XANES and the electronic structure of Actinide oxide

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Background

Americium (Am)

- Minor actinide (MA) accumulated in the irradiated nuclear fuel
- High and lasting radiotoxicity ⇨ Requirement of its reduction

⇨ **Transmutation to stable or short-lived radionuclide**

⇩

Development of Am-oxide fuel

Evaluation of the change of properties of the oxide fuel with Am supplementation

Local structure and chemical state around Am in the oxide fuel

⇩

Analysis of X-ray absorption near edge structure (XANES)

Purpose

XANES analysis of AmO_2 and UO_2

- Basic data for the evaluation of Am-oxide fuel
- Assumption of the origin of AmO_2 and UO_2 XANES peak structure
- Evaluation of the electronic state of AmO_2 and UO_2

Behavior of Am and U in the oxide fuel

- Comparison between the electronic structure of AmO_2 and that of UO_2
- Electronic states of Am and U in the mixed oxide ($Am_{0.5}U_{0.5}O_2$)

Calculation method

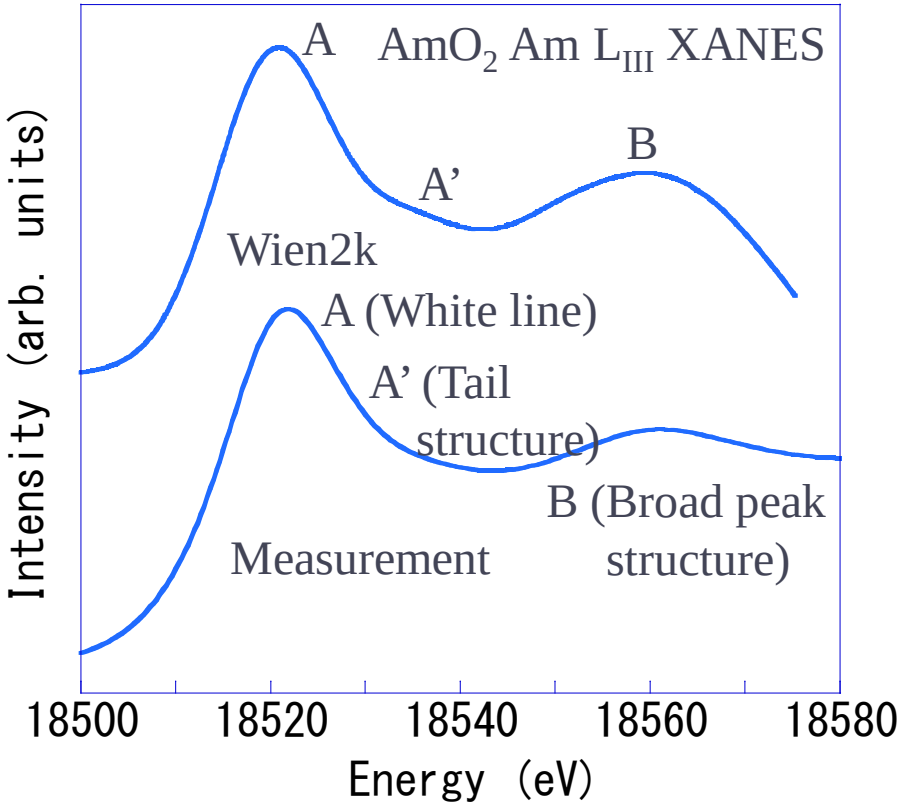
Wien2k

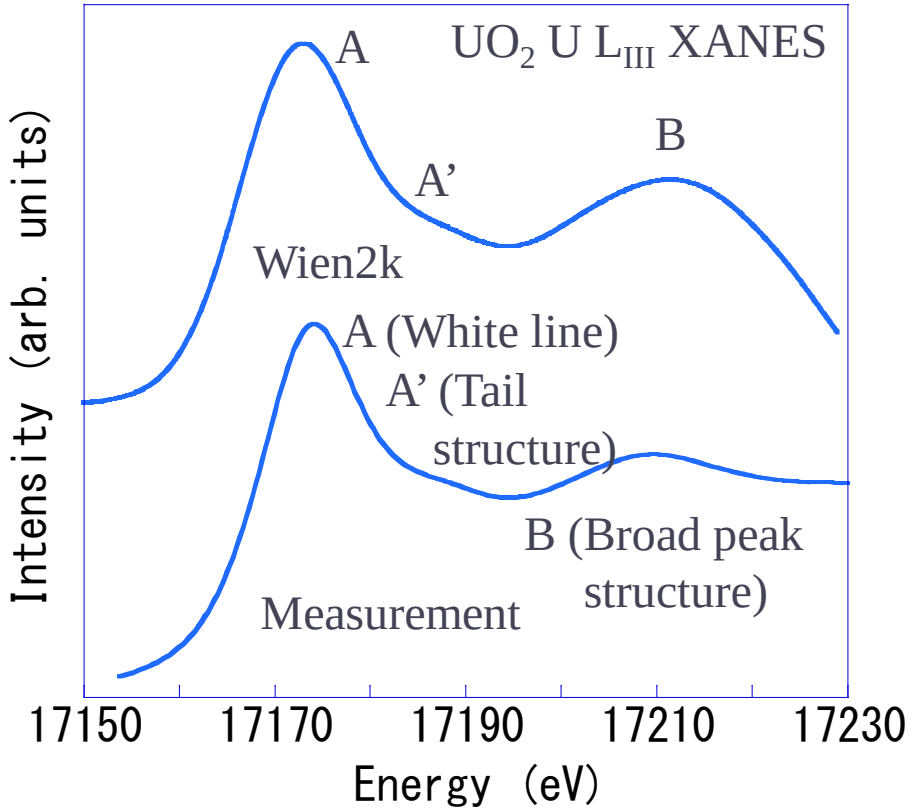
- Relativistic calculation which is necessary for actinide compounds
- Calculation and analysis for AmO_2 and UO_2 XANES
- Electronic structure of AmO_2, UO_2, and the mixed oxide

Relativistic DV-Xα molecular orbital method

- Calculation considering the relativistic effect
- Charge transfer in the mixed oxide (Effective charge)

Actinide oxide L_{III} XANES

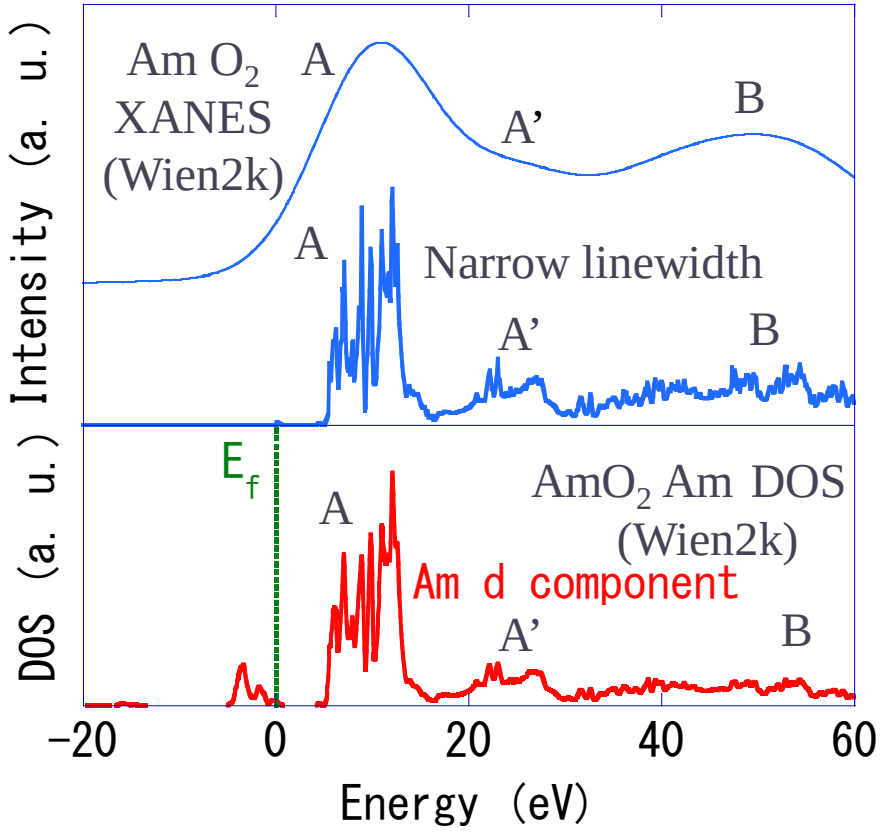


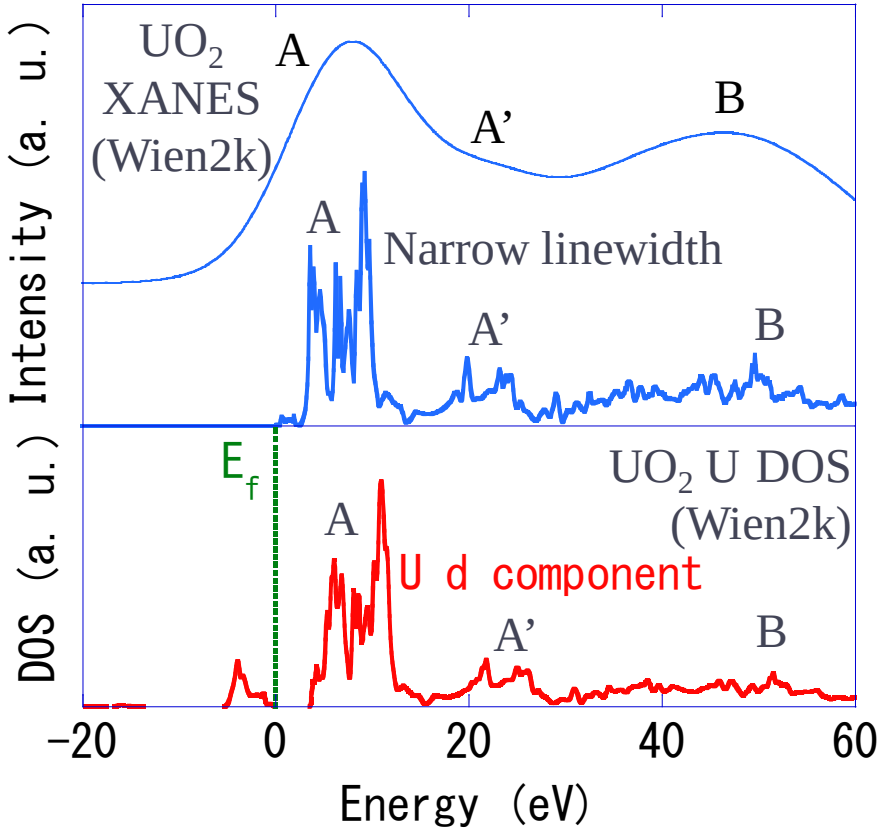


- **XANES are well reproduced with the calculation.**
- **AmO_2 Am L_{III} XANES and UO_2 U L_{III} XANES are similar.**

➡ **Analysis of XANES using the first principles calculation**

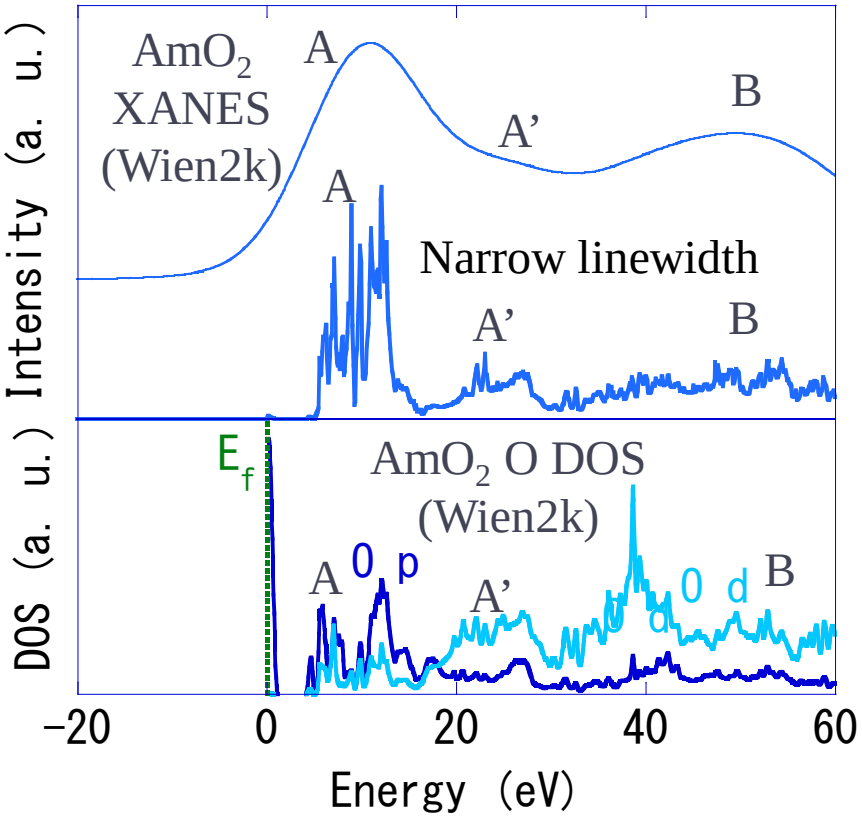
XANES and Am and U d component





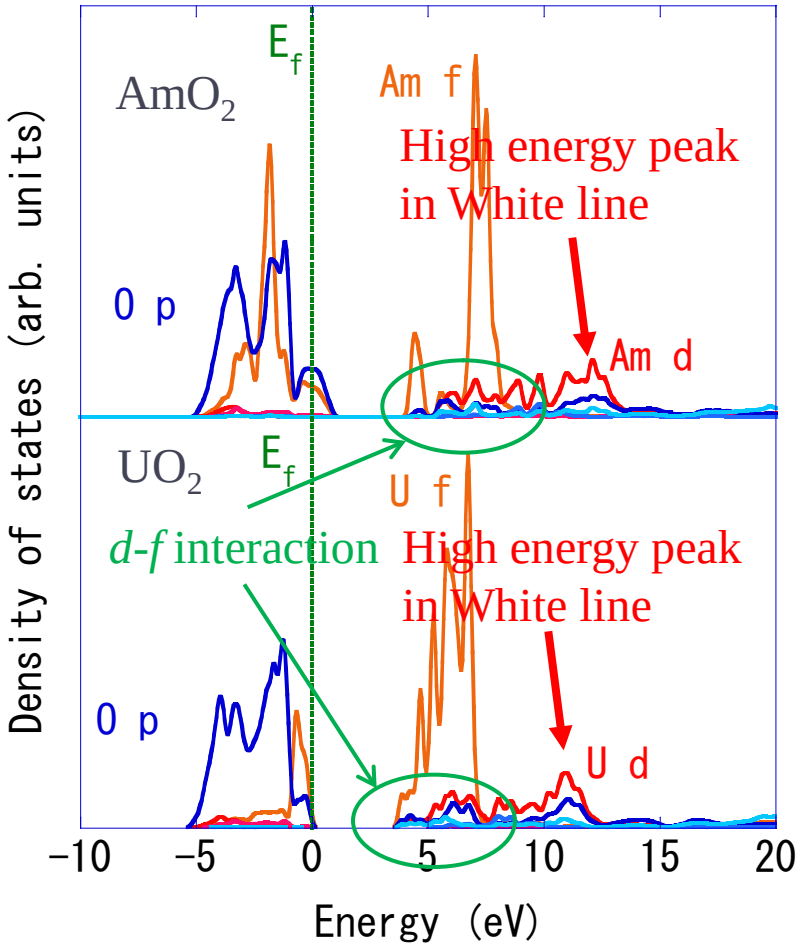
- **Am and U L_{III} XANES reflect Am and U *d* component.**
- **Theoretical spectra of AmO_2 and UO_2 are similar.**

XANES and O component



- **White line is created due to Am *d*-O *p* interaction.**
- **The tail structure is created due to Am *d*-O *d* interaction.**
- **Broad peak structure is created due to Am *d*-O *d*.**

Analysis of XANES of AmO_2 and UO_2



Behavior of Am and U in oxide fuel

↓

Investigation of redox property

UO_2 U L_{III} and AmO_2 Am L_{III} XANES are similar

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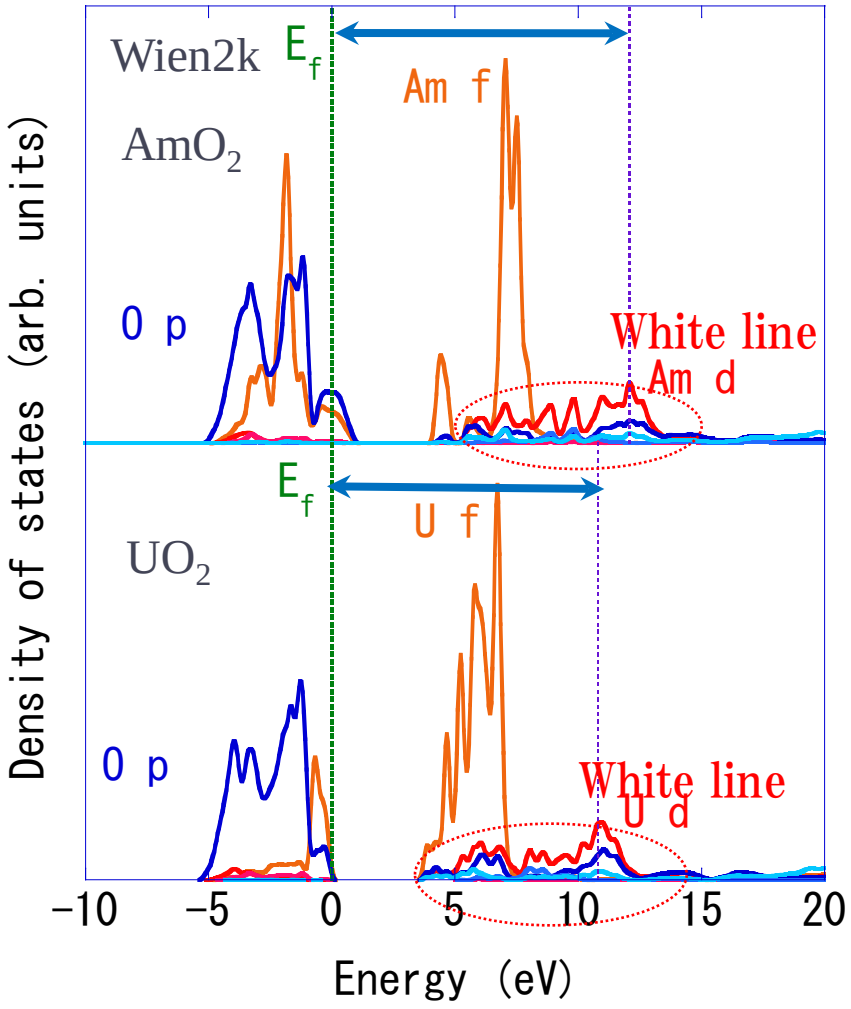
High energy peak in White lines are set as the standard energy

(free from *d-f* interaction)

Electronic structure of AmO_2 and UO_2



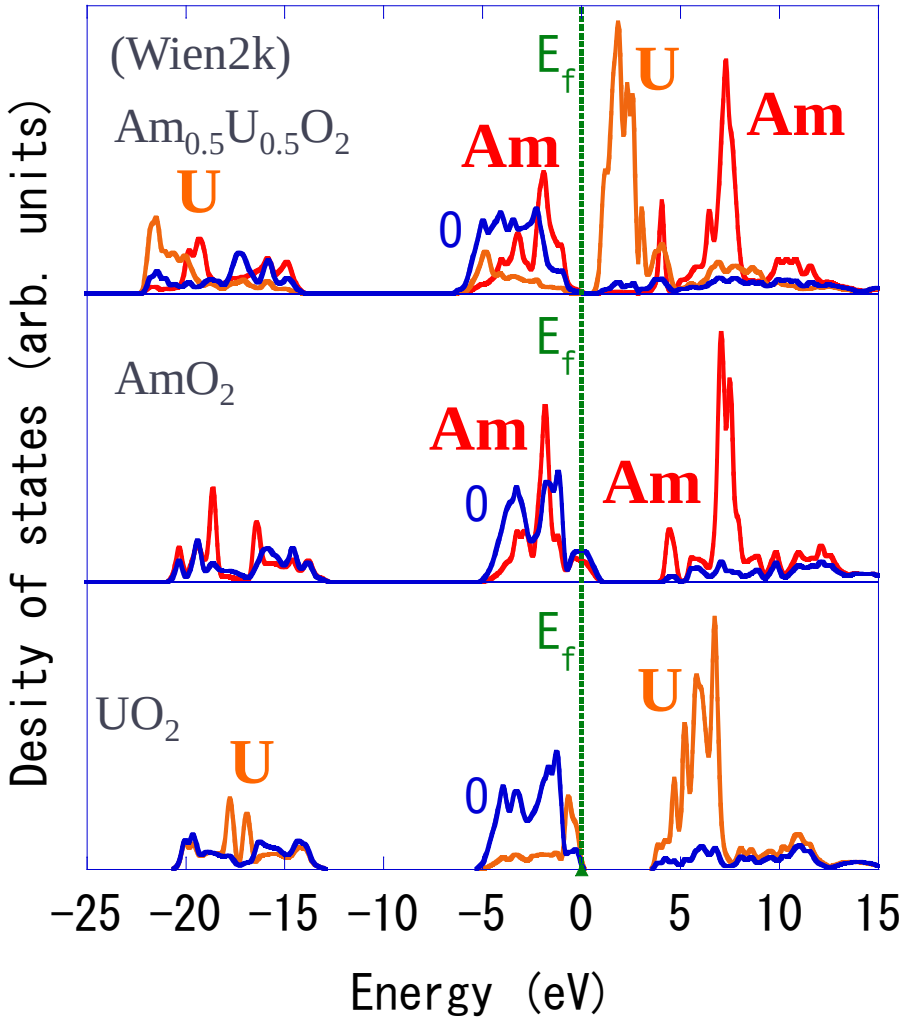
Energy of E_f → White line

AmO_2	UO_2
12.09 eV	10.80 eV

E_f of AmO_2 is deeper than that of UO_2

Electrons are assumed to be transferred from U to Am in the oxide fuel

Electronic structure of $Am_{0.5}U_{0.5}O_2$



Effective charge (DV-Xα method)

	Am	U
AmO_2 or UO_2	+3.33	+3.40
$Am_{0.5}U_{0.5}O_2$	+3.29	+3.55

The change of the electronic state of U is more remarkable than that of Am.

Summary

1. **AmO_2 Am L_{III} and UO_2 U L_{III} XANES are similar and well reproduced with the calculation.**
2. **Am and U L_{III} XANES reflect Am and U *d* component.**
3. **Am L_{III} XANES peak structures are created due to Am d-O p interaction in White line and due to Am d-O d interaction in the tail structure and the broad peak structure.**
4. **Fermi level of AmO_2 is deeper than that of UO_2.**
5. **The change of the electronic state of U is more remarkable than that of Am in the mixed oxide.**

Further consideration

1. XANES measurement and calculation for Am_2O_3, $Am_{0.5}U_{0.5}O_2$, and $Am_{0.05}U_{0.95}O_2$ (simulated as practical Am-oxide fuel).
2. Evaluation for the local structure by XANES analysis using charge density distribution
3. Clarification of the behavior of Am and U in $Am_{0.05}U_{0.95}O_2$
4. Development of the evaluation methods for the local structure and chemical state of MA in the oxide fuel using XANES and the theoretical calculation.