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X-RAY PHOTOELECTRON SPECTROSCOPY OF 5f ELECTRONS
IN DIOXIDES OF NEPTUNIUM AND PLUTONIUM*

B. W. Veal, D. J. Lam, and H. Diamond

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ABSTRACT

The $5f$ electron spectra in NpO_2 and PuO_2 were studied by XPS. Using intensity measurements and multiplet structure, the configuration $5f^3$ was assigned to NpO_2 . Although NpO_2 exhibits anomalous magnetic behavior similar to TmSe (a valence fluctuation system), XPS results do not support the valence fluctuation model for NpO_2 .

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1. Introduction

The magnetic properties of NpO_2 have been studied by low temperature specific heat [1,2], magnetization [3], neutron diffraction [4,5], and nuclear gamma-ray resonance (NGR) [6] measurements. Both the magnetic susceptibility and specific heat measurements show a maximum at ~ 25 K similar to that of UO_2 at ~ 30 K. The magnetic susceptibility [7] and specific heat [2] maxima in UO_2 are indications of long range antiferromagnetic ordering of the uranium 4+ ions as determined by neutron diffraction experiments [8]. On the other hand, no long range magnetic ordering could be detected in NpO_2 by neutron diffraction experiments. NGR results show a broadening of the resonance line below 22 K which is interpreted to be a small, unresolved magnetic splitting. From the size of the magnetic hyperfine field, the magnetic moment of the Np ion is estimated to be $\sim 0.01 \mu_B$. Such a small Np magnetic moment would not be detected in a neutron diffraction experiment. The anomalous magnetic behavior of NpO_2 is very similar to the bulk magnetic properties of TmSe determined by magnetic susceptibility [9], low temperature heat capacity [9], NGR [10], thermal expansion and magnetostriction [11] measurements. The anomalous magnetic behavior of TmSe is believed to be caused by the temporal fluctuations between the divalent and trivalent state of the Tm ion. Both valence states are clearly shown in x-ray photoelectron spectroscopy [12].

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XPS spectra of the valence band and outer core levels of NpO_2 and PuO_2 are reported in this paper. The possibility of temporal valence fluctuations in NpO_2 is investigated by systematically comparing XPS spectra obtained on the actinide oxides ThO_2 through PuO_2 .

2. Experimental

The XPS spectra were obtained with a Hewlett-Packard 5950-A spectrometer using a monochromatized aluminum x-ray source with a resolution capability of ~ 0.55 eV. The samples were prepared by oxidation of thin metal films which were deposited onto platinum substrates with a mass spectrometer. The neptunium was converted to NpO_2 by heating to 820°C and slowly cooling in an atmosphere of O_2 . Plutonium was allowed to become PuO_2 in air at room temperature.

3. Results and Discussion

Fig. 1(a) shows the XPS spectra of ThO_2 , UO_2 , NpO_2 , and PuO_2 within 50 eV of the Fermi level. The prominent narrow peak near E_F results from localized $5f$ electrons. The three peak structure centered around -25 eV are the An (actinide) $6p_{1/2}$, $6s$, and $6p_{3/2}$ lines. The "bonding" band derived from $6p$ electrons can be clearly observed near E_F in ThO_2 and between the $5f$ peak and the $6p_{3/2}$ line in UO_2 . The $5f$ spectrum moves toward higher binding energy and merges with the $6p$ -derived bonding band in NpO_2 and PuO_2 .

The shape of the $5f$ electron spectra is determined by the final-state multiplet structure [14]. Fig. 1(b) shows the free ion final state multiplet structure of the appropriate final state for the Np^{4+} and Pu^{4+} ions. The $5f$ electron spectrum of NpO_2 is essentially a single narrow line. It is thus unlikely that the $5f$ electrons of NpO_2

are fluctuating between $5f^3$ and $5f^2 6d$ configurations (the TmSe analogy). For a fluctuating system, one would expect superimposed spectra corresponding to the individual configurations and separated by the correlation energy difference of the two configurations [12]. This conclusion is further reinforced by examining the integrated intensity of the combined valence band normalized to the integrated intensity of the oxygen 2s and An 6p lines in the three oxides. (A consistent procedure was used to extract the background of inelastically scattered electrons.) As shown in Fig. 2, the intensity varies smoothly from ThO_2 to PuO_2 . Since the magnetic properties of ThO_2 , UO_2 , and PuO_2 can be accurately described in terms of $5f^0$, $5f^2$, and $5f^4$ configurations, respectively [2,7,8,13], we see that the normalized intensity (Fig. 2) depends linearly on 5f electron occupation. (This is a reasonable result since the XPS cross section for 5f emission is high.) These results indicate that the Np ions in NpO_2 are in the +4 state with the $5f^3$ configuration. The XPS data do not support the valence fluctuation model for NpO_2 . For the $5f^3$ configuration, however, there is no mechanism, which is purely electrostatic, that can produce such a large reduction in moment if NpO_2 is magnetically ordered below 25 K. The susceptibility and specific heat anomalies may be caused by a structural phase transition, e.g., noncubic distortion and the line broadening below 22 K observed in the NGR experiment may be caused by quadrupole interactions.

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Figure Captions

- Fig. 1. (a) XPS spectra for dioxides of Th, U, Np, and Pu within 50 eV of the Fermi level.
- (b) Calculated final state multiplet spectra compared with XPS spectra for NpO_2 and PuO_2 .
- Fig. 2. Integrated intensity of the valence electrons normalized to the integrated intensity of the An 6p's and O2s core lines as a function of 5f electron occupation.

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