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EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) STUDIES OF THE ACTINIDES*

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Extended X-ray Absorption Fine Structure (EXAFS) Studies of the Actinides*
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Abstract

The basic EXAFS parameters of the backscattering amplitude and phase shift have been computed as a function of k for the neutral atoms of Th, U, Np and Pu. It is found that an anomalous variation of the backscattering phase shift with respect to k occurs for the actinide elements at approximately $k=7\text{\AA}^{-1}$. However, this variation is monotonic, unlike those for Pb and a few other lighter elements. It is also found that the detailed behavior of the parameters is sensitive to the distribution of electrons in the 5f open shell. Comparison with experiments on uranium arsenide and selenide emphasizes the need for careful modeling of the 5f electronic configuration.

At the present time, there are no calculations of the EXAFS parameters beyond the element Pb ($Z=82$). Such calculations are of interest for two reasons. First, we have an extensive program to study actinide containing materials. Second, TEO and LEE [1] showed that the backscattering phase shifts became almost discontinuous near $k=7\text{\AA}^{-1}$ for atoms with $78 < Z < 82$, so that it is interesting to see what happens to the phase shifts and amplitudes of the higher Z elements. In this paper, exploratory results will be presented for the neutral atoms of Th, U, Np and Pu. A comparison with the experimentally determined parameters for UAs and USe will be made.

Scattering phase shifts, δ_l for the individual partial waves of angular momentum l have been computed for the neutral actinide atoms by solving the one electron Schroedinger equation self-consistently in the Hartree-Fock approximation and matching the radial wave functions inside and outside a muffin-tin radius, $R_0=1.5$ times the covalent radius. The charge densities of core electrons were obtained from Herman-Skillman wave functions [2]. Wave functions of electrons in the outer shells were truncated when they exceeded R_0 . Electrical neutrality outside R_0 was maintained by adding an appropriate uniform charge density to the spherical region inside. To check for relativistic effects, the self-consistent potential obtained for Th has been compared with the result from a relativistic calculation [3]. The difference is found to be insignificant and does not influence the individual partial waves phase shifts. The total backscattering amplitude A and phase shift ψ are finally obtained from

$$f(\theta=\pi) = Ae^{i\psi} = \frac{1}{k} \sum_l (2l+1)(-1)^l e^{i\delta_l} \sin\delta_l \quad (1).$$

The results for the neutral atoms Th, U, Np and Pu are presented in Figs. (1a) and (1b).

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Fig. 1. Backscattering amplitude (a) and phase shift (b) as a function of k for neutral atoms of Th, U, Np and Pu

The backscattering amplitudes A as a function of k show decreasing modulations with three maxima and two minima interposed between one another within the range $k=3.7$ to $15.2 \text{ \AA}^{-1}$. The corresponding curves of the backscattering phase shifts ψ are more monotonic but do exhibit changes in their slopes. Of particular interest is the region around $k=7 \text{ \AA}^{-1}$. There the phase shifts have the largest slopes. This behavior represents the remnant of the gradual build up and steepening of the "precipice" that occurs for elements with Z near 82, but the sign of the slope is opposite here. The reason for this change of slope is that when this near-discontinuity exceeds π , it is more natural to shift the low k phase shifts by 2π so as to minimize the anomaly. (This is correct since ψ is defined to only 2π). Since $d\psi/dk$ has the meaning of a time delay in scattering theory [4], this result suggests that when the atomic number is near $Z=82$, the shape and size of the potential is such that a wave packet with $k=7 \text{ \AA}^{-1}$ satisfies a resonance condition and is trapped for a long time between the rather steep walls of the potential.

The results of the backscattering amplitude A and phase shift ψ are sensitive to the distribution of electrons in the $5f$ open shell of the actinide elements. As an illustration, A and ψ for a neutral uranium atom were calculated under two different assumptions to mimic two different electronic configurations. First, all electrons in the $5f$ shell were assumed to hybridize with the more extended $6d$ and $7s$ electrons and became delocalized. The deficiency in charge is compensated by an appropriate charge density so that electrical neutrality is achieved outside R_0 . The results are indicated by the solid curves in Figs. (2a) and (2b). Next, two of the $5f$ electrons were allowed to remain localized as in a free atom and the rest replaced by an appropriate uniform charge density to maintain electrical neutrality outside R_0 . The corresponding backscattering amplitude and phase shift are shown by the dashed curves.

Fig. 2. Backscattering amplitude (a) and phase shift (b) as a function of k for neutral U atom ---- solid curve: $5f^0$ configuration; dashed curve: $5f^2$ configuration; dash-dot curve: experimentally determined for UAs

To test these model electronic configurations, we have made comparison with EXAFS measurements on UAs and USe at the arsenic and selenium absorption edges. The results are similar for both systems and we show only the parameters for UAs determined through the use of the standard EXAFS formula [5] and the As central atom phase shift calculated by TEO and LEE [1]. Experimental results for the Th, Np and Pu arsenides are similar to those of UAs and will be presented later in a full paper. The experimentally obtained A and ψ values are shown by the dash-dot curves. Due to the limitations coming from the plane wave approximation and the exclusion of inelastic scattering effects, we might not expect better agreement. Clearly, neither of the two models is able to mimic the experimentally determined parameters. What is apparent is that the experimental results show similar structure in the amplitude (displaced in k) and the increased slope in the phase near $k = 7 \text{ \AA}^{-1}$ in qualitative agreement with theory. These results emphasize the sensitivity of the EXAFS parameters to the $5f$ electronic configurations and point to the need of close coordination between experimental and theoretical efforts.

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