Mott insulating state of ultrathin epitaxial $LaNiO_3$ thin films detected by hard x-ray photoemission

Alexander Gray[1,2]

[1]Department of Physics, University of California, Davis

[2]Materials Sciences Division, Lawrence Berkeley National Laboratory

with

A. Janotti,[3] J. Son,[3] J. M. LeBeau,[3] S. Ueda,[4] Y. Yamashita,[4] K. Kobayashi,[4] A. M. Kaiser,[1,2] R. Sutarto,[5,6] H. Wadati,[5,*] G. A. Sawatzky,[5] C. G. Van de Walle,[3] S. Stemmer,[3] and C. S. Fadley[1,2]

[3]Materials Department, UC Santa Barbara; [4]NIMS Beamline Station at SPring-8, Japan,
[5]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada*

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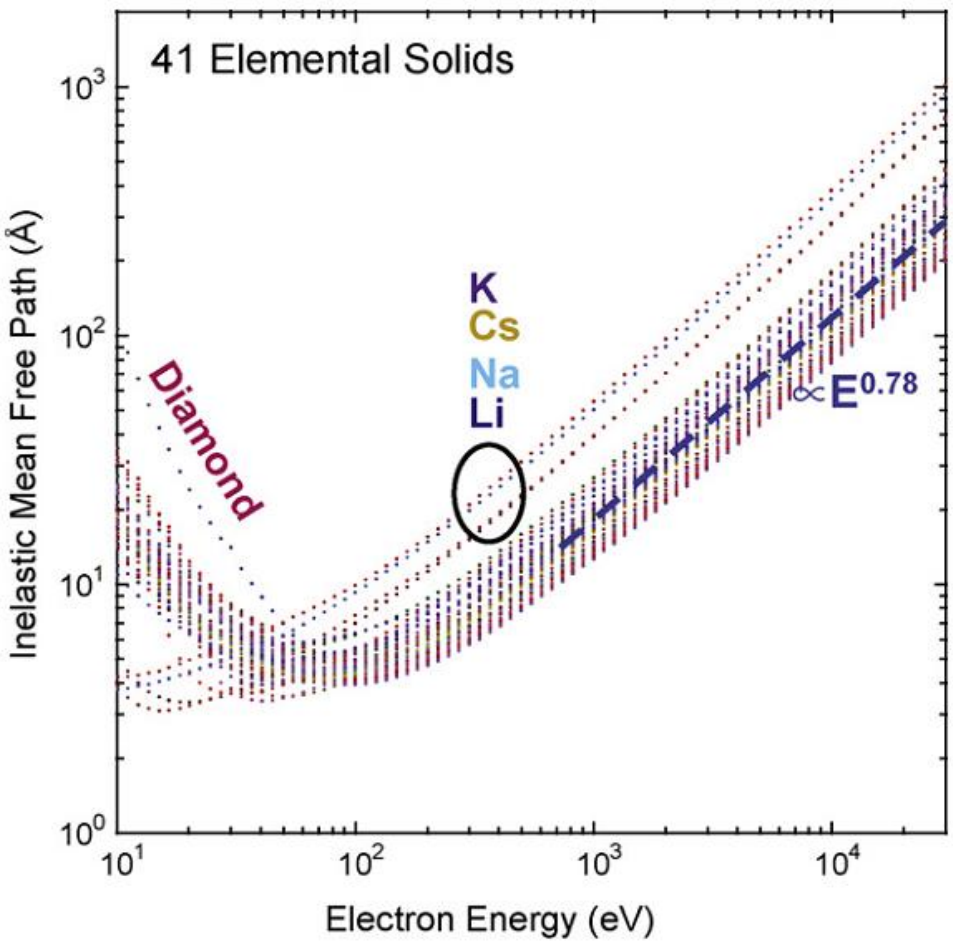
Outline

- **Motivation: Why Hard X-ray XPS?**
- **Application: Electronic Properties of $LaNiO_3$**
- **Determination of Effective Attenuation Length in LNO**
- **Extraction of Thickness-Dependent DOS of LNO**
- **Comparison to Theory and Conclusions**

Motivation

How much Deeper does Photoemission Probe with Hard X-Rays?

Inelastic Mean-Free Path VS E_{kin}



Traditional soft X-ray XPS is heavily influenced by surface effects

With multi-keV excitation

~ 4-5× deeper than soft x-ray XPS

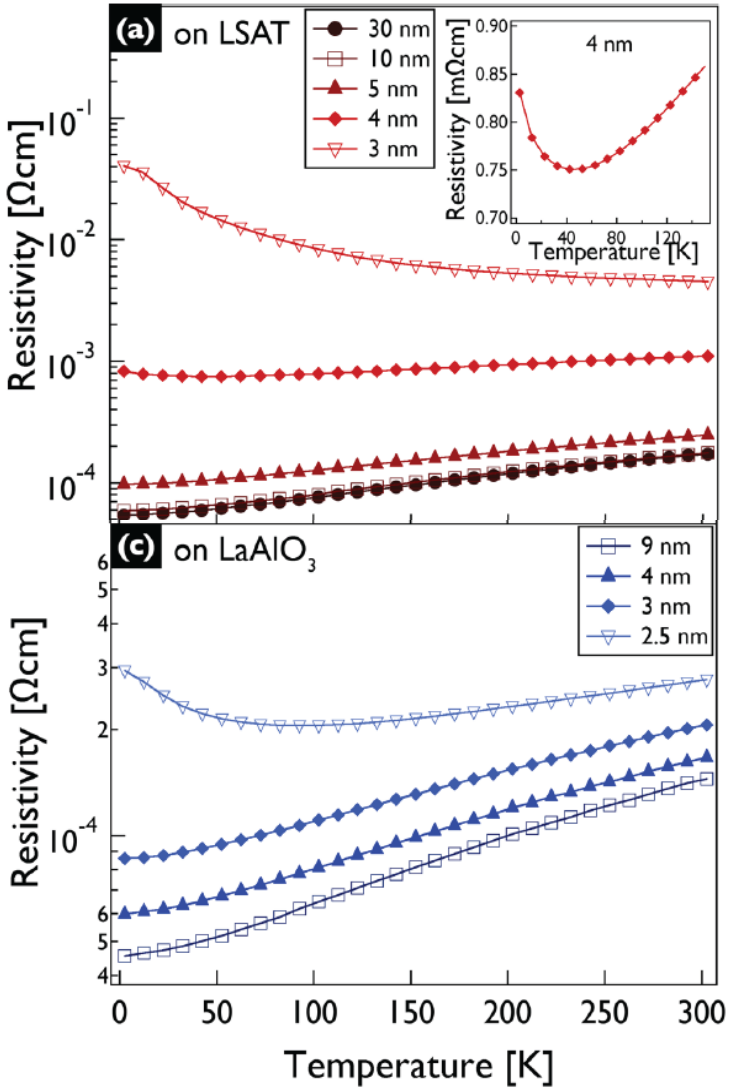
⇩

We can obtain more accurate BULK electronic structure

S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 43, 689 (2010).

Mott Behavior in $LaNiO_3$ Thin Films

Conductivity (J. Son, S. Stemmer)



J. Son et al., APL 96, 062114 (2010)

Mott Materials

- For ultra-thin films, strong electron correlations cause an insulating state when conventional theory predicts metallic behavior.
- This has great promise for applications, if the transition can be controlled.
- Materials are on the verge of metal-to-insulator transition.
- Dramatic Changes in properties: electrical, optical and magnetic.
- Among the least understood phenomena in condensed matter physics.

Mottronics

Mott Behavior in $LaNiO_3$ Thin Films

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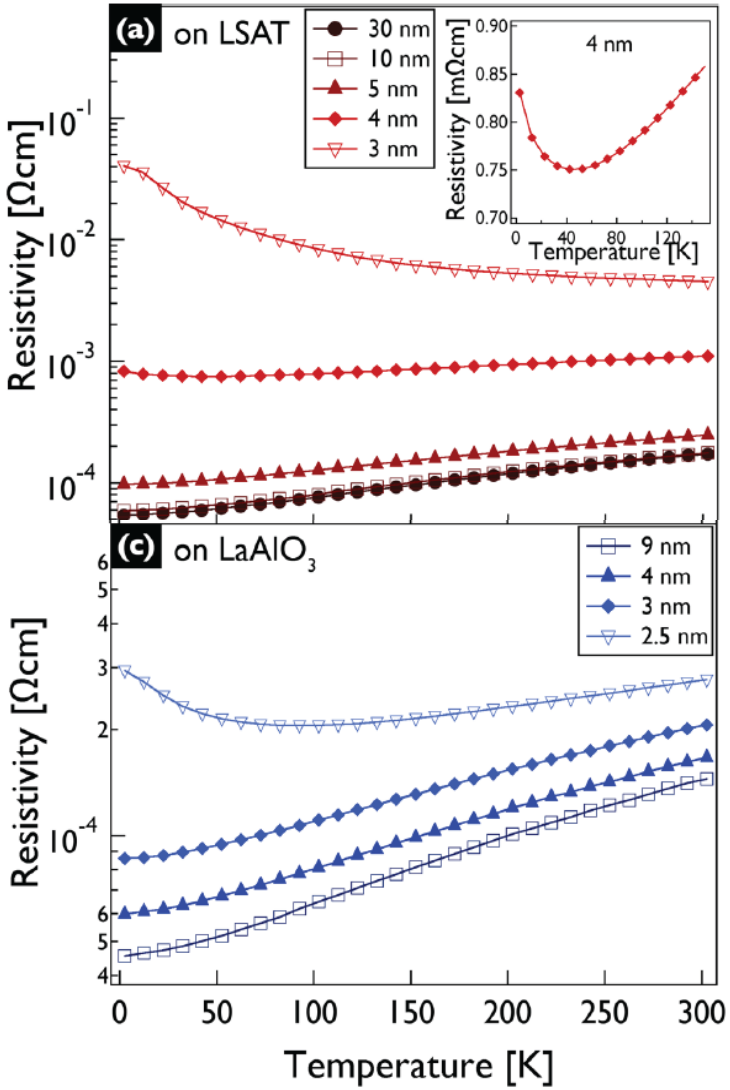
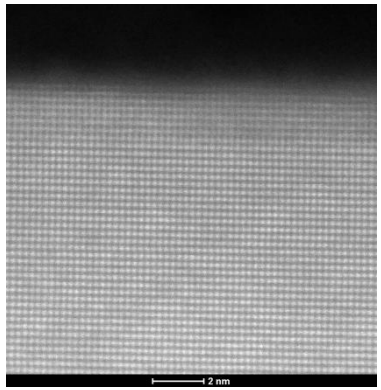
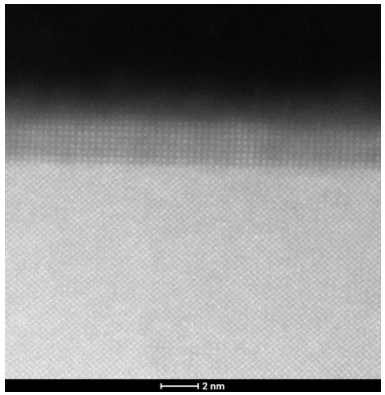


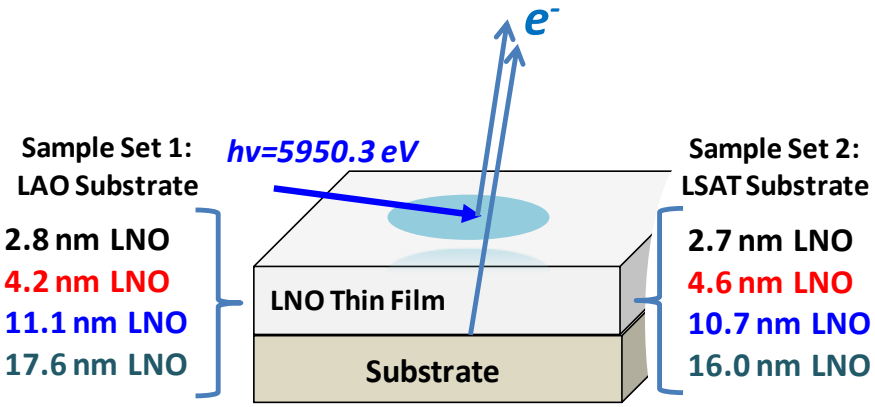
Epitaxial layers with TEM thickness det'n. (J. Son, J. LeBeau, S. Stemmer)



LNO/LAO
~ 7 unit cells = 2.8 nm



LNO/LSAT
~ 7 unit cells = 2.7 nm



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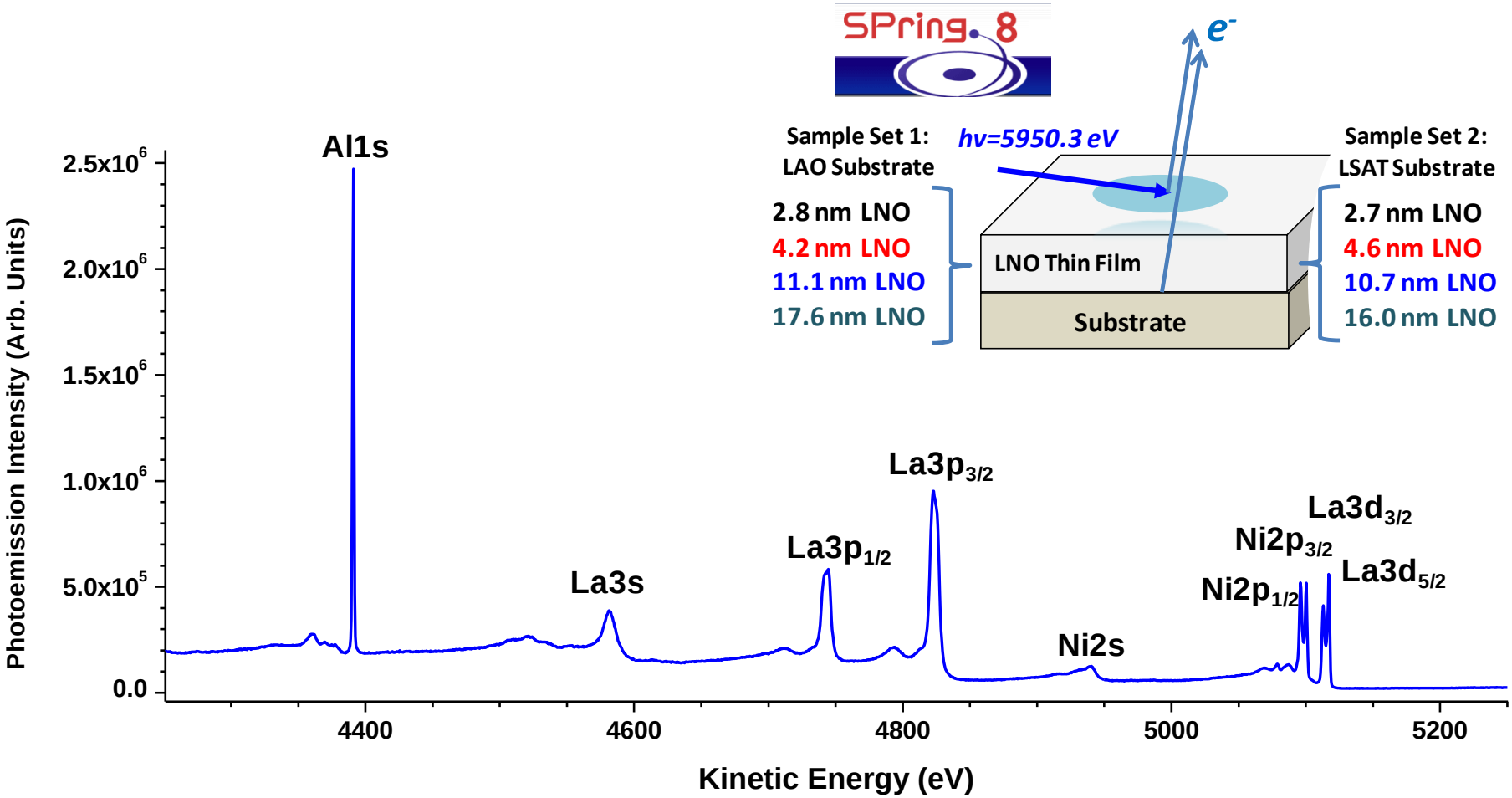
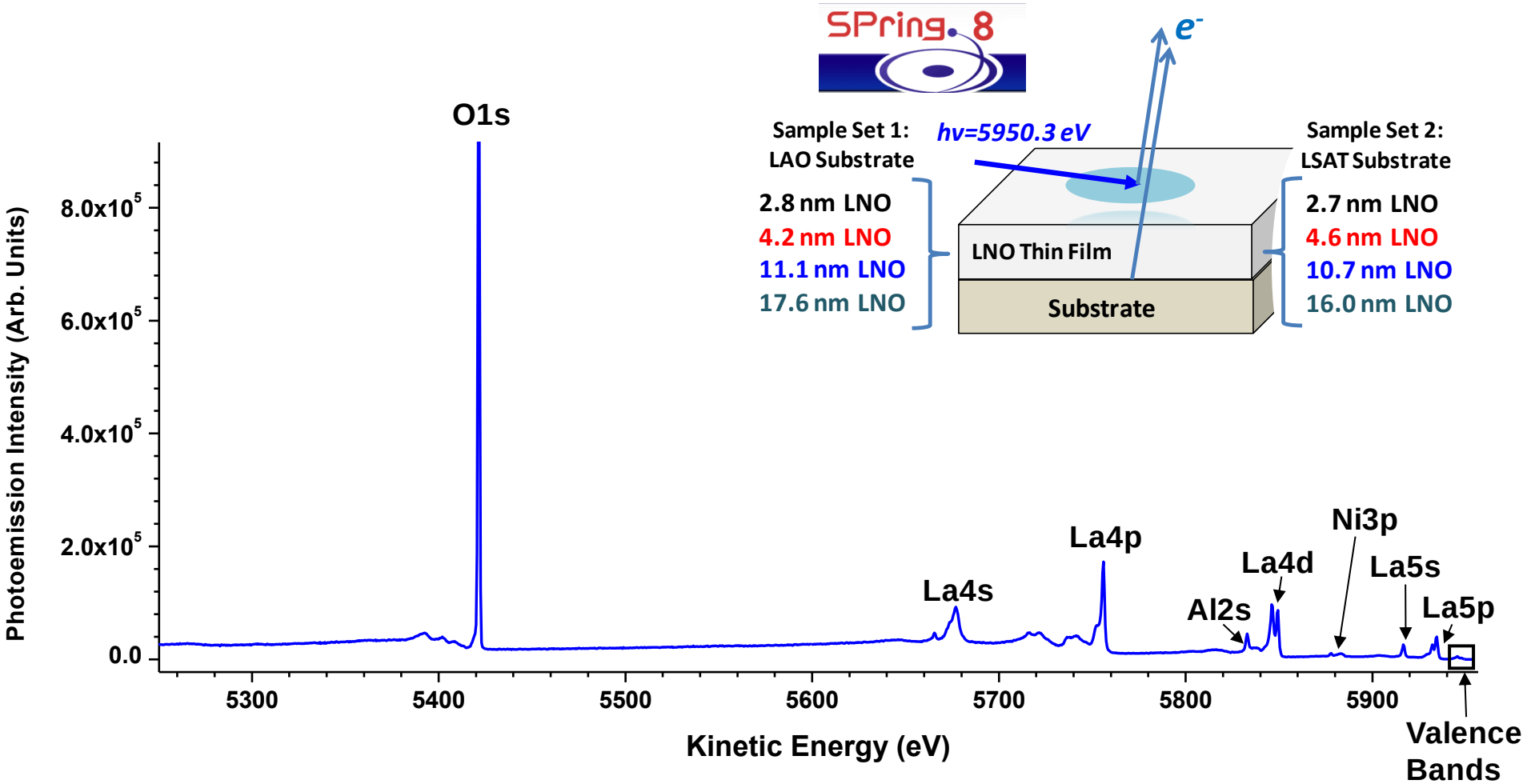
Hard X-ray Photoemission at *hv*=5.95 keV



Probing ~70 Å into the sample

Experiment with S. Ueda, K. Kobayashi

Hard X-ray Photoemission at *hv*=5.95 keV



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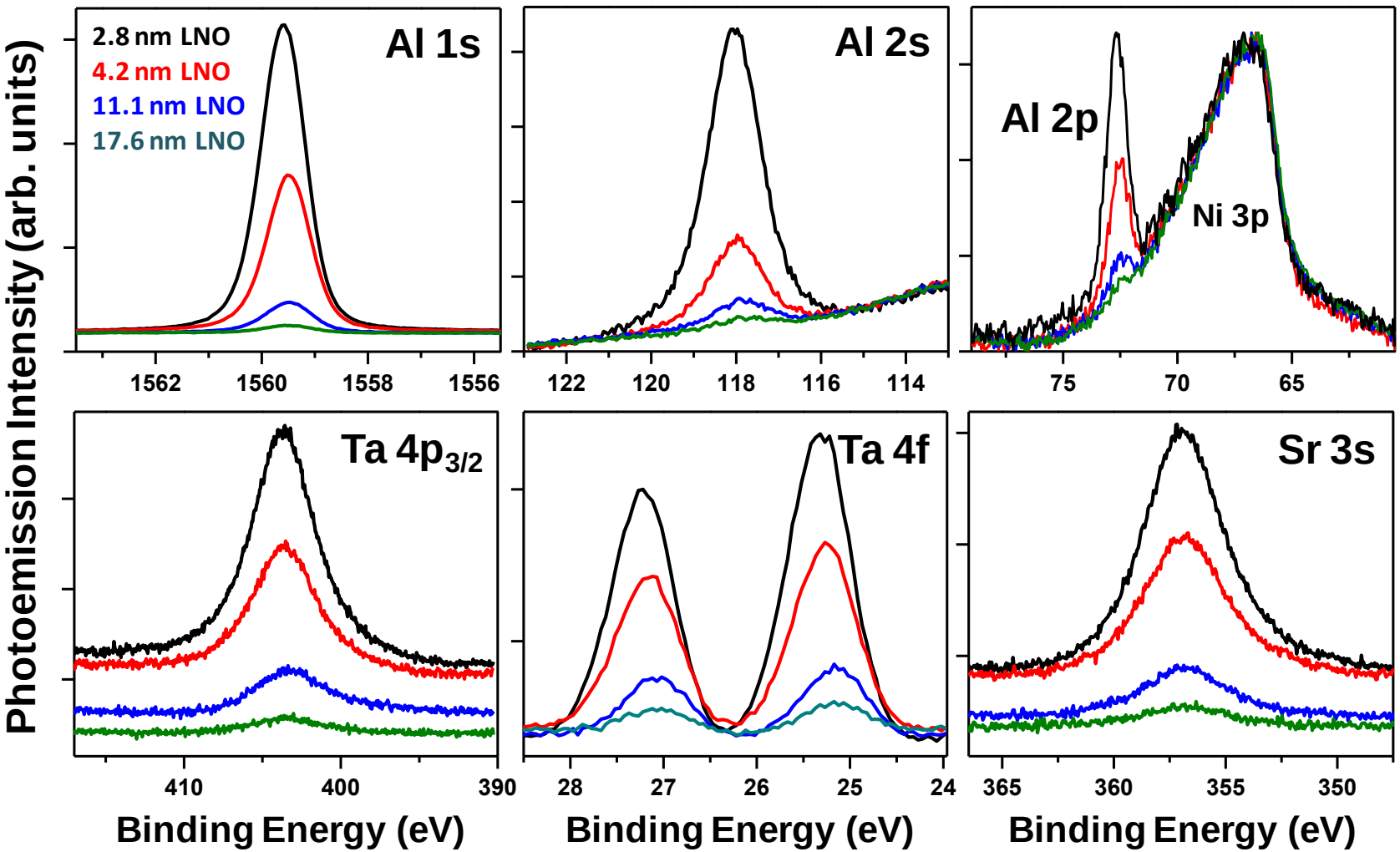
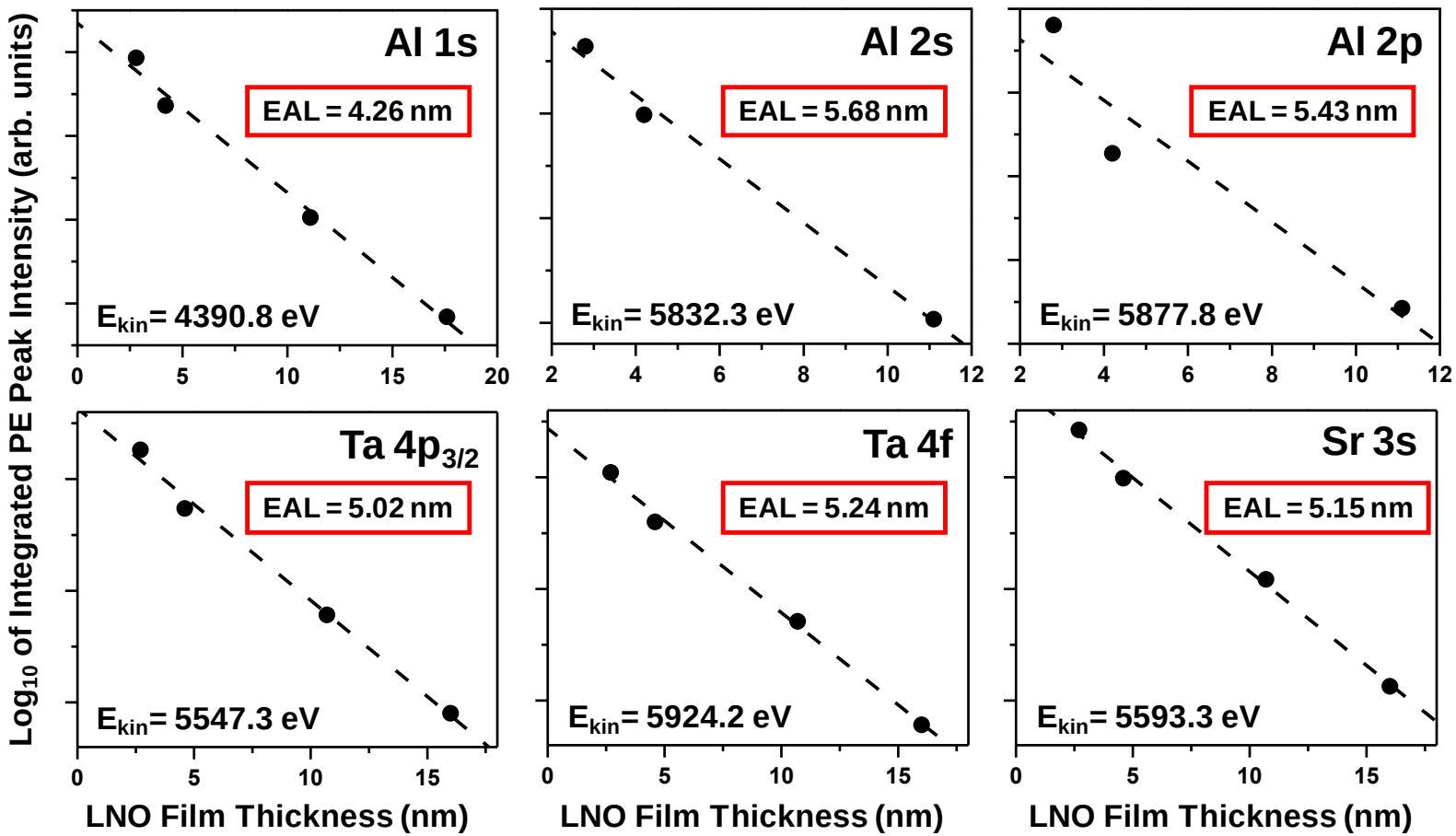
Substrate Core-Peak Photoemission Spectra

Core peaks originating from the substrate lose intensity as the overlayer thickness becomes larger: $I_{LSAT} \propto e[t_{LNO}/\Lambda_{EAL,LNO}]$

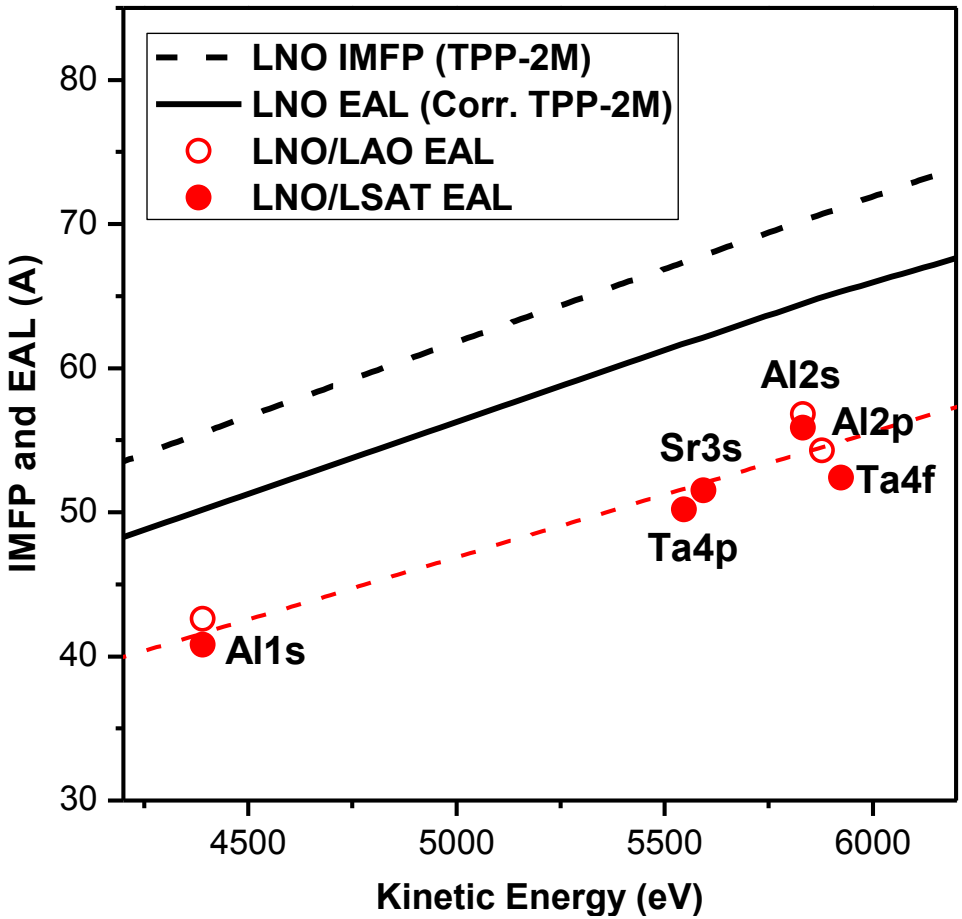


Calculating Effective Attenuation Lengths

Effective attenuation lengths for the photoelectrons can be calculated by analyzing core peak intensities according to: $I_{substrate} \propto e^{-t/\Lambda_{EAL}}$



Experimentally Determined EALs



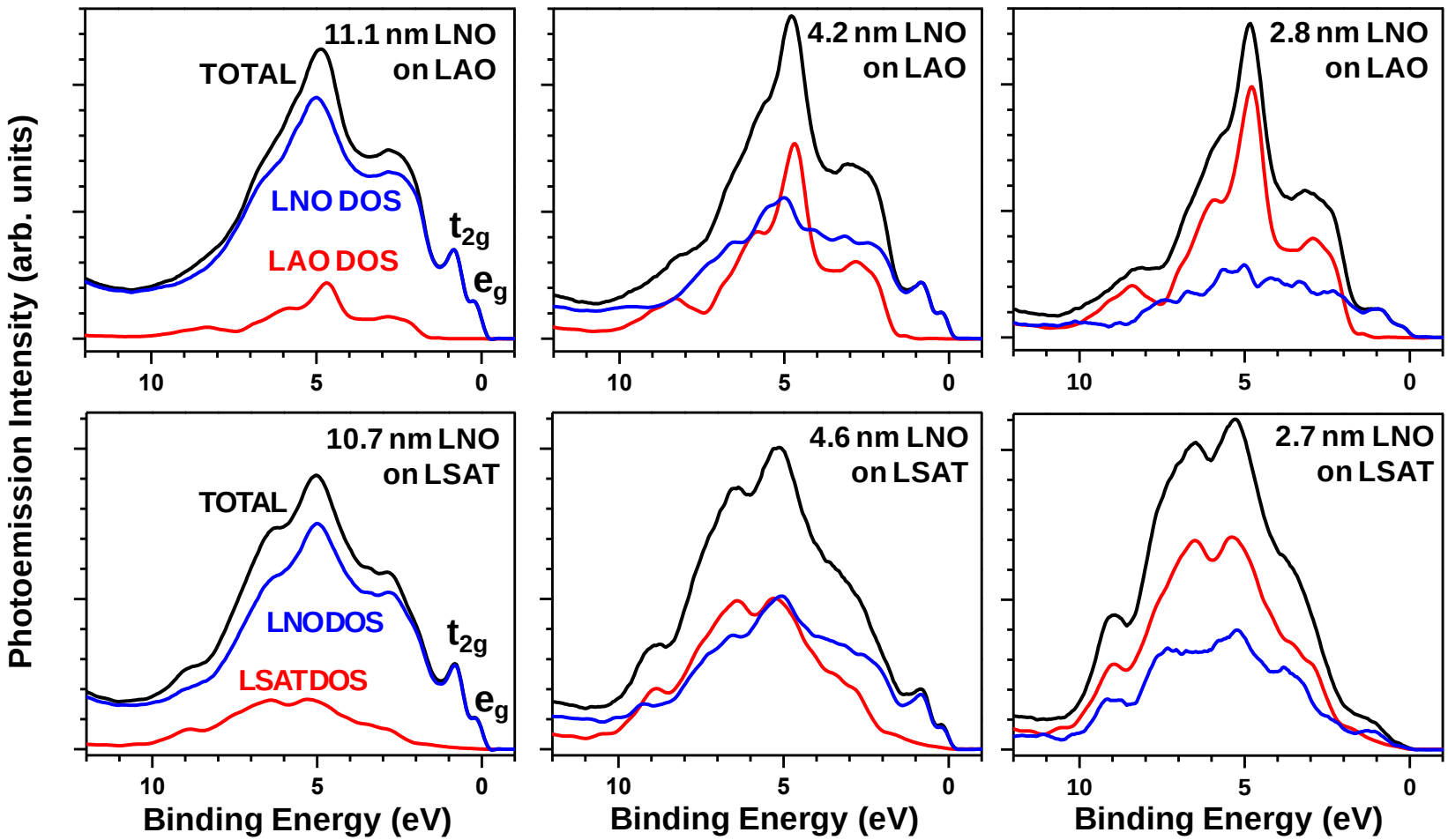
S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* 43, 689 (2011).
A. Jablonski and C. J. Powell, J. Vac. Sci. Technol. A 27, 253 (2009).

- **LNO EALs within ~20% of the much-used semi-empirical TPP-2M formula, if corrected for elastic scattering**

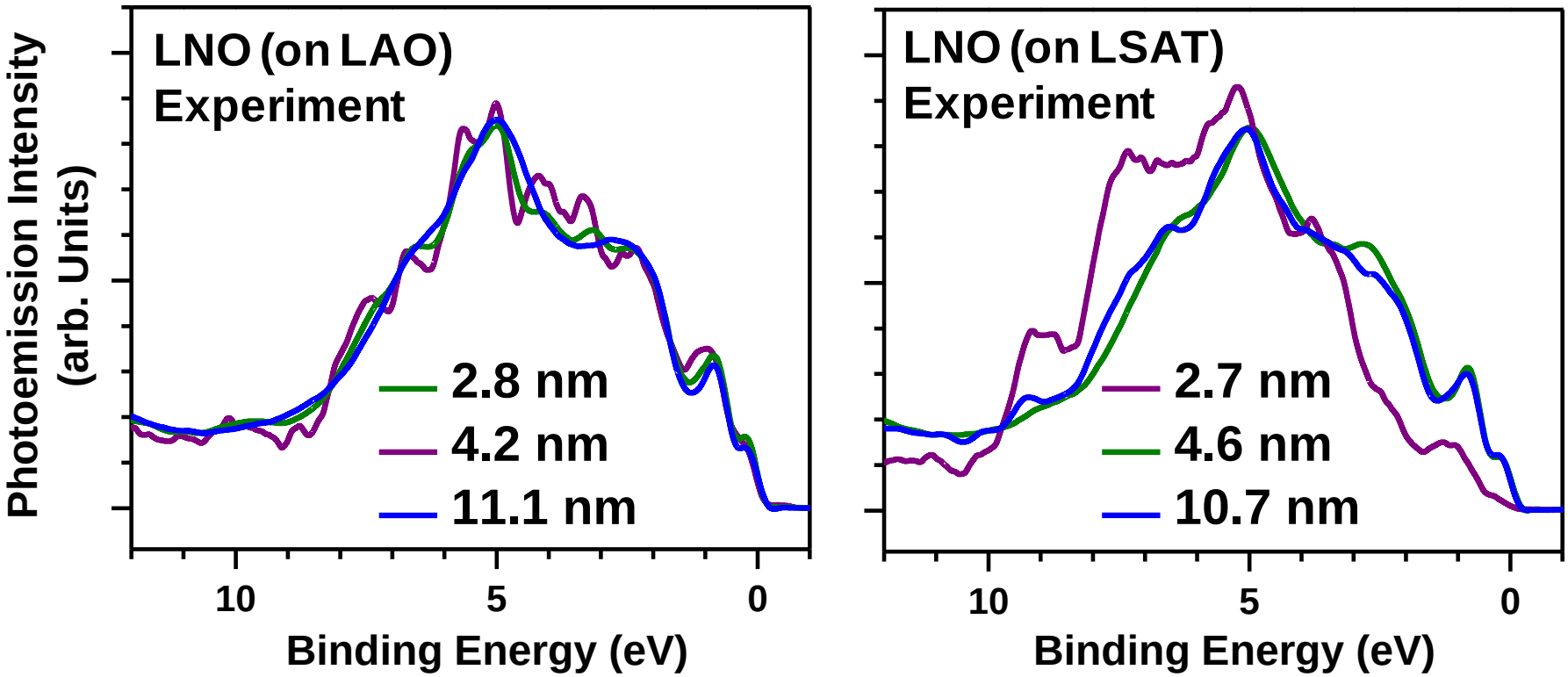
- **Remaining expt./theory discrepancy may be due to lack of resonant absorption edges in theory: an effect not considered previously**

Valence-Band Decomposition

Valence band spectra can now be decomposed into the film and substrate DOS components using the EALs and $I_t^{(0)} = [1 - e^{-t/\Lambda_{EAL}}]I_{LNO,t} + e^{-t/\Lambda_{EAL}} I_{LAO(LSAT),t}$

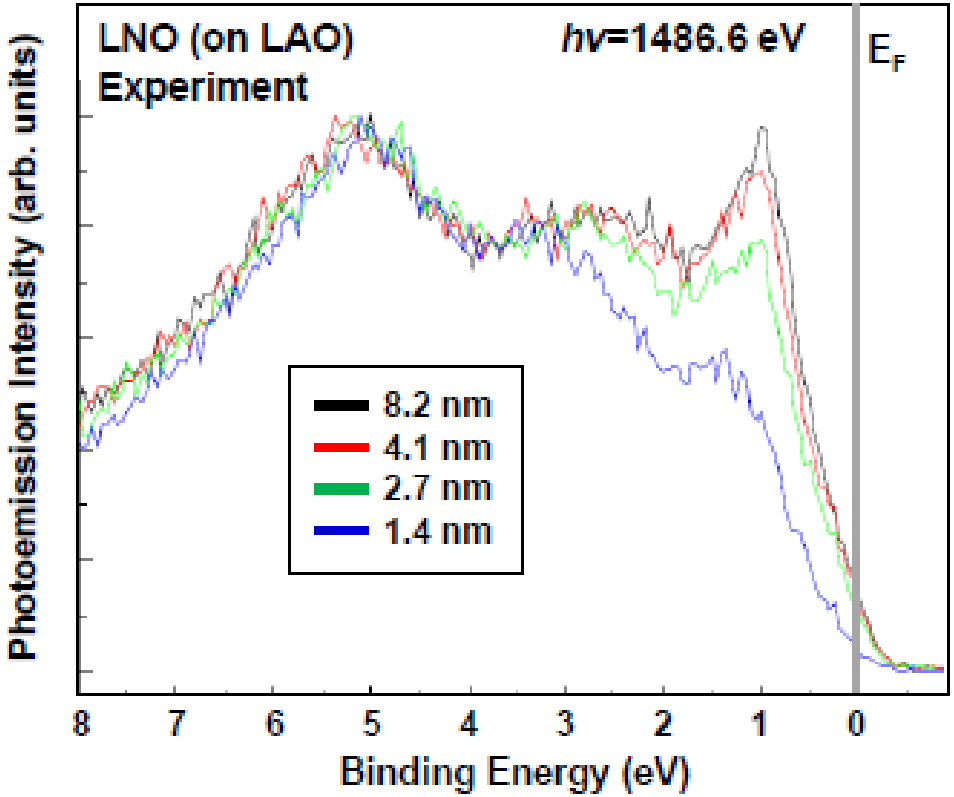


Thickness and Substrate Dependence of LNO DOS



A gap opening consistent with a metal-to-insulator transition is observed for the thinnest (2.7 nm) $LaNiO_3$ film on an LSAT substrate.

Thickness and Substrate Dependence of LNO DOS

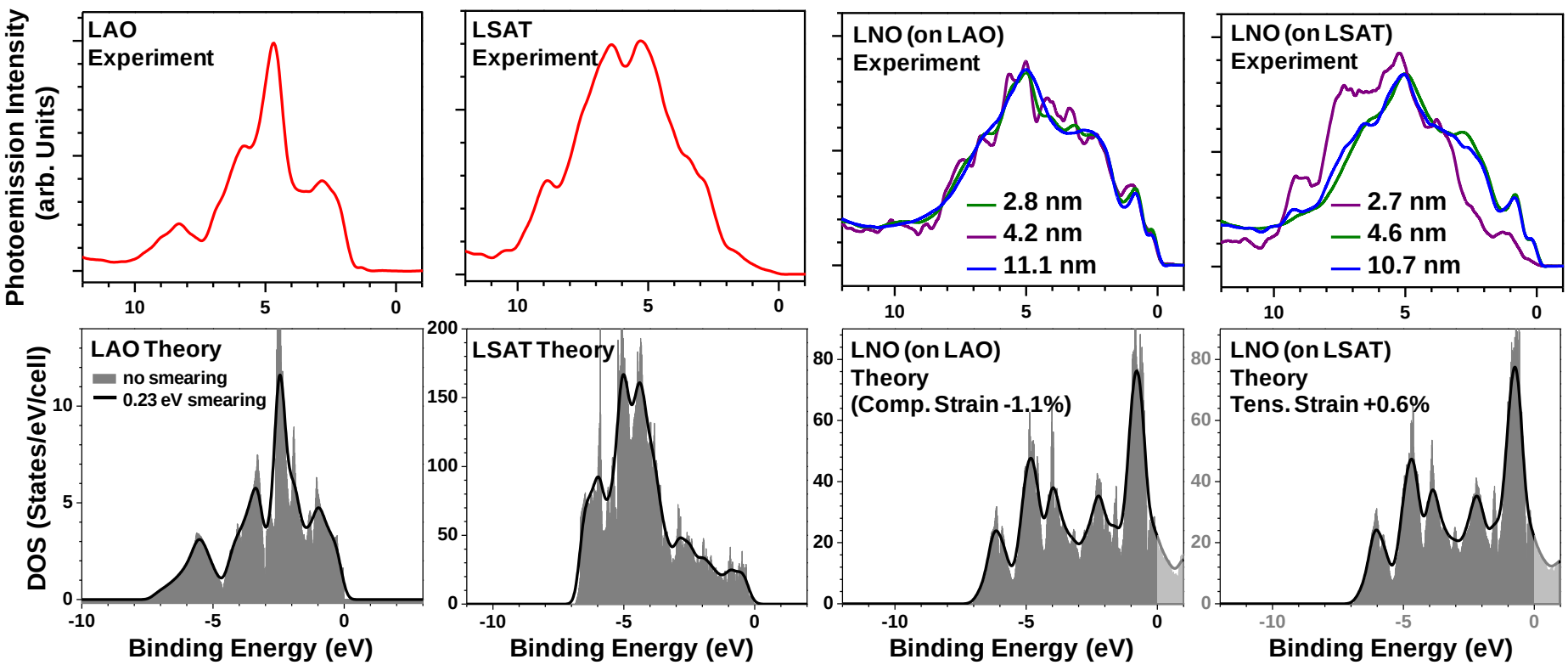


Similar gap opening is observed for a thinner (1.4 nm) $LaNiO_3$ film on an LAO substrate with soft x-rays.

Experimental data from R. Sutarto, H. Wadati and G. Sawatzky

Layer-Specific DOS Compared to DFT

Experimental layer-specific decomposed DOS

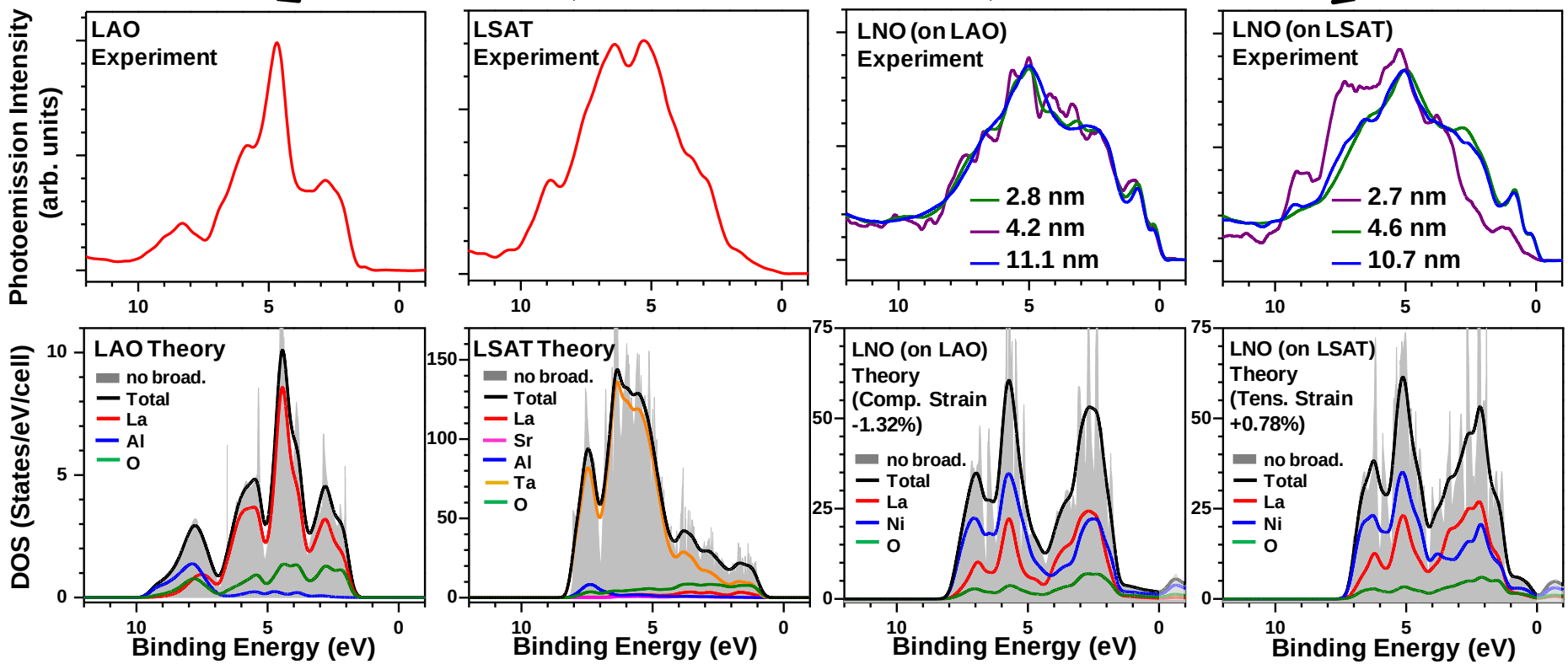


DOS Calculated using conventional DFT

Theory by A. Janotti and C. Van de Walle, UCSB

Layer-Specific DOS Compared to HSE DFT

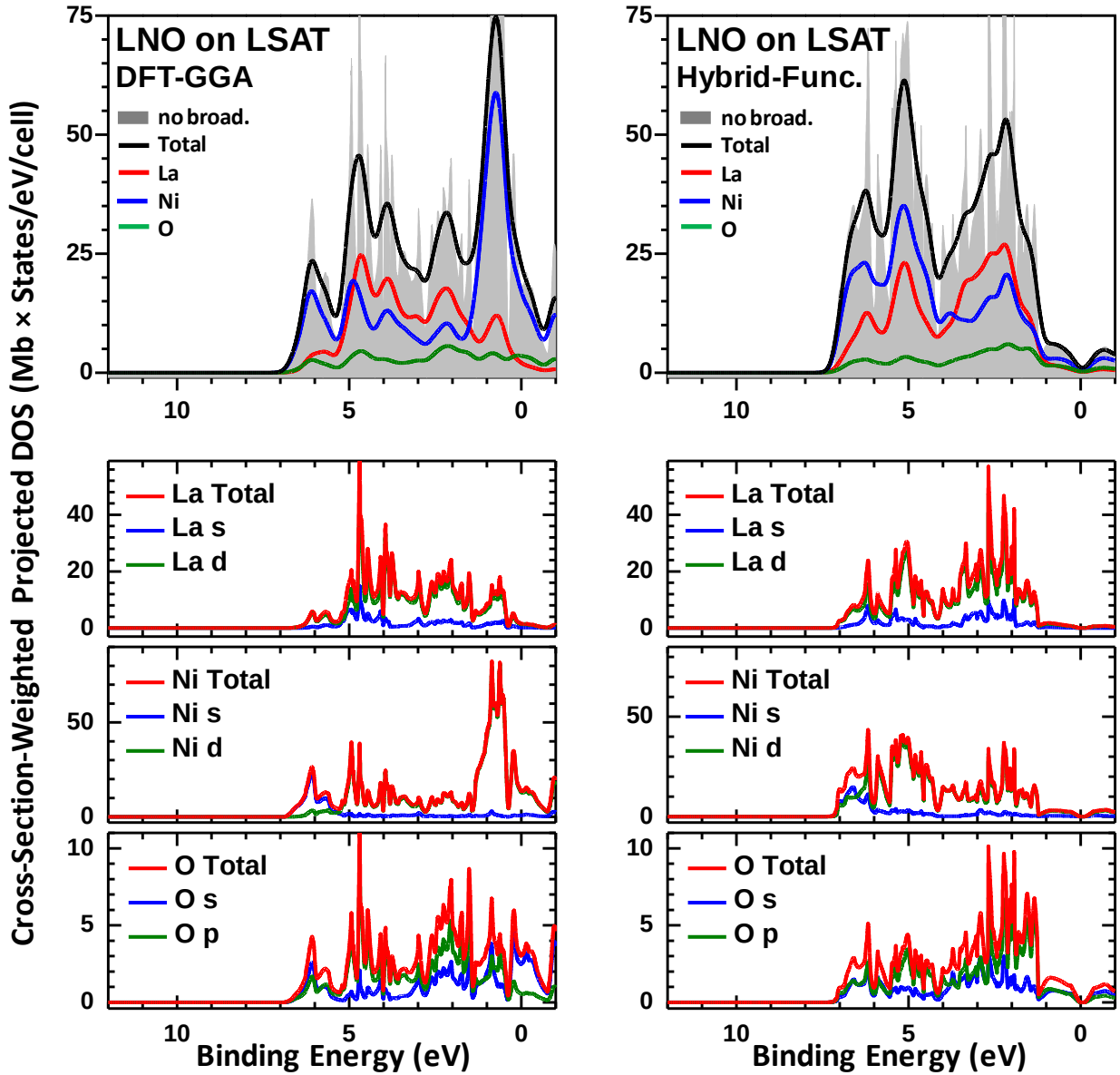
Experimental layer-specific decomposed DOS



DOS Calculated using hybrid functional HSE DFT

Theory by A. Janotti and C. Van de Walle, UCSB

Comparison between DFT-GGA and HSE DFT



Summary

- Derived accurate experimental values of the effective attenuation lengths (EAL) in LNO via core-level HXPS analysis of a series of LNO thin-film samples with varying overlayer thickness

- The resultant EAL values were then used to decompose the valence-band HXPS spectra into DOS contributions from thin film and substrate

- The resultant thin-film LNO DOSs were compared for various thicknesses and substrate materials

- Significant differences in the spectral weights are observed for the thinnest epitaxial film on the LSAT substrate (as well as on LAO substrate via soft x-ray XPS)

- Strong suppression of the DOS just below the Fermi level suggests a metal-to-insulator transition, as recently observed in similar thin LNO films via electron transport measurements