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Crystal fields in UO₂ - revisited

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Abstract. We performed inelastic neutron scattering (INS) in order to re-investigate the crystal-field ground state and the level splitting in UO₂. Previous INS studies on UO₂ by Amoretti et al. [Physical Review B 15, 1989, 1856] uncovered four excitations at low temperatures in the 150-180 meV range. Considering the dipole-allowed transitions, only three of these transitions could be explained by the published crystal-field model. Our INS results on a different UO₂ sample revealed that the unaccounted peak at about 180 meV is a spurious one, and thus not intrinsic to UO₂. In good agreement with Amoretti’s results, we corroborated that the ground-state of UO₂ is the \( \Gamma_5 \) triplet, and we computed that the fourth- and six-order crystal field parameters are \( V_4 = -116 \) meV and \( V_6 = 26 \) meV, respectively. We also studied the INS response of the non-magnetic \( \text{U}_0.4\text{Th}_0.6\text{O}_2 \). The splitting for this thorium-doped compound is similar to the one of UO₂, which orders antiferromagnetically at low temperatures. Therefore, we can conclude that magnetic interactions only weakly perturb the energy level splitting, which is dominated by strong crystal fields.

1. Introduction
Uranium dioxide (UO₂) crystallizes in the cubic CaF₂ structure (space group: Fm\( \overline{3} \)m) and it is an important nuclear fuel material [1]. In basic sciences, UO₂ attracted much attention because it is one of very few actinide compounds, for which some properties are consistent with localized 5f electrons [2]. The cubic crystalline environment of the \( \text{U}^{4+} \) ions and application of Hund’s rules result in a nine-fold degenerate \( \text{H}_4 \) ground state for the 5f\( ^2 \) electrons in UO₂ [3]. Strong crystal fields lift the degeneracy into a \( \Gamma_1 \) singlet, a \( \Gamma_3 \) doublet, and two triplets, \( \Gamma_4 \) and \( \Gamma_5 \). Here, \( \Gamma_n \) represents the different states of the irreducible representation of the cubic point group.
The cubic crystal field Hamiltonian in the Russell-Saunders or the intermediate coupling (IC) schemes is given by \[ H_{CF} = V_4 \beta [\hat{O}_4^0(J) + 5\hat{O}_4^+ (J)] + V_6 \gamma [\hat{O}_6^0(J) - 21\hat{O}_6^+ (J)], \]

where \( \hat{O}_n^w \) are the Stevens operator equivalents, \( \beta \) and \( \gamma \) are the reduced matrix elements of the \( J \) manifold, and the parameters \( V_n \) are the coefficients of the crystal field potential.

Using a point charge model, Rahman and Runciman [5] successfully diagonalized the complete Hamiltonian for paramagnetic UO\(_2\) taking into account \( J \) mixing due to crystal field effects. Combining the matrices of the cubic crystal field potential for the \( f^2 \) configuration with the electrostatic and spin-orbit matrices, they predicted that \( \Gamma_5 \) is the ground state for UO\(_2\) and they computed \( V_4 = -409 \) meV and \( V_6/V_4 = 0.06 \). It should be noted, however, that the point charge model tends to underestimate the sixth-degree term, as it does not take into account overlap and covalency effects.

### 2. Previous neutron scattering data and analysis

With the advent of spallation sources and chopper spectrometers, UO\(_2\) was one of the first materials to be examined for high-energy excitations. Kern et al. (1985) [6] reported excitations near 160 meV. Later, with the better resolution of HET at ISIS, a more detailed study was reported [7].

The experimental results corroborated the theoretically predicted \( \Gamma_5 \) ground state; however, the values for \( V_4 = -123 \) meV and \( V_6/V_4 = 0.22 \) determined from experiments were very different from the theoretical predictions above. Moreover, for temperatures below 40 K, the experimental data did provide evidence for four excitations with energy transfers of 149, 157, 169 and 179 meV. Cubic symmetry does not permit four transitions.

On the other hand, it is well established that the oxygen sublattice in UO\(_2\) exhibits a dynamical Jahn-Teller distortion, when the compound orders antiferromagnetically at \( T_N = 30.8 \) K [8, 9]. Both effects reduce the point symmetry at the U site. Nevertheless, even a sophisticated lattice-sum point charge model (PCM) assuming a triple-\( k \) monoclinic distortion and intermediate coupling (IC) predicts only three transitions at 147, 154 and 165 meV [7], while the fourth excitation around 180 meV is still unaccounted for.

### 3. Motivation and experimental approach

It is possible to avoid the complication due to magnetic ordering and the accompanied structural distortions by diluting the uranium sublattice so that magnetic long-range order is suppressed. In a study of UO\(_2\)-ThO\(_2\) solid solutions, it was found that the Néel temperature decreases linearly, and magnetic order vanishes when about half of the uranium is replaced by thorium [10].

The Institute for Transuranium Elements (Karlsruhe, Germany) provided two high-quality samples, pure UO\(_2\) and U\(_{0.4}\)Th\(_{0.6}\)O\(_2\). The latter composition was chosen as a non-magnetic counterpart to the magnetic UO\(_2\).

Inelastic neutron scattering experiments were performed using the time-of-flight spectrometer PHAROS at the Los Alamos Neutron Science Center. For the studies, we used powdered samples of UO\(_2\) with total mass of about 190 g and U\(_{0.4}\)Th\(_{0.6}\)O\(_2\) with mass of about 170 g. Data for UO\(_2\) were collected at 30 and 50 K and data for U\(_{0.4}\)Th\(_{0.6}\)O\(_2\) were collected at 17 and 50 K. Data were collected for 12-24 hours at each temperature, and we used incident beam energies of 243 meV. Correction for background, incident beam intensity, detector efficiencies and absorption was applied.

### 4. Results and discussion

All of the PHAROS data exhibit three distinct sets of features: a strong elastic peak around zero-energy transfer, three phonon peaks between 30 and 75 meV energy transfers, and multiple crystal-field excitations in the 145-175 meV range. For this contribution, we concentrate on the features arising from the crystal fields in both compounds.
Figure 1 shows the INS data for U$_{0.4}$Th$_{0.6}$O$_2$ at 17 K (left) and pure UO$_2$ at 50 K (right). It should be noted that we observed only very little difference in the response at 17 and 50 K for the non-magnetic U$_{0.4}$Th$_{0.6}$O$_2$, as expected. As can be seen in figure 1, there are two clear excitations in the INS response of U$_{0.4}$Th$_{0.6}$O$_2$ at energy transfers of ~149 and 169 meV. Comparing the results of the thorium-doped sample with the INS data on pure UO$_2$ at 50 K (paramagnetic region), we find that the positions of the two excitations are essentially unchanged and that the integrated intensities scale roughly with the uranium content, although the peaks are slightly broader in UO$_2$ (not resolution-limited). Nevertheless, our comparison provides evidence that the energy level splitting in UO$_2$ is only marginally affected (if at all) by short-range magnetic correlations at temperatures just above T$_N$.

Figure 2 shows the INS data on pure UO$_2$ taken at 30 K (just below T$_N$). Unlike the 50-K UO$_2$ data, fitting the observed spectrum at that temperature requires at least three Gaussians, and we were able to achieve a good fit assuming Gaussians centered at energy transfers of ~150, 158 and 170 meV. The peak positions of the three excitations and the overall shape of our INS curve are in excellent agreement with the previously published data taken at comparable temperatures [7] with one important exception: namely, the peak around 180 meV is absent. Therefore, we conclude that the previously observed excitation at ~180 meV is not intrinsic to UO$_2$.

**Figure 1.** Normalized inelastic neutron scattering spectra for U$_{0.4}$Th$_{0.6}$O$_2$ at 17 K (left) for pure UO$_2$ at 50 K (right), as taken on PHAROS. The experimental data were fitted using the two Gaussians shown. Note the different scales for the two samples.

**Figure 2.** INS spectrum of UO$_2$ taken at 30 K (below T$_N$). The experimental data were fitted using the three Gaussians shown.
We used our data then to compute the crystal-field coefficients for cubic symmetry given in equation (1). The crystal-field energy matrices were calculated using the Stevens’ operator equivalent method. We used a computer code by Crosswhite and Crosswhite [11] to determine the crystal field parameters for UO₂. Results for \( V_4 \) and \( V_6 \) in UO₂ for this and previous studies are listed in table 1.

| | experimental data (this result) | experimental Data [7] | PCM with \( J \) mixing [5] | lattice-sum PCM and IC [7] |
|---|---|---|---|---|
| \( V_4 \) (meV) | -116.2 | -123.0 | -409.0 | -80.9 |
| \( V_6 \) (meV) | 25.8 | 26.5 | 24.8 | 8.7 |
| \( V_6/V_4 \) | -0.22 | -0.22 | -0.06 | -0.11 |

Our crystal-field coefficients are in very good agreement with values determined from previous experiments, but neither theoretical model provides a satisfactory agreement with the experimental data. Both theoretical models assumed that the ground state is the \( \Gamma_5 \) triplet, followed by the \( \Gamma_3 \) doublet, the \( \Gamma_4 \) triplet and the \( \Gamma_1 \) singlet. In that sequence, one would label \( \Delta E_1 \sim 150 \text{ meV} \) as due to transitions between \( \Gamma_5 \) and \( \Gamma_3 \), \( \Delta E_2 \sim 158 \text{ meV} \) as due to transitions between \( \Gamma_5 \) and the lower two energy levels of \( \Gamma_4 \), and \( \Delta E_3 \sim 170 \text{ meV} \) as due to \( \Gamma_5 \) and the third level of the \( \Gamma_4 \) triplet.

Considering the transition strength between energy levels in UO₂, we calculated theoretical ratios of \( \Delta E_2/\Delta E_1 = 0.57 \) and \( \Delta E_3/\Delta E_1 = 0.29 \), while our experimental values (determined using the integrated intensities) are essentially reversed, i.e. \( \Delta E_2/\Delta E_1 = 0.26 \) and \( \Delta E_3/\Delta E_1 = 0.55 \).

In general, for the light actinide dioxides, the transition energies are consistent with the crystal-field scheme [12]. However, the individual matrix elements, especially those involving the ground states, still present a problem. Despite their simple crystal structure and many investigations, a full understanding requires consideration of higher-order terms [13].

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