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Magnetic structure and electric-field gradients of uranium dioxide: An *ab initio* study

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The magnetic structure of uranium dioxide has been investigated using linear augmented plane wave *ab initio* calculations, taking into account spin-orbit coupling, strong Coulomb correlation (using the LDA$+U$ approach) and noncollinear magnetism. The collinear 1-**k** antiferromagnetic type-I structure and the noncollinear antiferromagnetic 2-**k** and 3-**k** orderings have been tested. The 1-**k** and 2-**k** structures can be excluded by a comparison between the calculated and experimental uranium electric field gradients (EFG). It is shown that the measured EFG agrees with theory only in the 3-**k** structure and an additional deformation of the oxygen cage with an oxygen displacement of $\Delta_O=0.16$ a.u. Also the magnetic moments and the corresponding hyperfine fields agree reasonably well with experiment.

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UO_2 is a very important material for use in nuclear power production and is a particularly interesting material for which the type of noncollinear antiferromagnetic (AF) ordering has not been reliably determined, despite experimental efforts during four decades. It is also a very challenging compound for calculations since a proper theory must include spin-orbit coupling (SOC) interaction (due to the heavy actinide element) and must be able to properly treat the localized and strongly correlated $5f$ electrons of U. In addition a full theoretical description must also explore possible noncollinear magnetic ordering.

Almost 40 years ago Frazer *et al.*,[1] using neutron diffraction, established that UO_2 undergoes a discontinuous transition at $T_N=30.8$ K from a paramagnetic to an AF-I state with the quantization axis within the alternating ferromagnetic XY sheets. Subsequent measurements[2] showed that the elastic constant c_{44} begins to soften near 200 K, which is evidence of a strong electron-phonon coupling. Moreover, inelastic neutron scattering data were interpreted as evidence of a large magnon-phonon interaction.[3] Faber and Lander[4,5] proposed on the basis of neutron diffraction a 2-**k** type of ordering, where the moments are aligned in $\langle 110\rangle$ directions. They also found a 1-**k**-type distortion of the oxygen cage, where the oxygen atoms are displaced about 0.014 Å from their equilibrium positions in $\langle 100\rangle$ direction. Further analysis[6] and neutron diffraction under a magnetic field[7] suggested a 3-**k** magnetic ordering with the moments pointing along the $\langle 111\rangle$ directions and a 3-**k** distortion of the oxygen cage (oxygens are displaced in $\langle 111\rangle$ directions). On the other hand, a 1-**k** magnetic structure was found in agreement with magnetic x-ray diffraction measurements.[8] Polarized inelastic neutron scattering experiments are compatible with a 1-**k** uncorrelated Jahn-Teller distortion above T_N.[9] Below T_N the correlations between phases of the corresponding vibrations build up until a static 3-**k** distortion is obtained, suggesting 3-**k** type of magnetic ordering. This agrees with the recent nuclear quadrupole resonance study,[10] which reported electric field gradients (EFG) and hyperfine fields (HFF) supporting a 3-**k** magnetic ordering.

In previous theoretical calculations the major problem has been that the local density approximation (LDA) gives an even qualitatively incorrect description of the strongly correlated f states, leading to metallic instead of insulating behavior.[11,12] Orbital-dependent functionals like the LDA $+U$,[13] the self-interaction correction,[14] and recently hybrid Hartree-Fock–density-functional calculations[15] are known to correct this kind of problems. Dudarev *et al.*[16] showed that the LDA$+U$ method of Anisimov *et al.*[13] improves the calculated ground state. More recently Kudin *et al.*[15] performed hybrid density-functional calculations, resulting in very good agreement with experimental photoemission data. Both of these studies successfully obtain an insulating ground state, stabilize a 1-**k** AF ordering versus ferromagneting and predict an equilibrium lattice constant in good agreement with experiment.[15,16] This showed that a proper treatment of electron-electron correlations is essential for the description of the electronic structure of UO_2. However, despite the debate on the precise ordering of the magnetic moments and the oxygen displacement, both studies[15,16] assumed a collinear 1-**k** AF ordering with the oxygens at the ideal fluorite positions. Furthermore, they did not take SOC into account, which cause large orbital moments on the uranium site.

In this paper we show that *ab initio* calculations can provide a consistent picture of UO_2 on the electronic, nuclear, and magnetic structure by taking into account spin-orbit interactions, possible noncollinear magnetism, and strong correlations. We investigate the proposed magnetic orderings by comparing total energies and our calculated EFGs to the experimental ones.[10] For this purpose we have implemented the full treatment of noncollinear magnetism together with spin-orbit coupling and the LDA$+U$ method into the WIEN2K package.[17]

The WIEN2K[17] package is an implementation of density-functional theory using the all electron linearized augmented plane wave plus local orbitals method, where linearization is done by additional local orbital (L/APW+lo).[18] The latter expands the Kohn-Sham orbitals in atomiclike orbitals inside atom-centered spheres and plane waves in the interstitial region. The atomic sphere radii were set to 2.3 and 1.6 a.u. for

U and O, respectively. Additional local orbitals were added for U $6s$,$6p$,$4d$,$5f$ and for O $2s$ states. The basis-set size corresponding to $R_{MT}K_{MAX}=6$ (R_{MT} is the smallest atomic sphere radius, K_{MAX} is a cutoff for the basis functions wave vector), and a k sampling with a $4\times4\times4$ mesh in the full Brillouin zone turned out to be sufficient (the irreducible wedge contains four k points for 3-**k**, and eight k points for 1-**k** and 2-**k** structures).

Our implementation of noncollinearity is based on a mixed spinor basis-set approach.[19,20] In the interstitial region the basis functions are pure spinors given in a global spin coordinate frame. Inside the atomic spheres they are nonpure spinors given in local spin coordinate frames with quantization axes pointing along average magnetizations, which can be different for each sphere. In this setup, it is possible to use the spin-polarized radial part of the basis functions inside the spheres. Because, the energy dependence of the radial function is strong for the *f* orbital, this approach is an advantage. We have extended the original implementations in order to treat the spins fully noncollinearly also inside the spheres. Since, in order to treat the noncollinearity, we have to deal with the full Hamiltonian (2×2 matrix in spin space), the SOC (Ref. 21) is added to the scalar relativistic Hamiltonian directly in the first variational step.

The LDA+U calculations were performed with the LDA exchange-correlation potential by Perdew and Wang.[22] LDA+U can be formulated with different double-counting corrections (DCC), namely the "fully localized limit" (FLL),[13] "around the mean field" (AMF),[23] and the recently proposed interpolated DCC scheme (DFT-DCC).[24] We varied the average effective Coulomb interaction parameter U from 0.15 to 0.45 Ry. A generally accepted choice for J is $J=U/7\text{-}U/4$. According to our tests, values of J in this range do not change EFGs and, therefore, our final conclusions. Thus we adopted $J=U/5$.

We calculated the total energies of various magnetic structures with different U values and DCC schemes. For each magnetic ordering the positions of the oxygens were optimized. The total energy of the collinear ferromagnetic structure is always above all three AF cases, the exact energy difference depends on the details of the calculations but is never less than 0.1 Ry. In the 1-**k** AF ordering the undistorted oxygen positions are most stable. For the 2-**k** magnetic ordering a 1-**k** O deformation is preferred, while for the 3-**k** ordering the O deformation is also of 3-**k** type. This shows that the oxygen cage deformation strongly depends on the magnetic ordering and can be interpreted as evidence of strong magnon-phonon coupling, already mentioned in the experimental literature.[3] Figure 1(a) illustrates the difference of total energies of the collinear 1-**k** and the non-collinear 2-**k** and 3-**k** orderings as a function of U. It shows that for almost all calculations the 1-**k** magnetic ordering is energetically favorable. The only exceptions are AMF-DCC calculations with U larger than 0.35 Ry, where 3-**k** becomes most stable. The total energies are slightly affected by the choice of J, i.e., a very large value ($J\approx U/3$) can further stabilize the 3-**k** magnetic structure versus the collinear one. On the other hand, very small values of J ($J\approx U/10$) have an opposite effect. Figure 1(b) shows the effect of U on the oxygen displacement for 3-**k** ordering only. The displacement increases with U, more for AMF-DCC than for FLL-DCC, which is important for the electric field gradients discussed below. In addition, the energy gained by optimizing the oxygen positions, ΔE_{relax} [Fig. 1(b)] increases with the displacement. We find that the 3-**k** structure is stabilized in AMF-DCC only by this energy gain.

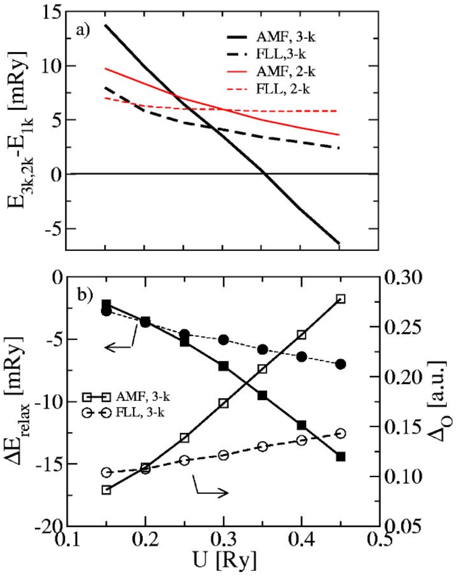

FIG. 1. (a) Total-energy differences (per four UO_2) between noncollinear and collinear structures vs the effective Coulomb interaction U. (b) Energy gain E_{relax} by relaxing the oxygen positions (closed symbols, left scale) and equilibrium oxygen displacements Δ_O from the ideal fluorite position calculated for the 3-**k** magnetic ordering (open symbols, right scale). The squares and circles are AMF and FLL-DCC calculations, respectively.

The exact magnetic ordering has still some experimental uncertainty, whereas the total magnetic moment is well known and about $1.74\mu_B$. Standard spin-polarized LDA calculations of collinear AFM UO_2 obtain a much too small magnetic moment of $0.62\mu_B$, with spin and orbital moments of $0.7\mu_B$ and $-1.32\mu_B$, respectively. LDA+U calculations with $U=0.35$ Ry give for the collinear 1-**k** structure almost the experimental moment ($1.75/1.81\mu_B$ for FLL/AMF versions of LDA+U), where the spin ($1.80/1.71\mu_B$) and orbital ($-3.55/-3.53\mu_B$) contributions partially cancel each other. The dependency of the total moment on the value of U is quite small (less than $0.1\mu_B$ when U is reduced to 0.15 Ry). In the noncollinear 3-**k** structure the spin moments are almost the same, but the corresponding orbital moments are 0.2 (no oxygen displacement) to $0.4\mu_B$ (full displacement) bigger, resulting in somewhat larger, but still acceptable, total moments.

The calculated density of states (DOS) is in good agreement with previous calculations[15,16] and photoemission data.[25] It is dominated by the conduction and valence uranium *f* states and the lower-lying oxygen *p* states. The orbital potential of LDA+U splits the *f* band into narrow occupied and broad unoccupied bands. Not surprisingly the position of the narrow *f* peak (between the conduction and the oxygen *p* bands) strongly depends on the value of U changing the band

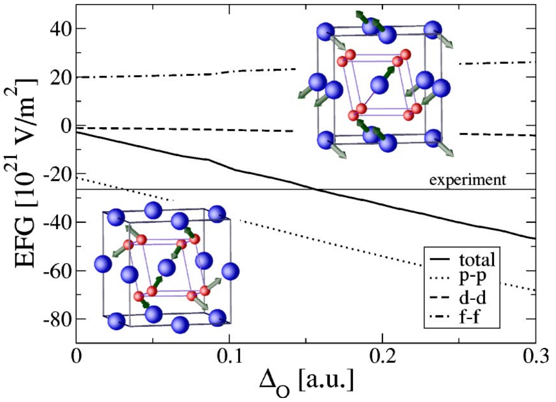

FIG. 2. Total U-EFG for the 3-**k** structure and its main angular contributions: p-p, d-d, and f-f as a function of O displacement. The s-d and p-f contributions are negligible. The upper inset presents the magnetic moments on U (large spheres) and the lower one the directions of oxygen displacements (small spheres).

gap from 0.6 eV for $U = 0.15$ Ry to the experimental gap of about 2 eV for $U = 0.4$ Ry.[26,27] This strongly supports the use of $U = 0.4$ Ry. The DOS does not significantly depend either on the DCC scheme or the magnetic ordering.

The EFG tensor is highly sensitive to the local coordination and anisotropy of the charge distribution close to a given nucleus and can be precisely calculated.[28,29] The recent measurements of EFGs in UO$_2$ by Ikushima *et al.*[10] give an opportunity to check the proposed structure and magnetic ordering.

Experimentally the nuclear quadrupole interaction is found as $\nu_q\ (\cos^2\theta - 1) = 392 \pm 11$ MHz,[10] where θ is the experimentally unknown angle between the principle EFG direction and the hyperfine field. From $\nu_q = 3eQV_{zz}/2hI(2I-1)$ (Ref. 30) we find the main EFG component $V_{zz} = 23 \pm 1 \times 10^{21}$ V/m^2, where we took our theoretical value of $\theta = 0$ and the most recent value of the nuclear quadrupole moment $Q(^{235}\mathrm{U}) = 4.936$ b.[31] Experimentally the EFG tensor for uranium showed axial symmetry ($\eta = |V_{xx} - V_{yy}|/|V_{zz}| = 0$).[10]

We performed EFG calculations for all three magnetic orderings, varying U and the oxygen displacements in noncollinear cases. We find that the calculated EFGs are insensitive to LDA+U details (for a given oxygen position), but depend strongly on the oxygen displacements. Thus the calculated EFGs allow a reliable determination of magnetic ordering and oxygen cage distortion. We find for all cases studied, that the direction of the principal axis of the EFG (V_{zz}) is parallel to the magnetic moment.

L/APW+lo showed it was precise enough[28,29] to let us, by comparing our calculated EFG to the experiment, to rule out the 1-**k** and 2-**k** magnetic orderings. For the 1-**k** ordering the calculated EFG, $V_{zz} = 6.4 \times 10^{21}$ V/m^2, is about four times smaller than measured and for the 2-**k** structure the EFG tensor is not axially symmetric, which is at variance with experiment.[10] The situation is different for 3-**k** ordering. The total calculated EFG for the undistorted structure is only -3×10^{21} V/m^2 with axial symmetry (Fig. 2). The EFG can be decomposed into contributions from different orbitals (see Ref. 28), and we find that the large p-p and f-f contributions cancel partly. The difference to 1-**k** is that in the 3-**k** ordering the oxygen atoms are displaced from their fluorite positions along the $\langle 111 \rangle$ directions, preserving the axial symmetry of the EFG tensor but resulting in a strong increase of the uranium $|V_{zz}|$, Fig. 2. This increase is caused by the p-p contribution, which strongly depends on the oxygen cage deformation. Note, that the p-p contribution to the U-EFG can be considered as coming from the tails of the O-2p wave functions (off site), or in the traditional point of view as the "lattice EFG" times an appropriate Sternheimer antishielding factor. On the other hand, the f-f (on-site) contribution has the opposite sign but remains almost constant when the O atoms are displaced (Fig. 2), a strong indication for the localized nature of the 5f states. The experimental value for the EFGs corresponds to the O displacement of $\Delta_O = 0.15$ a.u. in the calculation.

From the total-energy calculations (Fig. 1) we see that the displacement predicted by FLL-DCC for the 3-**k** ordering varies with U, and in the studied range is always slightly smaller than that required to give the experimental EFG. The variations are stronger for AMF-DCC, where a larger deformation then the 0.15 a.u. is predicted for U between 0.3–0.45 Ry. FLL and AMF are the extreme limits of DCC schemes for localized and delocalized electron shells,[24] respectively, and none of them is a perfect choice when applied to real systems like UO$_2$. According to a recent idea[24] an improved LDA+U potential (DFT-DCC) can be derived by interpolating between FLL and AMF schemes. If we use the value of $U = 0.4$ Ry, which gives a reasonable band gap of order 2 eV, the original DFT-DCC scheme[24] leads to a mixing parameter $\alpha = 0.75$. For this parameter the oxygen displacement is $\Delta_O = 0.15$ a.u. and the uranium EFG of value 23×10^{21} V/m^2 is in perfect agreement with experiment. However, the 3-**k** magnetic structure is slightly destabilized (0.2 mRy) corresponding to the collinear one. Adopting a smaller value of 0.5 for the mixing parameter α (making it more "AMF-DCC"-like) yields an oxygen displacement of $\Delta_O = 0.16$ a.u., an EFG of 25×10^{21} V/m^2 (which is still in very good agreement with experiment) and the 3-**k** ordering lies lower in energy than the 1-**k** by about 0.2 mRy.

Besides the EFGs also the hyperfine fields (HFF) on the U site have been measured by NMR.[10] As expected, the U-HFF has a very large value of about 253 T. We have calculated all three contributions of the HFF (Ref. 32) and obtain in the 1-**k** structure $-33/-290/+10/-313$ T for the contact/orbital/dipolar/total HFF, respectively. For the noncollinear 3-**k** structure the HFF at the U site is about 10% larger. The theoretically too large U-HFF (and magnetic moments discussed above) suggest that the localization of the U 5f electrons might be slightly overestimated in the current LDA+U method.

In conclusion, we have performed *ab initio* calculations of UO$_2$ in which we combined a full treatment of noncollinear magnetism, spin-orbit coupling, strong correlations, and oxygen cage distortions. We have investigated three different magnetic orderings proposed in the experimental literature. Our results strongly support a 3-**k** magnetic ordering with an oxygen cage deformation of the order 0.15–0.16 a.u. This ordering and deformation are essential to correctly predict the experimental EFG. EFGs determined for the collinear and noncollinear 2-**k** magnetic structures are in strong disagreement with experiment. The calculated EFG does not depend directly on the value of the Coulomb interaction U and the double-counting correction scheme but is very sensitive to the position of oxygens. These positions in turn depend on the details of LDA$+U$ setup. Considering density of states, $U=0.4$ Ry is a reasonable choice resulting in the band gap of order 2 eV. For this value of U, the calculated uranium EFGs are larger than the experimental values when AMF was applied and slightly smaller for the FLL scheme. The recent idea of interpolated LDA$+U$ functional (DFT-DCC) leads to a perfect agreement of calculated EFGs with the ones measured by Ikushima *et al.* The energetic stability of 3-**k** ordering relative to a collinear one depends on the details (AMF/FLL mixing factor), but the total energies stay close each other, which is reasonable considering the rather low ordering temperature (30.8 K). The EFGs being very sensitive to the magnetic ordering are a tool of choice for determining the actual magnetic structure.

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