Crystal-field transition in PuO_2

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A single peak at 123 meV has been found in the neutron inelastic-scattering spectrum of PuO_2 measured on the PHAROS chopper spectrometer at LANSCE. This is ascribed to the Γ_1 to Γ_4 transition of the ground-state crystal-field multiplet and quantitative agreement is obtained between the observed and calculated cross section. The peak is broadened beyond the instrumental resolution. A short discussion is presented on how this observation complements our understanding of the actinide oxides. [S0163-1829(99)02602-8]

I. INTRODUCTION

The tetravalent actinide oxides (with the cubic fluorite structure) have been perhaps the most studied of any actinide compounds. Their high-temperature properties are, of course, of technological importance, but much effort has been directed also at understanding their low-temperature properties, which are the focus of this paper. Despite considerable effort, many aspects remain poorly understood. Being insulators with well-localized $5f$ electrons,[1,2] we would expect that crystal-field (CF) theory would be immediately applicable. Indeed, a classic calculation reported for UO_2 in 1966 by Rahman and Runciman[3] provided the framework for much of the subsequent interpretation of the electronic structure. However, neutron experiments[4] which examined directly the CF level structure of UO_2 showed that the energy splittings were considerably smaller, by more than a factor of 2, than those predicted by Rahman and Runciman. Subsequent higher-resolution experiments at the ISIS spallation source in the UK showed remarkable ''fine'' structure in the CF levels[5] and this was interpreted as a result of the interactions between the electronic and lattice modes. That such effects are important in UO_2, which has of course been by far the most studied, had already been shown at lower energies by the spin-wave[6] and elastic constant[7] measurements, and by the considerations of the susceptibility of diluted systems performed by Sasaki and Obata.[8] Moreover, Allen[9,10] developed a theory of an interaction within the Γ_5 ground-state multiplet of UO_2 and this led to the prediction of a static Jahn-teller distortion at low temperature. The observation of an internal distortion of the oxygen sublattice,[11] although not the one predicted by Allen, led strong support to the ideas that the interaction between the lattice and electronic modes is significant, at least in UO_2.

The exact ground state of NpO_2 has remained an enigma since the discovery of magnetic effects in 1967,[12] but it is accepted that the CF ground state of the $5f^3$ ion must have Γ_8 character. Neutron inelastic experiments[13] established that there is a broadband of magnetic scattering extending from 30 to 80 meV, and this is assumed to arise from transitions between the ground and excited Γ_8 states. Much of this broadening may also arise from interactions between the phonon and electronic systems, in particular the Raman-active[14] mode at 58 meV.

For the purpose of this paper it is sufficient to note that the V_4 and V_6 CF parameters deduced for NpO_2 are consistent with those derived for UO_2 ($V_4 \sim -120$ meV; $V_6 \sim -20$ meV; Ref. 5). These values are only 30% of those predicted by Rahman and Runciman for UO_2.[3]

Even if the ground state of NpO_2 is not completely understood, both it and that of UO_2 have antiferromagnetic ground states. This complicates determining the CF parameters and the electronic structure. In particular, susceptibility measurements are difficult to interpret as they may exhibit effects of antiferromagnetic correlations. In PuO_2, on the other hand, with a $5f^4$ ionic state, and with $V_4 < 0$, the Γ_1 singlet should be the ground state.[15] Indeed, early measurements[16] confirmed that the susceptibility was independent of temperature but the samples contained a considerable amount of iron. Raphael and Lallement[17] reported the results from experiments up to 1000 K using high-purity samples and these reproduced the temperature-independent values, but the absolute value of the susceptibility was smaller at 536 μemu/mol. (This has been corrected for the calculated diamagnetic contribution of -56 μemu/mol.) This low value was independently confirmed at Argonne National Laboratory.[18] Using the weak-field approach,[19] which assumes negligible J mixing, this small value of the susceptibility implies a Γ_1 to Γ_4 energy separation of 284 meV, and a $V_4 \sim -320$ meV, much larger than the experimental value deduced from neutron inelastic-scattering results in UO_2 and NpO_2.

The simplicity of the PuO_2 ground state makes it particularly attractive. Dipole matrix elements exist between the ground state Γ_1 and the excited state Γ_4, but are zero with other excited states. Thus, only *one* transition should be ob-

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served within the ground-state manifold, and other manifolds are at energies of at least 0.5 eV. Additional transitions, if observed in PuO_2, would be a certain sign of more complicated interactions. The earlier neutron inelastic-scattering experiments[19] on PuO_2 were carried out with a sample highly enriched in the nonabsorbing isotope ^{242}Pu at the IPNS spallation source at Argonne National Laboratory. Two broad peaks at ~90 and ~120 meV were observed. However, the peak at 90 meV was ascribed to hydrogen impurities in the sample. The peak at 120 meV was almost 25 meV [full width at half maximum (FWHM)] broad and there was even a suggestion that two peaks might be present. These results suggested that higher-order effects might be important. The instrumental resolution was 6 meV (FWHM). In view of the pivotal importance in understanding the CF scheme in PuO_2 it seemed worthwhile to repeat these measurements with a better sample, higher neutron intensity, and better resolution.

II. EXPERIMENT AND RESULTS

The sample used in the earlier experiment at Argonne had apparently absorbed a large quantity of water, and possibly other hydrocarbons, on the large surface area of the small particles. To remove the absorbed water a part (29 g) of the original sample was heated to 800 °C and exposed to oxygen. The absence of hydrogen was verified by Fourier-transform infrared spectroscopy. The lattice parameter was 5.395 Å, compatible with stoichiometric PuO_2, and no other phases were detected. The sample was then resealed in the double-walled container. The neutron inelastic scattering was performed on the PHAROS chopper spectrometer at the Los Alamos Neutron Scattering Center (LANSCE) of Los Alamos National Laboratory. PHAROS is a high resolution, direct geometry, chopper instrument[20] with better resolution (and more intensity) than the spectrometers used for the earlier work.[19] The incident energy for these experiments was 184 meV, and the resolution at an energy transfer of 125 was 3.6 meV. Using a large vanadium sample as a standard we have been able to put the scattering cross section on an absolute scale. The sample was inside a closed-cycle refrigerator and could be cooled to ~30 K. Lower temperatures were not attained because of the double encapsulation required for safety considerations, the large thermal mass, and the poor thermal conductivity of this material.

Figure 1 shows the data at $T=30$ K. Except for a small broadening, the spectra are identical at 100 K. A small time-independent background has been subtracted. There is a single peak at 123 meV, and no significant signal in the range ~10–80 meV. A Gaussian fit with a full width at half maximum (FWHM) of 11 meV is indicated with the solid line. The peak seen at ~90 meV in the earlier work is absent.

III. DISCUSSION

The first point to remark is that the peak at ~90 meV is now unambiguously associated with H in the lattice. This was suspected, but not proved, in the earlier work.[19] We can now concentrate on the 123 meV peak as coming from the $\Gamma_1 \rightarrow \Gamma_4$ transition.

By using the superposition model[21] with $t_4=11$ and $t_6=7$ we may determine how the UO_2 CF parameters would

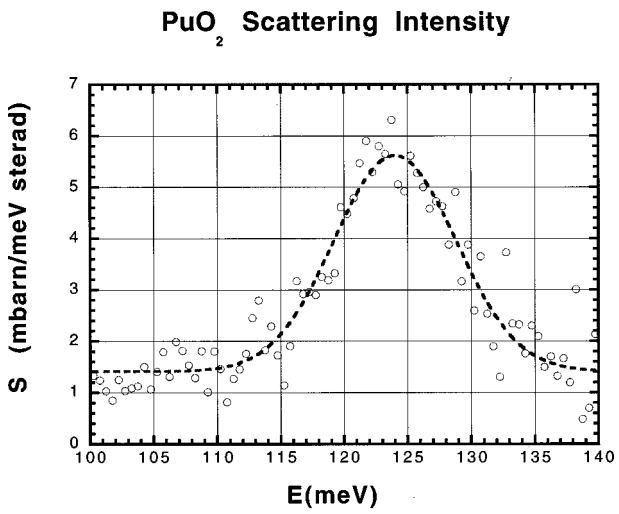

FIG. 1. Neutron inelastic spectra from PHAROS of $^{242}PuO_2$ at $T=30$ K after subtraction of a time-independent background and placed on an absolute scale by calibration with a vanadium standard. The incident energy was 184 meV. The dashed line represents a fit with a Gaussian of FWHM=11 meV. The resolution is 3.6 meV under these experimental conditions. There is no significant signal from the sample between ~10 and 100 meV. The momentum transfer at $E=124$ meV is ~4 $Å^{-1}$.

change for PuO_2 to take account of the small difference in the electron wave functions in going from U to Pu. We find $V_4=-1220$ cm^{-1} (−151 meV) and $V_6=+248$ cm^{-1} (+31 meV) as the cubic CF parameters; they generate a $\Gamma_1 \rightarrow \Gamma_4$ transition of 115 meV. The value of this calculated cross section is 81 mb/sterad. By fitting a Gaussian to the curve in Fig. 1 we obtain an experimental value for the absolute cross section of 84(5) mb/sterad. This agreement is unusually good for a neutron experiment considering the difficulties of calibration. Krupa and Gajek[22] calculated values that are less than this, giving a Γ_1 to Γ_4 splitting of 86 meV, but our results show that a consistent set of CF parameters are available for the light actinide dioxides—a situation we already discussed in our earlier paper. The calculated values of Rahman and Runciman[3] are too large for UO_2 because they attempted to make their ground-state moment agree with the experimental value of $\sim 1.8\mu_B$ rather than the $2\mu_B$ inherent in the Γ_5 ground state. We now know that the moment in UO_2 is reduced by the Jahn-Teller effects[10] rather than by mixing with higher CF states.

It is important to stress, however, that this value of the $\Gamma_1 \rightarrow \Gamma_4$ transition is in complete disagreement with that derived from the susceptibility measurements,[17] in which the transition energy is derived as ~284 meV. An alternative way to represent this is to take the experimental results of Raphael and Lallement (corrected by them for the diamagnetism of the core electrons) and plot the calculated susceptibility as a function of temperature for the CF parameters as deduced in our PuO_2 experiment. This is shown in Fig. 2. Indeed good agreement between experiment and the calculations can be obtained by using an orbital reduction factor of $k=0.905$. This is a large deviation from unity and would imply a reduced orbital moment, as might perhaps be produced by a dynamic Jahn-Teller effect. Such a Jahn-Teller effect can be simulated in a CF-type analysis by introducing a V_2 term in the Hamiltonian. In UO_2 the excited Γ_4 state is

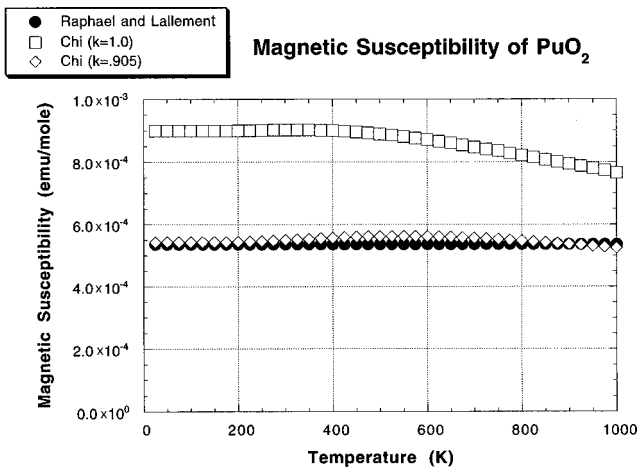

FIG. 2. Susceptibility as determined by Raphael and Lallement (Ref. 17) indicated by filled circles. The open squares represent the susceptibility deduced using the $\Gamma_1 \rightarrow \Gamma_4$ transition observed in Fig. 1. The higher lying J multiplets are automatically included by the CF program. The first three multiplets contribute ~87, 2, and 11 %, respectively, towards the full susceptibility. The open triangles are with the same calculation but with an orbital reduction factor of 0.905 (rather than $k=1$) introduced.

split by about 20 meV, and if we use the same parameters then the Γ_4 in PuO_2 splits by ~6 meV. PHAROS has sufficient resolution to allow such a splitting to be observed, but rather a general line broadening is found. This may, of course, be caused by a more complex process involving coupling between the lattice and electronic levels. It is important to remember also that the 123 meV line is now sharper (11 meV) than it was in the Argonne experiment (~20 meV) and that the resolutions were 3.6 and ~6 meV, respectively. The narrowing of the line in the recent experiment is probably associated with the removal of hydrogen rather than the improved resolution.

One possible other cause of line broadening should be mentioned. The sample consists of particles of ~12 nm in diameter. For particles of this size approximately 25% of the Pu ions would actually be within one lattice spacing of the particle surface. We cannot exclude therefore that a small change in the effective crystal-field occurs at the particle surface and this might well translate into a line broadening in the inelastic spectrum.

In conclusion, our experiments have fully confirmed the earlier interpretation of the discrepancy between the energy levels of the ground-state multiplet as deduced on the one hand from susceptibility measurements, and, on the other, directly from neutron inelastic scattering. The previous experiments were performed on a sample which contained a sizeable quantity of hydrogen, making the results not altogether clear. In view of the consistent CF parameters now deduced for all the three light actinide dioxides, UO_2, NpO_2, and PuO_2, a reliable basis has been established from which to depart theoretically. In spite of this it appears that the oxides are far from understood. It is not easy to accept the idea of so large an orbital reduction ($k \sim 0.9$), although we need more experiments on ionic actinide systems before rejecting such a hypothesis completely. Recently, Santini[23] has considered the anomalies presented by the PuO_2 measurements and suggested that Jahn-Teller couplings might account for the broadening of the transition and antiferromagnetic exchange *might* be sufficient to explain the discrepancy between the neutron and susceptibility results. We hope this work motivates this and other theoretical efforts.

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[1] M. S. S. Brooks and P. J. Kelly, Solid State Commun. **45**, 689 (1983).
[2] J. Schoenes, Phys. Rep. **63**, 301 (1980).
[3] H. U. Rahman and W. A. Runciman, J. Phys. Chem. Solids **27**, 1833 (1966).
[4] S. Kern, C.-K. Loong, and G. H. Lander, Phys. Rev. B **32**, 3051 (1985).
[5] G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn, and A. D. Taylor, Phys. Rev. B **40**, 1856 (1989).
[6] R. A. Cowley and G. Dolling, Phys. Rev. **167**, 464 (1968).
[7] O. G. Brandt and C. T. Walker, Phys. Rev. **170**, 528 (1968).
[8] K. Sasaki and Y. Obata, J. Phys. Soc. Jpn. **28**, 1157 (1970).
[9] S. J. Allen, Phys. Rev. **166**, 530 (1968).
[10] S. J. Allen, Phys. Rev. **167**, 492 (1968).
[11] J. Faber and G. H. Lander, Phys. Rev. B **14**, 1151 (1976).
[12] B. D. Dunlap and G. M. Kalvius, in *Handbook of the Physics and Chemistry of the Actinides; Vol. 2*, edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1985), p. 329.
[13] G. Amoretti, A. Blaise, R. Caciuffo, D. D. Cola, J. M. Fournier, M. T. Hutchings, G. H. Lander, R. Osborn, A. Severing, and A. D. Taylor, J. Phys.: Condens. Matter **4**, 3459 (1992).
[14] G. M. Begun, R. G. Haire, W. R. Wilmarth, and J. R. Peterson, J. Less-Common Met. **162**, 129 (1990).
[15] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).
[16] G. A. Candela, C. A. Hutchison, and W. B. Lewis, J. Chem. Phys. **30**, 246 (1959).
[17] G. Raphael and R. Lallement, Solid State Commun. **6**, 383 (1968).
[18] O. Kruger and H. Savage, J. Chem. Phys. **49**, 4540 (1968).
[19] S. Kern, C.-K. Loong, G. L. Goodman, B. Cort, and G. H. Lander, J. Phys.: Condens. Matter **2**, 1933 (1990).
[20] R. A. Robinson, M. Nutter, R. L. Ricketts, E. Larson, J. P. Sandoval, P. S. Lysaght, and B. J. Oliver, Proceedings of ICANS-XII, Rutherford Aplleton Laboratory Report RAL-94-025, 1994, Vol. 1, p. 44 (unpublished).
[21] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).
[22] J. C. Krupa and Z. Gajek, Eur. J. Solid State Inorg. Chem. **28**, 143 (1991).
[23] P. Santini (private communication).