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First-principles theory of multipolar order in actinide dioxides

Théorie *ab initio* de l'ordre multipolaire dans les dioxydes d'actinidesNicola Magnani^{a,*}, Michi-To Suzuki^{b,c}, Peter M. Oppeneer^d^a European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany^b CCSE, Japan Atomic Energy Agency, 5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8587, Japan^c RIKEN, Center for Emergent Matter Science (CEMS), Wako, Saitama, 351-0198, Japan^d Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden

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ABSTRACT

Magnetic phase transitions that involve multipolar degrees of freedom have been widely studied during the last couple of decades, challenging the common approximation which assumes that the physical properties of a magnetic material could be effectively described by purely dipolar degrees of freedom. Due to the complexity of the problem and to the large number of competing interactions involved, the simple (fcc) crystal structure of the actinide dioxides made them the ideal playground system for such theoretical and experimental studies. In the present paper, we summarize our recent attempts to provide an *ab initio* description of the ordered phases of UO_2 , NpO_2 , and AmO_2 by means of state-of-the-art LDA + U first-principles calculations. This systematic analysis of the electronic structures is here naturally connected to the local crystalline fields of the 5f states in the actinide dioxide series. Related to these we find that the mechanisms which lead to the experimentally observed insulating ground states work in distinctly different ways for each compound.

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R É S U M É

Les transitions de phases magnétiques impliquant des degrés de liberté multipolaires ont été beaucoup étudiées au cours des vingt dernières années, remettant en question l'approximation usuelle selon laquelle les propriétés physiques d'un matériau magnétique pourraient être convenablement décrites par des degrés de liberté purement dipolaires. Les problèmes à résoudre sont compliqués à cause du grand nombre d'interactions concurrentes concernées. C'est pour cette raison que les dioxydes d'actinides, avec leur structure cristallographique simple (cubique à faces centrées), représentent une classe de composés idéale pour aborder l'étude des ordres multipolaires, tant du point de vue théorique qu'expérimental. Dans cet article, nous résumons nos tentatives récentes, qui visent à fournir une description *ab initio* des phases ordonnées des composés UO_2 , NpO_2 , et AmO_2 au moyen de calculs LDA + U avancés. Cette analyse systématique de la structure électronique est ici intrinsèquement reliée au champ cristallin local qui détermine la composition des états 5f des ions actinides. Corrélativement à ceux-ci, nous mettons en évidence le fait que les mécanismes qui conduisent aux états fondamentaux isolants,

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observés expérimentalement, agissent de manière clairement différente pour chacun des composés de la série.

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1. A general introduction to multipolar order

Magnetically ordered materials have been used as navigational devices since long before a scientific understanding of their behavior was even attempted. As we now know, the basic necessary ingredient for magnetic order to occur is exchange interaction, a purely quantum-mechanical effect so called because the energy term associated with it arises from specific symmetry constraints on the wavefunction that is obtained when two indistinguishable particles are swapped (in the case of fermions, this is closely related to the Pauli exclusion principle). In one of the simplest pictures of interacting electrons, i.e., the molecular orbital model for the hydrogen molecule, this leads to a low-energy spectra composed of a singlet and a triplet, whose energy gap defines the exchange interaction. This result can be easily described in terms of the electron spins \mathbf{s}_i by the Heisenberg–Dirac Hamiltonian

$$H_{\text{HD}} = -2J_{12} \mathbf{s}_1 \cdot \mathbf{s}_2 \quad (1)$$

where J_{12} is the exchange constant. A generalization of (1) to atoms or ions with many electrons, having total spin S , reads:

$$H_{\text{HD}} = - \sum_{i>j} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2)$$

where i, j label the atoms and the J_{ij} are the inter-atomic exchange constants. This Hamiltonian can usually describe very well the magnetic properties of localized-electron materials if the orbital moment is quenched. If ligands shared by two magnetic ions are present, charge-transfer processes between the two ions are most likely mediated by the ligands rather than occurring directly between the ions. Some general features of this superexchange mechanism can already be described by the Heisenberg–Dirac formulation: for example the non-degenerate tight-binding Hubbard model with half-filling electron count, an effective hopping integral t describing charge transfer processes between pairs of nearest-neighbor sites (ij) and an intra-site Coulomb repulsion energy U that penalizes double occupation,

$$H_{\text{Hub}} = -t \sum_{(ij)} \sum_{\sigma=\uparrow,\downarrow} (a_{i,\sigma}^\dagger a_{j,\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3)$$

can be perturbatively mapped onto (2) with $J_{ij} = -2t^2/U$ in the limit $U \gg t$. The situation is more complex when orbital degrees of freedom cannot be neglected; even formally simple extensions of (3) which account for this feature contain a very large number of adjustable parameters and their use for quantitative studies is therefore unpractical [1].

One way to circumvent this problem is to replace the matrix elements appearing in these complex Hamiltonians by the use of conveniently defined effective operators with a strong physical identity. A typical, long-standing example is the commonly used formulation of the single-ion crystal-field potential in terms of Stevens' operator equivalents O_K^Q [2]:

$$H_{\text{CF}} = \sum_K \sum_Q C_K^Q O_K^Q \quad (4)$$

The O_K^Q operators are related to irreducible spherical tensors, and the number of adjustable parameters in (4) depends on the chosen set of basis states (for example, within a given configuration, terms with K larger than a certain value are ineffective and can be disregarded) and on the local symmetry of the system under study [3]. The same concept can be extended to two-ion interactions, which can take the general form:

$$H_{12} = \sum_{K,K'} \sum_{Q,Q'} I_{KK'}^{QQ'} O_K^Q(1) O_{K'}^{Q'}(2) \quad (5)$$

Because at the same time proper combinations of these irreducible spherical tensors can be associated with charge-like and magnetic-like observables, Eq. (5) can be interpreted as the sum of several contributions, each arising from the coupling between two specific electronic multipoles. Once again, the symmetry operations imposed by the original Hamiltonian affect which $I_{KK'}^{QQ'}$ coefficients are non-zero and the eventual relationships between them. For example, time-reversal invariance only allows coupling between multipoles with the same parity rank, and both the symmetry of the crystal and that of the bond between ions 1 and 2 must be considered as well.

Eq. (5) can drive a transition to a multipolar-ordered phase in very much the same way as (2) leads to conventional magnetic order under appropriate conditions. However, other terms in the Hamiltonian (in particular the single-ion crystal-field potential) usually reduce the active degrees of freedom at low temperatures, and therefore a strong interaction between two

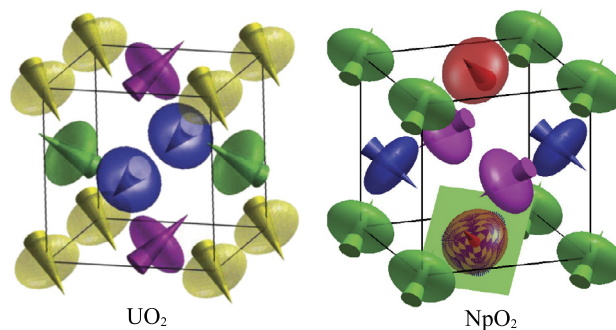


Fig. 1. (Left) Arrangement of the ordered magnetic moments (cones) and quadrupoles (ellipsoids) in the 3- \mathbf{k} phase of UO_2 . The four sublattices are labeled with different colors. (Right) Arrangement of the T_5 magnetic multipoles (MMPs) (cones) and of the induced T_5 quadrupoles (ellipsoids) in the 4-sublattices 3- \mathbf{k} ground state of NpO_2 . The slice displays the direction of the local magnetic field around one of the Np ions. The cones represent the local D_{3d} axes, and the direction in which they point illustrates the sign of the local multipole moment. Adapted from [1,11]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

multipoles does not guarantee that a purely multipolar-ordered state will be generated. As an example, consider a lattice of identical odd-electron magnetic ions, subject to a crystal-field potential that selects a well-isolated Kramers' doublet as the ground state. A phase transition driven by the interaction between magnetic multipoles breaks the time-reversal invariance of the crystal field, and therefore splits the ground doublet of each ion into two singlets, the lowest of which in general has a sizable dipole moment associated with it; as a consequence, magnetic dipoles also order and this multipole-driven transition might be experimentally indistinguishable from a conventional one. A different situation may occur when a magnetic transition is easily detected by peaks in bulk observables (such as susceptibility or specific heat), but the material shows no ordered moment when studied by local probes (such as Mössbauer, NMR or neutron diffraction), and it is often referred to as “hidden order” [4].

One of the reasons why actinide dioxides are regarded as archetypal systems to study multipolar order is that the O_h local symmetry at their crystallographically equivalent actinide sites means that the cubic crystal-field potential can lead to highly degenerate electronic ground states (threefold for U, fourfold for Np). Another reason is that the relatively large extension of their unfilled 5f electronic shell translates into a significant superexchange coupling (with respect for example to the lanthanide 4f orbitals), but at the same time these electrons remain mainly localized so that the orbital degrees of freedom are unquenched (unlike for the 3d electrons in most transition-metal-based compounds). Indeed, uranium dioxide shows a first-order transition to a transverse 3- \mathbf{k} state at $T_N = 31$ K driven by quadrupolar interactions [5–11]; in the ordered phase, the magnetic dipoles and the charge-like electric quadrupoles on four inequivalent sites are arranged according to different orientations along the cube diagonal (Fig. 1, left). Conversely, the transition at $T_H = 25$ K displayed by neptunium dioxide [12–16] is driven by a rank-5 magnetic multipole [1], which in turn triggers the order of electric quadrupoles in a longitudinal 3- \mathbf{k} arrangement (Fig. 1, right).

In the following, we will summarize the recent progresses in the theoretical study of multipolar order parameters in UO_2 , NpO_2 and AmO_2 by *ab initio* methods [17,18]. Apart for some brief remarks when necessary, we will not discuss the laborious experimental determinations of their order parameters (which is for the most part already covered by a comprehensive review paper [1]), nor recent theoretical work [19,20] on the same family of compounds that addresses some electronic structure aspects, but is unrelated to their multipolar ordered phases.

2. Uranium dioxide

As mentioned above, the low-temperature physics of UO_2 is dominated by a complex interplay of superexchange and magnetoelastic interactions, the latter essentially coupling lattice phonons with local electric quadrupoles [21]. Several different types of magnetically ordered structures were proposed as the ground state during the years [1], until the general consensus was reached on a transverse 3- \mathbf{k} arrangement of the dipole moments following neutron scattering experiments performed under an external magnetic field. Indeed, several years later, LDA + U *ab initio* calculations [22] that accounted for the noncollinear magnetic structure and distortions of the oxygen ligand cage showed that the electric field gradient calculated at the uranium sites is in agreement with nuclear quadrupole resonance measurements [23] only for a 3- \mathbf{k} magnetic structure. Nevertheless, both the value of the ordered moment and some distinctive features of the spin-wave spectra seemed to be better accounted for by a 1- \mathbf{k} order, at least until the separate roles of the Jahn–Teller and superexchange mechanisms as sources of quadrupolar interactions were properly accounted for [24]. Recently, the importance of these combined effects have been confirmed both experimentally, by polarized inelastic neutron scattering [11], and by *ab initio* electronic structure calculations by aspherical-self-interaction free DFT + U [20]; in the latter study all antiferromagnetic configurations are shown to be essentially degenerate as a result of the relatively weak and largely isotropic interactions between the magnetic centers, and only when lattice relaxations are properly taken into account, the 3- \mathbf{k} state becomes significantly lower in energy with respect to the others.

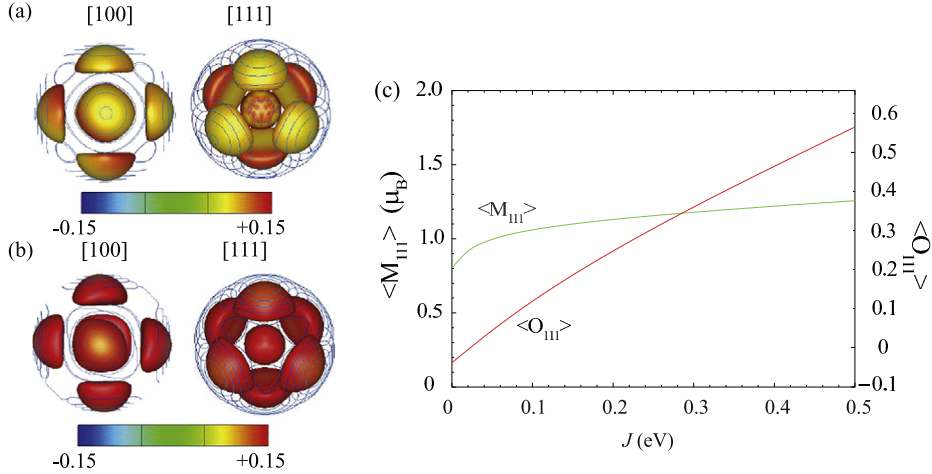


Fig. 2. (Color online.) Charge and magnetic distributions of the U-5f electrons in UO₂, *ab initio* computed with (a) $U = 4$ eV and $J = 0$ and (b) $U = 4$ eV and $J = 0.5$ eV. The distributions are viewed from the [100] direction and from the [111] threefold axis, as indicated above the corresponding panels. The charge distributions are depicted by the isosurface, and the distributions of magnetic moments $M_{111}(\mathbf{r}) = \frac{1}{\sqrt{3}}\{M_x(\mathbf{r}) + M_y(\mathbf{r}) + M_z(\mathbf{r})\}$ are shown by the color code and plotted on the isosurface of the charge density. (c) Computed expectation values of the total (orbital + spin) magnetic dipole moment and of the quadrupole moment $\langle O_{111} \rangle = \frac{1}{\sqrt{3}}[\langle O_{yz} \rangle + \langle O_{zx} \rangle + \langle O_{xy} \rangle]$ in UO₂ as a function of J . Adapted from [18].

The important role of electric quadrupolar ordering in the phase transition of UO₂ was studied by *ab initio* methods [18] by expressing the calculated LDA + U energy in terms of its multipole decomposition [25]. LDA + U electronic structure calculations were performed with an initial density matrix corresponding to the non-ordered state and allowing for self-consistent convergence to a symmetry-broken ordered phase. The value of U is fixed at 4 eV, a magnitude which is largely accepted as valid for this type of compounds and which, in the ordered phase, correctly reproduces the energy gap of about 2 eV measured for UO₂. Hund's coupling parameter J is varied between 0 and 0.5 eV. Fig. 2 shows the calculated charge and magnetic distributions of the U-5f electrons in UO₂ for the two limiting values of J ; the calculated ordered magnetic moment is significantly reduced with respect to that expected for the paramagnetic Γ_5 ground triplet, and a clear quadrupolar order parameter develops in the calculations and grows with J . One point that might be interesting to notice is the change in the quadrupole arrangement (shown by the change of sign in the expectation value in Fig. 2) for small values of J ; although this choice is apparently in contrast with experiment, we must remark that quadrupolar superexchange in UO₂ that is included in the calculations [18] is apparently on the same energy scale as spin–lattice-mediated interaction, and it has recently been suggested that the former is actually ferromagnetic [26], whereas the competition with the latter determines the overall antiferro-quadrupolar ordered structure.

3. Neptunium dioxide

After teasing physicists for more than 50 years [1], the “hidden order” parameter in the low-temperature phase of NpO₂ was recognized to be a magnetic (odd-rank) multipole [12]. Shortly thereafter, its symmetry was clarified by directly observing the associated antiferro-quadrupolar order [13]. Initially thought to be an octupole (rank 3), the primary order parameter was later suggested to be a rank-5 triakontadipole by careful studies of the low-energy excitation spectra [15,16]. An attempt to quantify the relative magnitude of different multipolar superexchange interactions from the microscopic point of view was made by means of a Hubbard-type model, whose hopping part H_{hop} has the same basic structure as that of Eq. (3), but takes into account that hopping between different orbitals m on neighboring sites generally has a different amplitude [1]:

$$H_{\text{hop}} = \sum_{(ij)} \sum_{mm'=-3}^3 \sum_{\sigma} t_{i,j}^{mm'} (a_{i,m\sigma}^{\dagger} a_{j,m'\sigma} + \text{h.c.}) \quad (6)$$

As discussed above, assuming that the energy cost of a double occupation U (which, unlike the hopping amplitude, has been considered as independent of the specific state), charge-transfer processes can be eliminated by second-order perturbation theory. The resulting Hamiltonian was then projected on the lowest $^4I_{9/2}$ manifold of Np⁴⁺ and the multipolar superexchange coefficients appearing in (5) were determined. Since no estimate of the individual hopping parameters is available, this procedure was repeated varying the ten independent hopping parameters relative to a bond of C_{2v} symmetry on a hypercubic grid; the results are given in Fig. 3 and clearly show the importance of the interactions between almost all higher-order multipoles, in particular those of rank 5 (and 6). Some energy terms involving two multipoles of different ranks, not shown in Fig. 3, were also found significant [1].

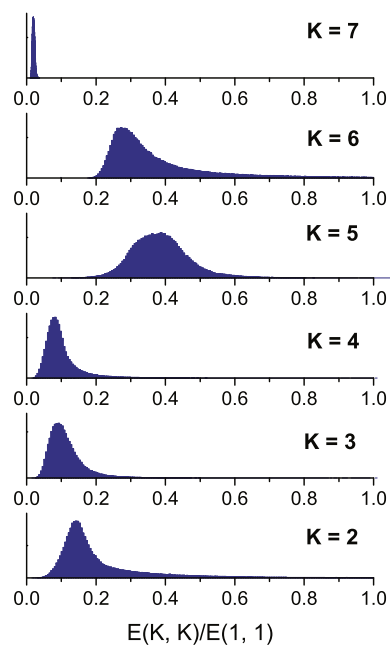


Fig. 3. (Color online.) Distribution of the ratio $E(K, K)/E(1, 1)$, with $E(K_i, K_j)$ being the ground-state energy of a dimer (C_{2v} bond) of Np^{4+} ions associated with a specific pair of ranks K_i, K_j . The relative values of ten independent $t_{i,j}^{r_i r_j}$ coefficients (which refer to the hopping integrals between the orbitals of the magnetic ions labeled by definite irreps of the C_{2v} symmetry group, and define the $t_{i,j}^{m m'}$ hopping parameters of Eq. (6) through linear combinations) are varied on a hypercubic grid. Adapted from [1].

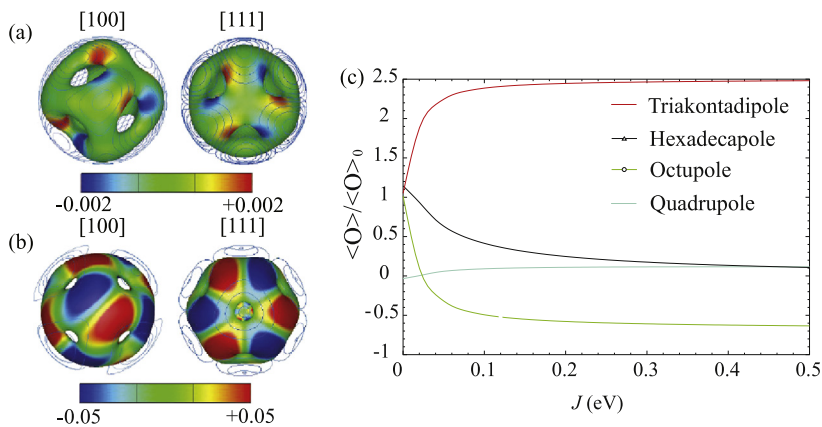


Fig. 4. (Color online.) Charge and magnetic distributions of the Np-5f electrons in NpO_2 , computed with (a) $U = 4$ eV and $J = 0$ and (b) $U = 4$ eV and $J = 0.5$ eV (for details see the caption of Fig. 2). (c) Computed expectation values of four possible J_5 multipolar order parameters in NpO_2 as a function of J . Adapted from [17,18].

Naturally, the fact that multipolar superexchange interaction is sizable is not the only factor that must be taken into account to understand the ordered phase, since the single-ion crystal-field potential can strongly affect the multipolar susceptibility [15]. For this reason, LDA + U calculations of the electronic structure density in the ordered phase of NpO_2 have been performed and the expectation values of multipolar operators of various ranks have been extracted as already discussed for UO_2 . Fig. 4 clearly shows that, when Hund's rule J is turned on, the magnetic distribution is dominated by odd-rank multipoles as several close areas with opposite directions of the local magnetic vector alternate around the Np ion. The plot also shows that the main contribution arises from the rank-5 triakontadipoles, a first-principles confirmation of the important role of this unique parameter in the hidden-order phase of NpO_2 .

4. Americium dioxide

Mostly because of the experimental difficulties involving minor actinides, the low-temperature properties of AmO_2 are not yet as well-known as for its U and Np counterparts [27]. The signature of an antiferromagnetic transition is visible

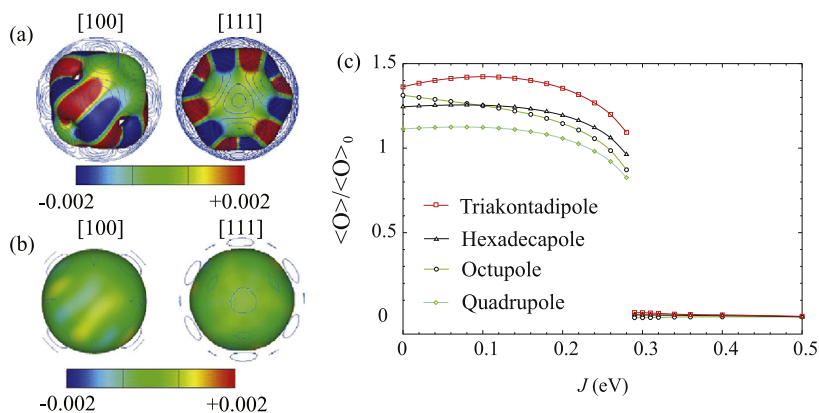


Fig. 5. (Color online.) Charge and magnetic distributions of the Am-5f electrons in AmO₂, computed with (a) $U = 4$ eV and $J = 0$ and (b) $U = 4$ eV and $J = 0.5$ eV (for details see the caption of Fig. 2). (c) Computed expectation values of four possible Γ_5 multipolar order parameters in AmO₂ as a function of J . Adapted from [18].

at 8.5 K in its magnetic susceptibility curves as well as in ¹⁷O NMR spectra [28], but no evidence of dipolar order was found by Mössbauer or neutron diffraction [1]. It seems then natural to suggest that this is a case of magnetic multipolar order not unlike NpO₂, but there are some questions to consider. Crystal-field calculations [29] and EPR measurements [30] suggest that the ground state in the paramagnetic phase is the doubly degenerate Γ_7 (rather than the Γ_8 quartet as in NpO₂), which does not support multipolar order without the concurrent ordering of magnetic dipoles. However, a Γ_8 ground state cannot be ruled out on the basis of available data [31].

In the case of AmO₂, LDA + U calculations (see Fig. 5) lead to a 3- \mathbf{k} ordered state with a sizable contribution from higher-rank multipoles only for relatively small values of the Hund's coupling parameter J . Whereas increasing J makes a magnetic solution more favorable [18], for $J > 0.3$ eV the expectation value of all higher-rank multipoles drops to zero. Even for smaller values of J the relative weight of the different multipolar components is very different from that found for NpO₂ [17], where increasing J above a certain threshold rather stabilizes the non-zero triakontadipole expectation value, despite the same symmetry of the ordered phase. The possible involvement of multipolar degrees of freedom is especially interesting in the light of recent measurements performed on a freshly-prepared sample in order to avoid lattice distortions due to self-irradiation effects; in fact, the rapid broadening of the ¹⁷O NMR spectra seems to indicate a short-range, spin-glass nature of the transition [32].

5. Conclusions

First-principles LDA + U calculations can reproduce the low-temperature multipolar ordered phases characteristic of the actinide dioxides family, using values of the U and J parameters within the usually accepted range. These calculations selfconsistently treat the actinide–ligand hybridization effects and provide access to the multipole–multipole superexchange coupling that is responsible for the long-range order. The active multipoles in the ordered states are found to be strongly dependent on the orbital occupation. The strong electronic correlation typical of 5f electrons, in terms of their spin-orbit and Coulomb repulsion, is found to be a crucial ingredient to reproduce the insulating ground states of these compounds [18].

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