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Shake-up satellites in the U4f E.S.C.A. spectra of NaCl-type uranium monocompounds: UN, UP, UAs and US

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Résumé. — Les spectres E.S.C.A. des niveaux U4f de quatre composés d'uranium, tous de structure NaCl, sont décrits et discutés en vue d'une approche du caractère de la liaison chimique.

Abstract. — The U4f E.S.C.A. spectra of four NaCl-type uranium monocompounds are reported, and discussed in an attempt to relate them to the character of the chemical bond.

1. Introduction. — The study of uranium monocompounds with group Va and Via elements was undertaken in order to extend the understanding of chemical bonding of this metal with elements of different electronegativities.

All the studied compounds: UN [1], UP [2], UAs [3] and US [4], have cubic (fcc, NaCl-type) structure and present semi-metallic electrical properties. The uranium electronic state in these solids is still questioned. On one side indeed, neutron diffraction experiments on UN [5], UP [6], UAs [7], confirm the existence of the U(III) state with [Rn] 5f³ configuration; but on the other hand, a discussion of magnetic properties [8] leads to the conclusion that uranium is rather in the +4 state. For US, Suski [9] recently noted that the electronic configuration of uranium is still a matter of discussion.

It was therefore tempting to tackle these problems with a technique which produces a direct look at electronic states: X-ray photoelectron spectroscopy (Electron Spectroscopy for Chemical Analysis) of core and valence levels.

2. Results. — All spectra were obtained on a Hewlett-Packard 5950 A instrument, using monochromatized AlKα radiation (hv = 1 486.6 eV). The spectrometer’s sample inlet chamber is equipped with a stainless steel glove box, in which a dry nitrogen atmosphere is maintained by recycling the gas over appropriate catalysts which eliminate residual water and oxygen.

In spite of drastic operating conditions, all powdered samples presented severe oxidation, marked by the presence of O1s and O2s peaks around 532 and 22 eV in the spectra, and by a marked broadening of the normally sharp U4f peaks.

Attempts to sputter the oxidized layer off the sample by Ar⁺ (1 kV) ions were unsuccessful or worse. Better experimental data could probably be obtained by studying single crystals, which could be cleaved and scraped in vacuo. Powders indeed have high reactivity due to their large specific area in contact with the surrounding atmosphere.

Of all core and valence spectra, which have been obtained, we will only discuss here a noteworthy fraction: the U4f levels show indeed much stronger shake-up satellites than those already known for

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Table I. — Comparison of E.S.C.A. results on NaCl-type uranium compounds. Description of U4f peaks and their satellites (symbols used are the same as in figure 1).

<table>
<thead>
<tr>
<th>U4f peaks</th>
<th>Shake-up satellites</th>
<th>% ionic character</th>
<th>Atomic polarizabilities[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, shift (eV) relative to UX</td>
<td>Separation (eV) from main peak</td>
<td>Intensity ratio to main peak</td>
<td>(10^{-26} cm^3)</td>
</tr>
<tr>
<td>UX</td>
<td>UX</td>
<td>U4f_{1/2}</td>
<td>U4f_{5/2}</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UN</td>
<td>—1.2</td>
<td>A' = 4.3</td>
<td>A = 4.8</td>
</tr>
<tr>
<td>UP</td>
<td>—1.6</td>
<td>B' = 9.6</td>
<td>B = 8.8</td>
</tr>
<tr>
<td>UAs</td>
<td>—1.3</td>
<td>C' = 6.3</td>
<td>C = 5.1</td>
</tr>
<tr>
<td>US</td>
<td>—1.0</td>
<td>D' = 6.6</td>
<td>D = 6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E' = 3.3</td>
<td>E = 3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F' = 5.9</td>
<td>F = 6.1</td>
</tr>
</tbody>
</table>


uranium oxides [10]. We wanted to investigate the possible relations between position and intensity of such satellites and nature of the anion and bonding.

Failing at present to have oxygen-free spectra, we have analysed the existing data, using standard mathematical procedures. The U4f main peak components were first located by reconstructing the spectrum from Gaussian curves. The scaled components were first located by reconstructing the main characteristic (UP and UP and UN and UN) characteristics. This conclusion may seem rather disappointing at this point; forthcoming results on single crystals, eventually cleaned in vacuo, should confirm or correct these observations.

Comparing the compounds of highly covalent character (UP and UAs) the explanation might be sought in the different polarizabilities of the anion. This property is known indeed to affect in several ways the aspect of E.S.C.A. spectra, as observed in the series of M'UO, alkali metal hypouranates [11].

On the reverse, the ionic fraction of the chemical bond certainly is one of the determining factors of shake-up satellites. Asada and Sugano [12] have calculated in the case of transition-metal compounds that their intensity is a result of the relative increase of covalency upon departure of a metal core electron. Finally, the satellite-to-main peak separations are to be associated with energy gap values in the valence band, observing the monopole selection rule [10]. Band structure calculations would in this view be particularly welcome.

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