Crystal-field spectroscopy of PuO$_2$: further complications in actinide dioxides

LETTER TO THE EDITOR

Crystal-field spectroscopy of PuO_2: further complications in actinide dioxides

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Abstract. Neutron spectroscopy has been performed on a sample of PuO_2, enriched to 94% with the non-absorbing isotope ^{242}Pu, to measure the crystal-field potential. We find levels consistent with the weak-field case crystal-field parameters recently derived for UO_2 and NpO_2, but inconsistent with a weak-field interpretation of the magnetic susceptibility measurements on PuO_2. In the light of these discrepancies we believe that the conventional crystal-field model is inadequate. PuO_2 is probably the simplest material to test any new ideas because the ground state is a non-magnetic singlet.

The advent of spallation neutron sources has meant that large electronic energy transfers (up to ∼1 eV) can be measured for the first time by neutron spectroscopy. So far experiments have been performed on the rare-earth and actinide dioxides [1–3] and on the rare-earth metals [4, 5]. These experiments are difficult because of the restrictions imposed on the momentum transfer, Q, in the scattering process. For dipole electronic transitions $|Q| \leqslant 4$ Å so that incident neutron energies of above 1 eV have to be used in some cases. Neutrons of such energies are unavailable at a conventional reactor source.

In this letter we draw attention to already published results for the inelastic neutron scattering of the tetravalent actinide dioxides UO_2 [2, 3] and NpO_2 [6, 7], and we present new results for PuO_2. The level structure now observed for PuO_2 is consistent with the conventional, weak crystal-field interpretation of the levels found in these other dioxides. But our observed level structure for PuO_2 is completely *inconsistent* with the corresponding weak crystal-field analysis of the magnetic susceptibility of PuO_2 [8]. We offer some qualitative remarks on this contradiction and introduce evidence from the magnetic susceptibility of CmO_2 ([9] and references therein) to suggest a new theoretical viewpoint that shows promise in resolving this contradiction.

According to the weak-field approach, the crystal-field (CF) potential arising from the arrangement of electrostatic charges in a solid acts to lift the degeneracy of the electronic ground state of an open-shell ion such as the tetravalent actinides. In cubic materials this potential may be characterised by two terms, V_4 and V_6, the fourth- and sixth-order potentials, respectively. In a classic paper Rahman and Runciman [10] used a modified point charge model together with strong coupling (i.e. leading to a ground state with mixed J composition) to obtain values of $V_4 = -409$ meV, and $V_6 = +25$ meV

for UO_2. For the f^2 system this model predicts the Γ_5 triplet to be lowest, with allowed transitions to Γ_3 (170 meV) and Γ_4 (624 meV).

The early work on UO_2 at the Argonne National Laboratory showed that there were at least two neutron inelastic scattering peaks [2] in the energy range 140–180 meV. However, the recent high-resolution experiments at the ISIS [3] spallation source (Rutherford Appleton Laboratory, UK) have shown that there are *many* (at least 4) peaks in this energy range, and that there are no other transitions of any appreciable strength up to ~800 meV. This work on UO_2 has been interpreted according to the weak-field approach to show that both Γ_3 and Γ_4 excited states are below 200 meV and that the $|V_4|$ potential is considerably smaller than estimated by Rahman and Runciman. In fact, Osborn and co-workers [3] proposed that $V_4 = -123(5)$ meV and $V_6 = 27(10)$ meV. The hyperfine splitting of the main peaks is postulated as arising from quadrupolar effects in the magnetically ordered state ($T < 30$ K). The important parameter, V_4, is thus only 30% of that estimated by Rahman and Runciman [10]. This lowering of V_4 has the consequence, in at least the conventional model, that the extent of J-mixing is decreased substantially. Thus, the experiments *appear* to suggest that the ground state wavefunctions can be expressed almost entirely within a simple single J ground-state manifold [3], much as is commonly accepted for lanthanide systems. For NpO_2 the situation is more complex because a number of experimental investigations suggest a strong coupling between the electronic and vibronic states [11], but the neutron experiments seem consistent with $V_4 \sim -120$ meV [6, 7].

We anticipate that within the conventional weak-field approach the V_4 values should be fairly constant across the series UO_2, NpO_2 and PuO_2, so we may now examine the latter compound. Tetravalent Pu^{4+} has a $5f^4$ configuration with a $J = 4$ ground state ($^5I_4$). For $V_4 < 0$, $V_6 > 0$ (cubic coordination) the ground state is a Γ_1 non-magnetic singlet with the Γ_4 triplet being the first excited state. In the weak-field approach and using the notation of Lea and co-workers [12] this corresponds to $W > 0$ and $x < 0.5$ and the Γ_1 state is stable over a wide range of x. PuO_2 should therefore be non-magnetic and this is confirmed by magnetic susceptibility [8, 13] and heat capacity [14] work. These measurements, both performed up to at least 1000 K can also give us information on the excited states. Raphael and Lallement [8] found a flat temperature independent susceptibility with a value (after correcting for small diamagnetism) of 536 μemu mol^{-1}. Using the simple formulation of Lea and co-workers [12] they deduced a splitting (which we shall call Δ) between the Γ_1 ground and Γ_4 excited states of 284 meV. In this formulation

$$X \propto |\langle \Gamma_1 | J_z | \Gamma_4 \rangle|^2 / \Delta \tag{1}$$

where X is the susceptibility and J_z is the matrix angular momentum operator. No orbital reduction factor is used here. This simple formula relies on the fact that matrix elements between Γ_1 and the other states arising from $J = 4$ (which will be at higher energies) are zero. Such a large value of Δ implies a $V_4 \sim -320$ meV; a value much larger than the recent interpretations of the UO_2 spectra discussed above.

We have used an intermediate-coupling crystal-field calculation that includes the 100 lowest-energy states of the f^4 configuration to confirm the reliability of the susceptibility calculation [12] for this weak-field case. We have also verified that one can use an orbital reduction factor of 0.625 to calculate the susceptibility and thereby obtain the values 111 and −125 meV for Δ and V_4, respectively. It is important to note, however, that introduction of such a substantial orbital reduction factor would be a significant departure from the weak-field approach.

A value of Δ as large as 284 meV is also inconsistent with the accepted interpretation of the high temperature ($T > 500$ K) heat capacity data. Fink [15] has reviewed the work on actinide oxides and it is clear from the excess heat capacity of the non-5f electron system ThO_2 that additional contributions for PuO_2 are already apparent by 500 K. In fact, they exceed those observed in UO_2 over the range 500–1500 K. Although defect formation plays a role in the oxides at above $\sim$1500 K, the excess contributions over the ThO_2 value at lower temperature are almost certainly magnetic in origin. If $\Delta = 284$ meV with the first Γ_4 state at 3300 K, there would be a negligible contribution to the heat capacity at 500 K. The heat capacity data [14, 15] and *weak-field interpretation* of the magnetic susceptibility (with equation (1) and $k = 1$) are therefore inconsistent.

We now present the neutron spectroscopy results for PuO_2. The experiments were performed at the Intense Pulsed Neutron Source, Argonnne National Laboratory, with two different chopper spectrometers. The experimental conditions have been described previously [2, 6]. The sample was a finely divided powder (75 g) of PuO_2, enriched to 94% in the non-absorbing isotope ^{242}Pu, and held in a double-walled Al container. The sample thickness was 0.4 cm parallel to the beam, and the transmission was 0.82. The sample was cooled in a Displex cryostat to a temperature of 20 K. The lattice parameter is 5.395(1) Å, which is consistent with an oxygen/Pu ratio of 2.0. The particles are of very fine grain with a radius (as determined by the line-broadening observed in the x-ray diffraction patterns) of $\sim$120 Å. Chemical analysis (by weight) of the sample just before the neutron experiment gave 0.9% of Am, 30 ppm Fe, 130 ppm U, and <20 ppm of all other metals.

Figure 1 shows the intensity of the scattered neutrons between 40 and 160 meV with the sample at $\sim$20 K. These data were collected on the LRMECS spectrometer which has the advantage of a continuous bank of detectors so that Q-values from 3 to 14 Å^{-1} may be examined. The incident neutron energy was 200 meV. This allows a separation of phonon or nuclear vibration effects that arise from the neutron–nuclear interaction and have an intensity

$$I_N \propto Q^2 \exp(-\alpha Q^2) \tag{2}$$

where the exponential factor represents the Debye–Waller factor, and magnetic effects that arise from the interaction between the magnetic moment of the neutron and the magnetic moments in the sample. This latter may be written as

$$I_M \propto \langle M_n \rangle^2 f^2(Q) \exp(-\alpha Q^2) \tag{3}$$

where $\langle M_n \rangle^2$ represents the neutron matrix element, $f(Q)$ is the atomic factor, and the exponential term is the Debye–Waller factor. The magnetic form factor may be simply approximated as

$$f^2(Q) \simeq \exp(-0.06\, Q^2) \tag{4}$$

for Pu^{4+}. The result of these Q dependences is that nuclear and magnetic interactions may be separated easily for modest (<12 Å^{-1}) Q-values; the scattering from nuclear interactions *increase* with Q, whereas that from magnetic interactions *decrease* with Q. The LRMECS data on PuO_2 show clearly that the peak at $\sim$90 meV is nuclear in origin, and that at $\sim$120 meV is magnetic in origin. Further analysis of the 90 meV peak shows that it arises from atomic hydrogen in the sample. The α derived from equation (2) is 0.012 Å^{-2} corresponding to B (in the conventional Debye–Waller notation) $\simeq$1 Å^{-2}. This signal peaks at $Q \sim 9$ Å^{-1}. At this temperature this behaviour is characteristic of atomic hydrogen. It should be recalled that hydrogen has an incoherent cross section
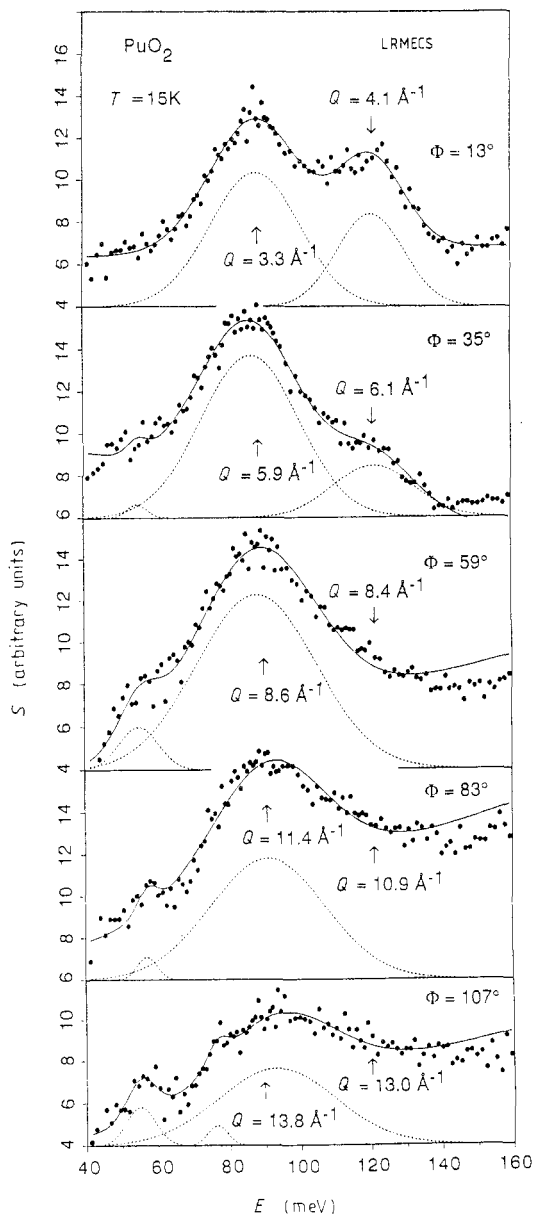
Figure 1. Neutron spectra as a function of scattering angle Φ taken at the LRMECS spectrometer on the sample of PuO_2 ($T = 15$ K). The Q-values are marked on the plot. The full curve is the best fit to the data points and the individual Gaussian peaks making up the calculated line are shown by dotted curves. The 90 meV peak arises from atomic hydrogen in the sample, whereas the 120 meV peak is magnetic in origin. Peaks below 80 meV arise from oxygen phonons.

almost two orders of magnitude greater than any other element, so neutron experiments are extremely sensitive to small amounts of hydrogen. The fine particle nature of the sample makes it quite likely that OH has been absorbed on the large surface area. A similar signal was observed in early experiments on Pr and Nd metal [4] but was not observed previously in experiments on oxide systems [1, 2, 5, 6, 7]. The one-phonon spectrum of UO_2 extends to $\sim$80 meV [16] and will be similar for PuO_2. It is clear that neither of these peaks arises from the phonons in PuO_2, and this is consistent with our observations of ThO_2, for which the phonon spectra should be very similar.
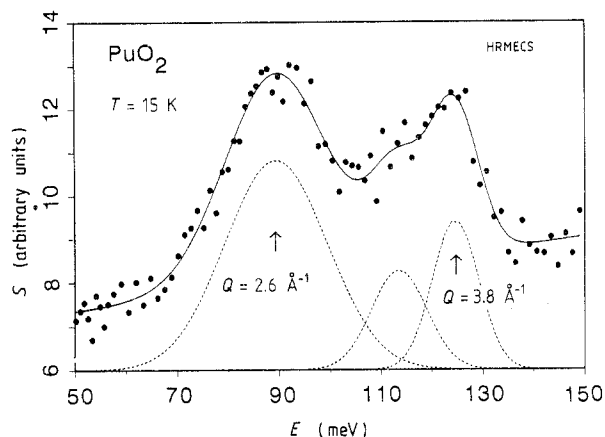
Figure 2. Higher resolution data taken on the HRMECS spectrometer (incident energy 200 meV, $T = 20$ K, resolution ~ 6 meV) showing the possible splitting of the magnetic peak at 120 meV.

We now concentrate on the 120 meV peak; the Q-dependence of this peak in figure 1 clearly indicates that it is magnetic in origin. Using the HRMECS spectrometer with higher resolution ($\Delta E = 6$ meV at $E_0 = 200$ meV) we show the best fit in figure 2. As expected, the peak at 90 meV is still present at $Q \sim 3$ Å^{-1}, but the 120 meV peak is clearly broad. A single peak fit (not shown) gives a width of 25 meV. Figure 2 shows a fit with two peaks, one at 114 ± 4 meV and one at 125 ± 2 meV, both with a peak width of ~ 12 meV (i.e. twice the resolution). Higher incident energy neutrons were used to establish that no other strong transitions exist up to 300 meV. This is not surprising. Dipole matrix elements exist *only* between the Γ_1 and Γ_4 states—thus we expect a single peak giving unambiguously Δ, the Γ_1–Γ_4 separation.

The first point to note from figure 2 is that the excitation energy is ~ 120 meV, which, in the weak-field model, corresponds to $V_4 \sim -120$ meV. From our discussion above, this is clearly consistent with accepted values of V_4 for UO_2 and NpO_2, but completely inconsistent with the weak-field interpretation of the bulk susceptibility of PuO_2. The second point is that the 120 meV feature is at least noticeably broad and may represent more than one peak. At this stage the resolution and statistical information in figure 2 are not sufficient to establish whether there are two (or more) peaks in an electronic transition in the energy region 110–140 meV. This aspect remains an important point for future studies. More than one electronic transition in this energy range for PuO_2 with a cubic lattice could be a qualitatively important result that would indicate that the interactions between two or more Pu atoms need to be considered to explain these features. For now it is quantitatively significant that our observation of the first excited electronic state in PuO_2 at 120 meV leads to a factor of 2 disagreement between the observed and calculated magnetic susceptibilities within the accepted weak-field model for the actinide dioxides, a factor substantially greater than the usual level of agreement for this type of comparison [17].

We may summarise the problem of incorporating our neutron inelastic scattering results for PuO_2 into the conventional view of the electronic structure for actinide dioxides as follows. Assuming $V_4 \sim 120$ meV, which is the value derived from the weak-field analysis of the UO_2 spectra [3], we would expect a single, reasonably sharp excitation in the neutron inelastic experiment at ~ 110 meV together with a value of ~ 1200 μemu mol^{-1} for the low-temperature magnetic susceptibility and very little temperature dependence of this susceptibility. Such a small value of V_4 would suggest

that the coupling is weak and that the ground-state is predominantly $^5I_4$ with an orbital reduction factor near 1. The neutron experiments do indicate a broad peak in energy at about 120 meV. The position of this peak is in satisfactory agreement with our expectation from the weak-field model. Moreover, the V_4 parameter appears approximately the same for the early actinide tetravalent dioxides, again consistent with expectations. The width of the peak is somewhat of a problem, which will be made more serious if future experiments indicate a resolvable multiple peak structure. Having observed the excited state at the energy predicted by the weak-field model should give us increased confidence in the parallel prediction of the magnetic susceptibility. However, the experiments yield a value of 536 μemu mol^{-1} [8], roughly one half the predicted quantity.

In addition to the features of UO_2, NpO_2 and PuO_2 discussed above, we must also take into account the magnetic susceptibility of $^{248}CmO_2$, which has recently been carefully re-investigated and shown to yield an effective moment of 3.36 μ_B for *unambiguously stoichiometric* CmO_2 [9]. In the weak-field regime this result makes no sense. In this case, one starts from the $^7F_0$ ground state for an f^6 system in the weak-field regime and there is no sensible way to make this state yield an effective moment near 3 μ_B. In the strong-field limit, on the other hand, the seven-orbitals can split in a cubic crystal field so that the two sets of three-fold degenerate orbitals are much lower in energy than the non-degenerate orbital. In the case where the spin-pairing energy [18] is substantially larger than the separation between these two triply degenerate sets, the Hund rule ground state of the f^6 system is a $^7A_{1g}$ state. This state has an effective moment of 6.93 μ_B. Thus, somewhere between the weak-field and the strong-field limit one can anticipate that there occurs an intermediate value for the effective moment of order 3 μ_B.

We conclude that a growing body of results for the actinide dioxides seems to indicate that the crystal-field strength in these compounds may actually be larger, rather than smaller, than the range of parameters originally proposed by Rahman and Runciman [10]. One of us is currently developing this point of view into a more complete analysis [19].

References

[1] Kern S, Loong C-K, Faber J and Lander G H 1984 *Solid State Commun.* **49** 295
[2] Kern S, Loong C-K and Lander G H 1985 *Phys. Rev.* B **32** 3051
[3] Osborn R, Taylor A D, Bowden Z A, Hackett M A, Hayes W, Hutchings M T, Amoretti G, Caciuffo R, Blaise A and Fournier J M 1988 *J. Phys. C: Solid State Phys.* **21** L931; 1989 *Phys. Rev.* B **40** 1856
[4] Stirling W G, Mc Ewen K A and Loong C-K 1986 *Physica* B **136** 420
[5] Taylor A D, Osborn R, Mc Ewen K A, Stirling W G, Bowden Z A, Williams W G, Balcar E and Lovesey S W 1988 *Phys. Rev. Lett.* **61** 1309
[6] Kern S, Morris J, Loong C-K, Goodman G L, Lander G H and Cort B 1988 *J. Appl. Phys.* **63** 3598
[7] Fournier J M, Blaise A, Larroque J, Amoretti G, Caciuffo R, Hutchings M, Osborn R, Taylor A D 1989 *J. des Actinides* (Abstract C22) unpublished
[8] Raphael G and Lallement R 1968 *Solid State Commun.* **6** 383
[9] Morss L R, Richardson J W, Williams C W, Lander G H, Lawson A A, Edelstein N M and Shalimoff G V 1990 *J. Less-Common Met.* at press
[10] Rahman H U and Runciman W A 1966 *J. Phys. Chem. Solids* **27** 1833
[11] Friedt J M, Litterst F J and Rebizant J 1985 *Phys. Rev.* B **32** 257

[12] Lea K R, Leask M J M and Wolf W P 1962 *J. Phys. Chem. Solids* **23** 1381
[13] Lam D J cited in reference [14] below
[14] Kruger O L and Savage H 1968 *J. Chem. Phys.* **49** 4540
[15] Fink J K 1982 *Int. J. Thermophys.* **3** 165 (see figure 5 therein)
[16] Dolling G, Cowley R A and Woods D B 1965 *Can. J. Phys.* **43** 1397
[17] See, for example:
　　Guo M D, Aldred A T and Chan S K 1987 *J. Phys. Chem. Solids* **48** 229
　　Moore J R, Nave S E, Hart R C, Wilmarth W R, Haire R G and Peterson J R 1988 *Phys. Rev.* B **38**
　　　2695
[18] Griffith J S and Orgel L E 1957 *J. Chem. Phys.* **26** 988–92
[19] Goodman G L to be published