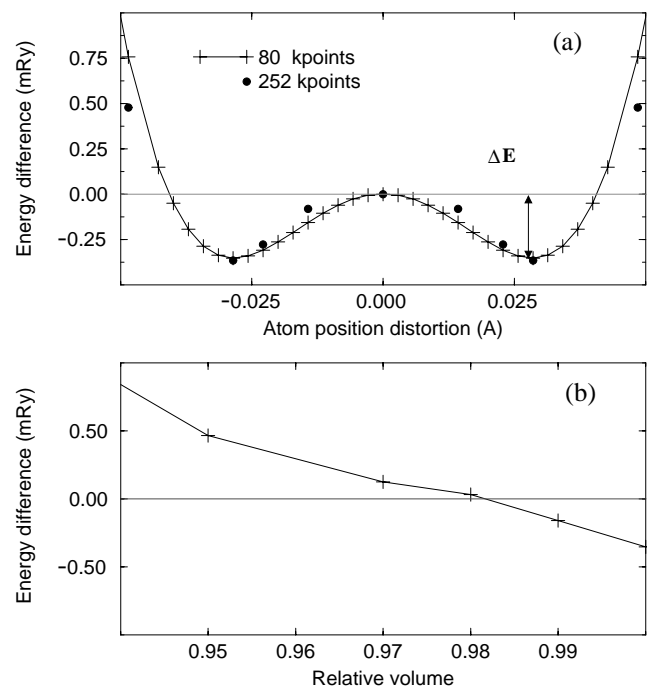

FIG. 1. Atomic arrangements of the α_1 CDW and of the α-U ($u = 0$) projected on the ab plane. The doubling of the unit cell is in the a direction and the size of the cell is indicated by the thin line. The open (filled) circles mark atoms situated in the $z = 0$ ($z = \frac{1}{2}$) layer.

FIG. 2. (a) The calculated energy as a function of the CDW distortion parameter u (see Fig. 1). Two different k-point sets were used. (b) The energy difference, ΔE, between the α-U and α_1-U ($u = 0.028$ Å) as a function of compression.

samplings of k space. Thus we conclude that the calculated total energy is converged in the number of k points. The calculated energy gain connected to the CDW distortion is very small (0.35 mRy, equivalent to 55 K). This finding is consistent with the fact that it requires only a temperature of 43 K to transform α_1-U to the undistorted α-U crystal structure.

In Fig. 2b we plot the energy difference between the undistorted and the distorted system for a constant distortion, $u = 0.028$ Å (which corresponds to the energy minimum of the α_1-U state) as function of volume. This difference, ΔE, is shown in Fig. 2a and we observe that our calculations give a phase transition at 98% of the equilibrium volume. Under compression, the transition from the α_1-U to α-U phase is observed to occur at a volume approximately 99% of the equilibrium volume. Hence experiment and theory agree very well also in this respect.

So far we have been able to reproduce the behavior of the optical phonon mode of the α-U structure that is responsible for the CDW state called α_1. In order to better understand the appearance of this CDW we investigated the Fermi surface (FS) of the distorted and undistorted structure. It is appropriate to mention in this connection that Freeman *et al.* [16] calculated the FS of α-U from a non-self-consistent density some 20 years ago. By slicing the Fermi surface, making 2D contour plots, we have analyzed the FS topology of the undistorted and the distorted systems. One particular cut was more informative than others. We found that the largest change of the topology of the Fermi surface occurs close to the point $(\frac{1}{2}, 0, \frac{1}{2})$ in the reciprocal space (in units of the Bravais lattice vectors). In Figs. 3a and 3b we present the Fermi level contour for the undistorted and distorted systems in the BZ of the 8 atom cell. When comparing Figs. 3a and 3b we notice that there is a clear change in the Fermi surface behavior close to the U point, an ellipsoid object has disappeared due to the distortion. If we plot the bands from Z to U, one band splits at the Fermi level at the corresponding k points. This kind of band splitting due to a symmetry breaking distortion is usually referred to as a Peierls distortion. Now we are at a stage where we know that there is a topological change of the Fermi surface close to the U point. In order to test the hypothesis that this is the driving source for the formation of the CDW, we excluded the k points closest to the U point in a separate set of calculations (for different k point densities, ensuring convergence). We found that such a restriction changed the sign of the energy difference, ΔE; that is, the CDW minimum in Fig. 2a disappeared. In order to decide that this was not an artifact due to a nonhomogeneous k-point sampling we excluded other k-point regions, randomly distributed (some of high symmetry, some not), and calculated the total energy. In all these cases the α-U structure was found to be unstable towards the formation of the CDW.
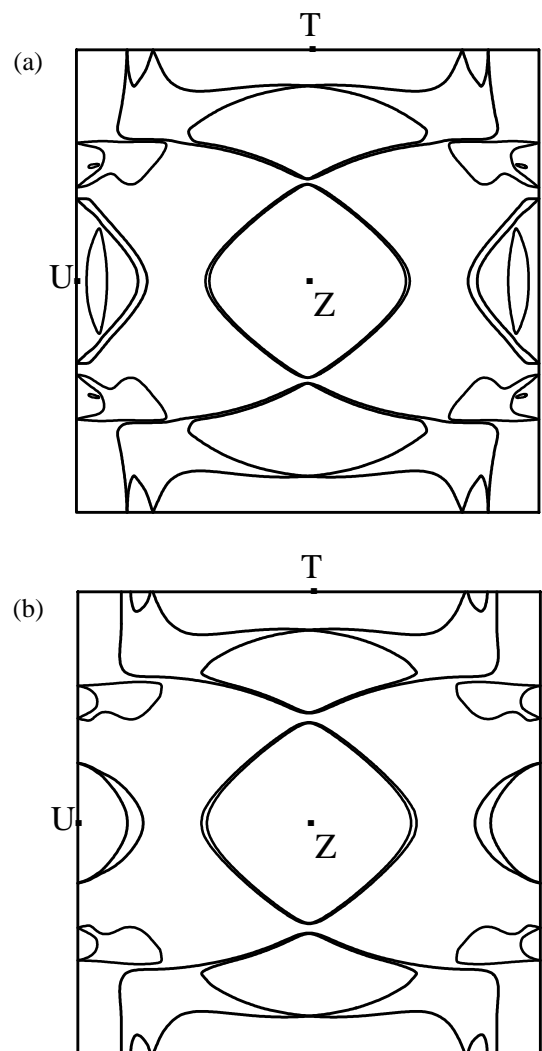

FIG. 3. The Fermi surface of the larger unit cell with eight atoms is shown for (a) $u = 0$ and (b) $u = 0.028$ Å. The cut is spanned by the vectors $(0, 1, 0)$ and $(1, 0, 0)$ and includes the symmetry points $(0, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, 0, \frac{1}{2})$, which are called Z, T, and U.

In Fig. 4 we show the FS of α-U with two atoms in the primitive cell (corresponding to the Bravais lattice of the α-phase), for a cut in reciprocal space which is corresponding to those shown in Fig. 3. The rather complex contour in Fig. 3a has changed to a much simpler contour, due to the unfolding of the BZ. There is a possibility for nesting of the Fermi surface in the a direction (indicated by the horizontal vector in Fig. 4). Comparing the distance between the almost parallel contours, with the distance of the reciprocal lattice vector of the α_1-U structure in the a direction, we notice that they are almost equal in length. That is, we have nesting vectors of length $\frac{\pi}{a}$, which by means of Peierls arguments will give rise to a lattice distortion, doubling the conventional unit cell, i.e., in complete agreement to the observed behavior of the α_1 phase. Experimentally it is known that the nesting vector
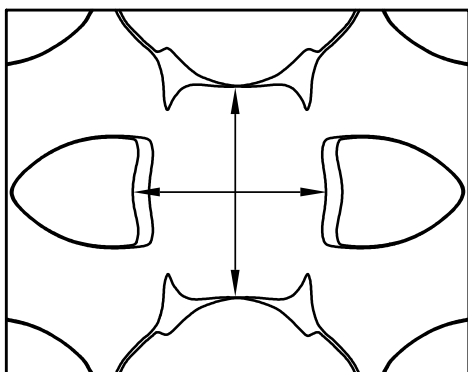
FIG. 4. A cut of the Fermi surface in the *ab* plane for $k_z = \frac{1}{2}$ is presented for the α-U structure. The arrows indicate possible nesting vectors in the *a* direction (horizontal) and the *b* direction (vertical).

q_x varies from 0.49 to 0.50 as the temperature drops from $\sim$47 to $\sim$37 K [5], which is consistent with the observed nesting. In addition we also observe nesting features in the *b* direction (indicated by the vertical vector in Fig. 4), which we suggest give rise to the the α_2 CDW phase of uranium. In Figs. 3a and 3b the corresponding almost parallel contours are found close to the *T* point. The nesting vectors in the *b* direction are of length $\sim \frac{\pi}{6b}$, which is consistent with a sixfold increase in the *b* direction of the α_2 phase as observed experimentally. Thus all our analyses, the FS nesting, electronical topological transition, and calculations excluding certain *k* points of the BZ, suggest that the α-U to α_1-U transition is a Peierls-like transition. The nesting parts of the Fermi surface are dominated by *f* character and the corresponding bands are quite narrow, i.e., there is a large number of electronic states involved in the opening of the Peierls gap which makes it energetically favorable. This is one reason why CDWs are observed in uranium but not in sp-like metals, since in these metals the appropriate bands are too broad.

In summary we have reproduced the most intricate lattice distortion of one of the CDWs of uranium and have shown that it may be understood as a Peierls-like distortion. The mechanism discussed here for the stabilization of the α_1-U phase is related to that discussed by us previously, when analyzing the structural properties of light actinides [11]. However, in the latter much larger parts of the BZ contain states which are active in driving the structural transition. In contrast to this, the structural distortion associated with the α_1 CDW state is well explained by the nesting features of the Fermi surface in the *a* direction.

In this connection it is of particular interest to notice that although uranium is an *f*-electron element, we are able to account for the CDW phase called α_1, which involves minute energy changes and puts extremely high demands on the theoretical treatment. This strongly favors a picture where the description of *f* electrons in uranium metal can be accurately obtained from density functional theory. We finally speculate that other *f* elements, such as plutonium, might possibly exhibit a CDW-like behavior provided sufficiently refined low temperature experimental probes are used for its detection. In addition we encourage experimentalists to perform de Haas–van Alphen experiments on uranium, both as function of pressure and temperature, in order to test our theoretical predictions, to continue the work of Ref. [17].

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