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High-energy spectroscopic study of the occupied and unoccupied 5f and valence states in Th and U metals

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X-ray photoemission spectroscopy and bremsstrahlung isochromat spectroscopy have been used to investigate the electronic density of states of metallic Th and U, below as well as above the Fermi level. In contrast to the discrete 4f levels observed in the rare earths, the 5f states in these metals are found to be delocalized and to form relatively narrow bands. The experimental spectra are compared to recent calculations of the density of states.

It is well established that the 4f states in the whole lanthanide series (except perhaps α-Ce) are localized. Their large Coulomb correlation energies U have been systematically determined in the metals by combining the results obtained by x-ray-photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS).[1] It appears interesting to apply the same techniques to the light actinide metals for which many arguments support an itinerant description of the 5f electrons.[2-5] These states are expected to be hybridized with other valence states and to contribute to the bonding.[6,7] They must form bands which are not far from the Hubbard limit since at the middle of the series they start to become localized in the metals and behave like 4f states in the lanthanides. An extensive XPS study of the oxides of the elements Np to Cf has recently been published[8] where the spectra are compared to the multiplet calculations assuming localized 5f electrons. Very important theoretical efforts have been made recently[9-13] to compute the electronic band structure of the light actinide metals which are at the limit of applicability of band theory.

We present in this paper XPS and BIS spectra of Th and U metals in the range of interest for the 5f electrons, below as well as above the Fermi energy E_F. These two metals have already been studied by XPS but the valence-band spectra are either poorly resolved[14] or distorted by the presence of contamination.[15,16] An appearance potential spectroscopy (APS) spectrum of U has recently[17] been compared to the one-electron density of states above E_F (Ref. 18). Such a comparison should be performed with care since the perturbation created by the deep hole as well as the possibility of a double 5f occupancy in the final state[19] have to be considered. As far as we are informed, BIS has never been applied to the study of the actinide metals. It is probably the most direct method to determine the density of the empty states.[1] Instrumental details on our apparatus have been given elsewhere.[20,21] Clean metallic samples have been prepared, as described in Ref. 14.

Th metal is tetravalent and the occupied part of the band has mainly d character with a much smaller s and p contribution. As indicated by the analysis of reflectivity data,[3,4] the 5f states are itinerant and a weak tail of this symmetry is occupied below E_F. Figure (1a) shows our XPS spectrum of Th metal. The agreement with previous measurements[14,15] is good if one makes allowance for the different resolutions and the presence of oxide which in this case does not affect the valence-band region of the pure metal. The densities of states (DOS) of Th computed by different authors[9,12] are in remarkable agreement. The most recent one,[12] shown in Fig. 1(b), has been convoluted with Lorentzian and Gaussian lines in order to simulate the XPS spectrum.[22] Other than a slightly broader width, the computed band is in very good agreement with the experimental spectrum. The two peaks correspond mainly to states with d character, whereas s states are rather concentrated at the bottom of the band. The contribution of the $l = 3$ projected DOS to the occupied part of the band is only 0.5 state per atom.[12] This

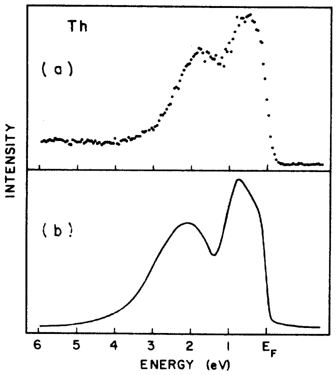

FIG. 1. XPS spectrum of Th, (a), compared to the convoluted (Ref. 22) total DOS of Ref. 12, (b).

low contribution, however, can be expected to bring a sizable intensity since the atomic cross section for the 5*f* states is much larger than for the 6*d* and 7*s* states.[23] For this reason the empty part of the band where the narrow and intense *f* states are concentrated will be compared to the calculated $l=3$ projected DOS. The other symmetries may increase the intensity somewhat in a small energy range above E_F. In the BIS spectrum, shown in Fig. (2a), the intensity at E_F is weak compared to that of the two main peaks located at 3.15 and 4.51 eV. The overall shape of the computed DOS in Fig. (2b) is rather similar to that of the experimental spectrum but the intensity ratio of the peaks is quite different; their separation is smaller (10%) and they are shifted by about 0.7 eV toward E_F. The width of the experimental peaks is mainly attributable to the final-state lifetime and it is not possible to draw conclusions about the large tails. The crystal field is probably responsible for the splitting (the spin-orbit splitting of 5*f* states in Th is[24] of the order of 0.5 eV).

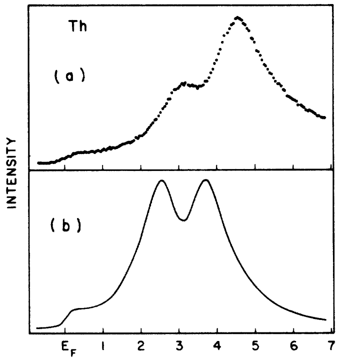

FIG. 2. BIS spectrum of Th, (a), compared to the convoluted (Ref. 22) $l=3$ projected DOS of Ref. 12, (b).

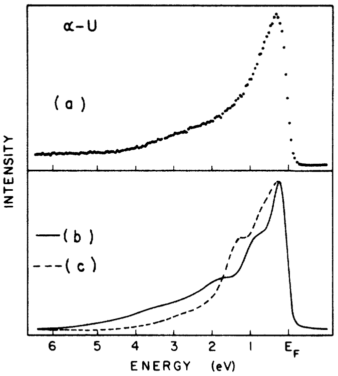

FIG. 3. XPS spectrum of U, (a), compared to the convoluted (Ref. 22) $l=3$ projected DOS of Ref. 10, (b), and of Ref. 13, (c).

In uranium, which has an orthorhombic structure (α-U) at room temperature, the $l=3$ projected DOS is occupied by somewhat more than two electrons.[5,7,10,12] These states are hybridized to some extent but they are still expected to be mainly concentrated in a narrow energy range. As a consequence of the high 5*f* cross section mentioned previously, the XPS spectrum of U [Fig. 3(a)] must be compared to the calculated $l=3$ projected DOS[10,13] [Figs. 3(b) and 3(c)]. Our spectrum is in agreement with results obtained at lower resolution on clean metallic samples[14] so that the shoulder[15] or even the peak[16] observed previously around 2 eV has to be ascribed to oxygen contamination. The narrow and intense peak located within 1 eV below E_F certainly accounts for the rather pure 5*f* states which become more hybridized at higher energies. *s* and *d* states might also bring a weak intensity contribution to the bottom of the XPS spectrum. The DOS obtained by the linearized augmented plane wave (LAPW) calculation[10] is in fair agreement with the experiment but it predicts too many *f* states at high energies. The result of another calculation based on the atomic sphere approximation (ASA)[13] is also shown in Fig. 3(b). The agreement is somewhat better but not perfect since more states are concentrated near E_F and the tail at higher energies falls off faster. For the unoccupied part of the band, the BIS spectrum is compared to the two previous calculations in Figs. 4(a)–4(c). The experiment shows that the 5*f* states form a relatively narrow band pinned at E_F with a shape rather similar to that found for Th but with a different peak intensity ratio and a smaller separation (1.15 eV). The agreement with the LAPW calculation is poor; the structures are different and the band is much too large. The ASA calculation yields a quite different DOS. A rather featureless peak is found in the correct energy range but the bandwidth is now too small, even if the lifetime broadening is

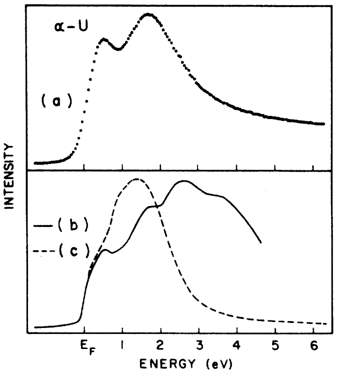

FIG. 4. BIS spectrum of U, (a), compared to the convoluted (Ref. 22) $l=3$ projected DOS of Ref. 10, (b), and of Ref. 13, (c).

underestimated in the convoluted theoretical spectrum. The fact that two theoretical approaches which both predict rather correctly the mean features of the DOS of Th yield so different results for U is certainly due to the difficulty in treating correctly the nearly localized $5f$ states of U in a band formalism.

The final states produced in XPS and BIS correspond to real variations of the orbital occupations and in metals a complete screening of the resulting change in the potential is achieved by the valence electrons. A band calculation of the ground state can account for such excited states only if the corresponding variation of the orbital occupations induces a negligible change of the single-particle eigenvalues. This approximation is certainly suitable for extended states but it fails completely for localized states like the $4f$ states in rare-earth metals.[25] The $5f$ states in the light actinides are even more localized than the $3d$ states in the first transition metals series so that the comparison of our spectra with computed DOS can be questioned. The renormalized atom scheme which has demonstrated the importance of this problem for the $4f$ states has also been applied to the calculation of the $5f$ states in the actinide metals.[5] It yields energy values which are consistent with our experimental results and, surprisingly, the one-electron eigenvalues are nearly identical to the multielectron estimates of the $5f$ energies. This result provides good evidence that this problem is not critical for the light actinides. A more conclusive answer could be given by a full band calculation using the transition-state method.

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