Uranium

Cold

Hot!
LEED and ARPES of α - Uranium (001)

Presented by:

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In collaboration with:


and

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Outline:

- U single crystal origin
- LEED patterns
- Splitting 6p bands (XPS) & DDOS(T) WIEN2K calculations
- Valence band (UVPS) DOS(T) data & DDOS(T) WIEN2K calculations
- U(001) ARPES & DDOS(T) WIEN2K calculations at 173 K
- Avenues ahead…
- Questions and Conclusions
Origins of Uranium Single Crystals (001)

Argonne National Laboratory

Nuclear Fuels Reprocessing
Three U allotropes: Crystal structure vs T (K)

- **Liquid**
  - 1406 K
- **Solid**
  - 1045 K
  - 935 K
  - 0 K

**Crystal Structure vs Temperature (T) (K):**

- **Orthorhombic**
  - Cmcm (4 ats/u.c.)
- **Tetragonal**
  - P42/mnm (30 ats/u.c.)
- **Body Centered Cubic**
  - Im -3m (2 ats/u.c.)

- **α**
- **β**
- **γ**

- **Highly ductile, no work hardening observed, little microstructural strain or impurities, RRR ~ 115 (3x better)**

- **Chemical Analysis (PPM)**
  - Si = 168, C = 40, with Ti, Cu, Mo, V, Zr, Fe, Al, Ta, Mg < Detectable Limit
LEED Apparatus

LEED = Low Energy Electron Diffraction

Used to examine ordered surface structure and effects of controlled surface doping
Real and reciprocal space U(001)

- $a = 2.854 \, \text{Å}$
- $b = 5.869 \, \text{Å}$
- $c = 4.955 \, \text{Å}$

LEEDpat analysis

- Basic 2D lattice/group : [5] Centred. Rect. cm
  - $a = 2.85400$, $b = 5.86900$, $\phi = 90.00$
- Superlattice/group : (None) Matrix = $(1, 0, 10, 1)$ [11] Oblique pl
  - $a_2 = 3.26807$, $b_2 = 3.26807$, $\phi_{22} = 128.13$, 1 unique domain(s)
LEED pattern of U(001) at T = 273 K

1st order
75 eV

2nd order
150 eV

- First U(001) LEED pattern, long range order bulk termination
- Calculation & Experiment < 2 % difference
- Structural reactivity studies: O$_2$, D$_2$, H$_2$
- I-V analysis underway
Photoelectric Effect and Photoemission Spectroscopy

Photons in

Light in

Electrons out

$E_f$

$2p$

$2s$

$1s$

$E = h\nu$

K.E.

B.E.

B.E. = $h\nu - \Phi_s - \text{K.E.}$
Photoemission Spectroscopy

Photons in

$$E = h \nu$$

Electrons out

K.E. = $$h \nu - \Phi_s - B.E.$$
Splitting of $6p_{3/2}$ and $6p_{1/2}$ bands

Depth profiling by angle resolved XPS:
Valence band DOS(T) at Fermi edge

**Experimental Parameters**
- PHI-5600 ESCA
- Spherical cap. analyzer
- Photon sources:
  - Al Kα (1486.6 eV)
    - [monochromated]
  - UPS - He I, He II
- P = 1.0 x 10^{-8} Pa
- Resolution = 28.5 meV
- Temp. ⇒ 173 - 1273 K
- Electron TOA = 90°
He I & II VB Data and WIEN2K Calculation

He I, (21.2 eV)

He II, (40.8 eV)
Directional Density of States (DDOS), at the $\Gamma_\Sigma$ point
**ARPES** - choose azimuthal $\theta$ to specify $k$-vector to probe, and then vary polar $\phi$ to collect DOS at various $k_{||}$ and observe dispersion of bands along $k$-vector.

$$E_{\text{kinetic}} = h\nu - e\Phi - E_{\text{binding}}$$

$$k_{||} = \sqrt{\frac{2m_e E_{\text{kinetic}}}{\hbar^2}} \cdot \sin \phi$$

Brillouin zone orientation

$$(100) \text{ plane}$$
Condensed Matter in a Nutshell

1. Real vs. Reciprocal Space

(Real) x-Space

(Momentum) k-Space

Localized core electrons
Delocalized valence band electrons

Constant-energy surface
Constant Energy Surfaces

\[ E_{\text{Bind}} = \frac{1}{2} mv^2 \]

\[ = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \]

\[ E_F \]

\[ \Gamma \quad X \quad \Gamma \quad X \quad \Gamma \]

e.g. Copper

\[ \Gamma \quad X \quad L \quad \Gamma \quad L \quad \Gamma \]

gap
Angle-Resolved Photoemission

Copper

Binding Energy, eV

momentum, k

Energy

photon

valence levels

core levels

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NISA
Brillouin Zone

Orthorhombic Space Group, b > a, α - Uranium

ARPES Raw Data Stack Plot

φ = 60 degrees

⊥ to U(001) surface
ARPES Raw Data Stack Plot

$\phi = 60$ degrees

$\perp$ to U(001) surface
ARPES $\Sigma$ to $\Gamma$, $\Gamma$ to $Y$, $U(001)$, $T = 173$ K
ARPES \( \Sigma \) to \( \Gamma \), \( \Gamma \) to \( Y \), U(001), \( T = 173 \) K
Uranium Band Map

Sigma to Gamma

Gamma to Y

$T = 173$ K
ARPES $\Gamma$ to $S \ U(001), \ T = 173 \ K$
ARPES $\Gamma$ to S U(001), $T = 173$ K
Uranium Band Map
Gamma to S
T = 173 K

Intensity [arb. units]

K// [unity], Gamma to S

Binding Energy [eV]
Uranium Band Map
Gamma to S
T = 173 K
Uranium Band Map
Gamma to S
T = 173 K

Intensity [arb. units]

Binding Energy [eV]

K// [unity]

Gamma to S
ARPES: Σ - Γ - Y, Γ - S

α-Uranium (001), T = 173 K
ARPES & WIEN2K

$\alpha$-Uranium (001), $T = 173$ K
Directional Density of States (DDOS), at the $\Gamma_\Sigma$ point
Data Maxima, WIEN2K Gap Calculations & Surface States

- Band Structure
- Band Structure, Low Intensity
- d-Band, Tamm surface states
- f-Band, f-like, Shockley surface states
- Plasmon ??
- Flat band near FE due to disorder ?

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Data Maxima, DDOS WIEN2K Calculations

Band Structure

Band Structure, Low Intensity

d-Band, Tamm surface states

f-Band, f-like, Shockley surface states

Plasmon ??

Flat band near FE due to disorder ?
Band crossing points
\[
\text{Reality} = \text{Matrix} \times \text{Theoretical Calculation}
\]

**Experimental Data, ARPES**

**Temperature Dependence and Electron-Electron Correlations**

**WIEN2K**
**Band Structure Calculations**
**& DMFT Modeling**
Low Temperature Sample Manipulator

Displex

Electric and Cryogen Ports

Axis Rotation

Triple Axis

Radiation Shield

Pot

Sample Puck

Mo Sample Jaws

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Low Temperature Sample Manipulator
surface chemistry, analytical surface science, electronic structure measurements, single crystal investigations, 
in-situ surface/thin film reactions, materials corrosion, in-situ thin film materials synthesis, analytical surface forensics
Conclusions:

★ Single crystal U(001) samples yield expected experimental LEED pattern (< 2% difference). Showing long range bulk termination.

★ XPS data on U(001) correlates well with 6p splitting shown in DDOS WIEN2K model calculations.

★ Valence band DDOS WIEN2K calculations correlates with UPS data at 173 K, E < 4 eV.

★ ARPES data exhibit band dispersion at 173 K and correlates with DDOS WIEN2K, if temperature and e⁻ correlations are considered.
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The following slides are supplementary to the presentation and will be used as needed.
Brittle-Ductile transition in Uranium


*Impurity mobility effects B-D trans.*

*Electronic and structural correlations*
Conclusions:

- Single crystal U(001) samples yield expected experimental LEED pattern (< 2% difference).

- XPS data on U(001) correlates well with 6p splitting shown in WIEN2K model calculations.

- Valence band WIEN2K calculations correlates with UPS data at 173 K, E < 4 eV.

- ARPES data exhibit band dispersion at 173 K and correlates with WIEN2K, if Temperature and e⁻ correlations are considered.

- %Elongation(T) and ψ (T) show a change in slope at ~ 400 K due possibly to impurity mobility.
WIEN2K Calculation for α Uranium with S-O coupling
WIEN2K Calculation for $\alpha$ Uranium with S-O coupling only s band

WIEN2K Calculation for $\alpha$ Uranium with S-O coupling only p band
WIEN2K Calculation for α Uranium with S-O coupling only d band

WIEN2K Calculation for α Uranium with S-O coupling only f band
WIEN2K Calculation for α Uranium with S-O coupling
At He I energy ($h\nu = 21.2$ eV) 6d states are emphasized.

At He II energy ($h\nu = 40.8$ eV) 5f states are emphasized.

**Back-reflection Laue**

In the back-reflection method, the film is placed between the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.