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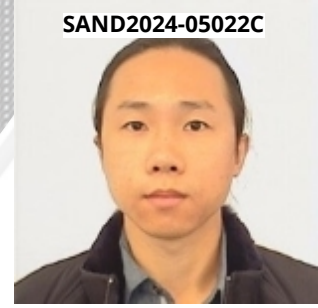


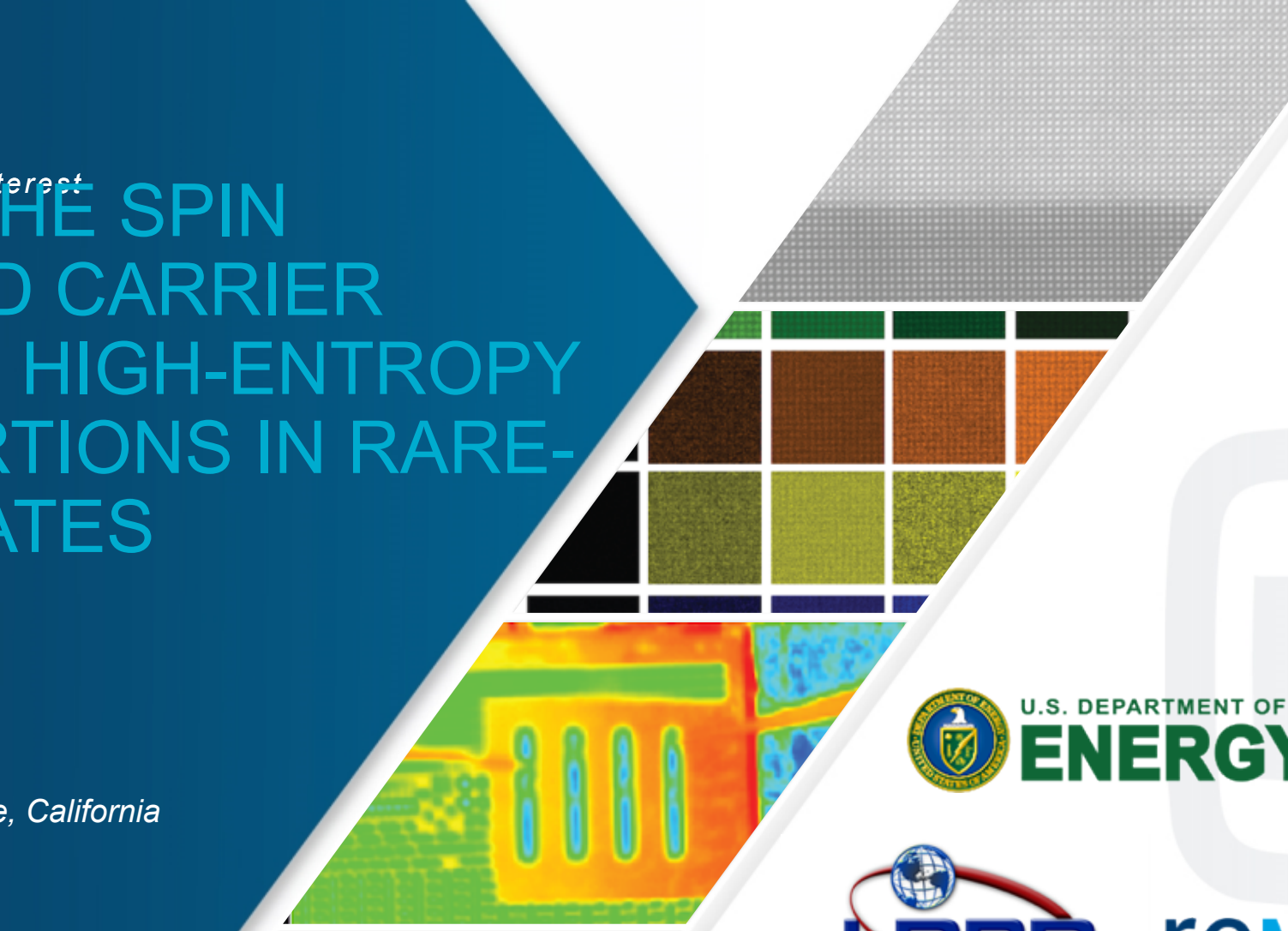
Alan Zhang

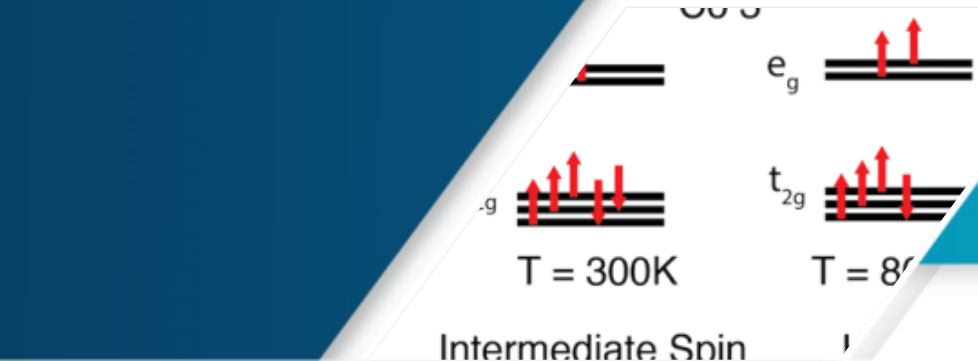
ENGINEERING THE SPIN TRANSITION AND CARRIER TYPE THROUGH HIGH-ENTROPY LATTICE DISTORTIONS IN RARE-EARTH COBALTATES

Elliot J. Fuller

Materials Physics Department, Livermore, California

MRS Spring Meeting 2024





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LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

reMIND

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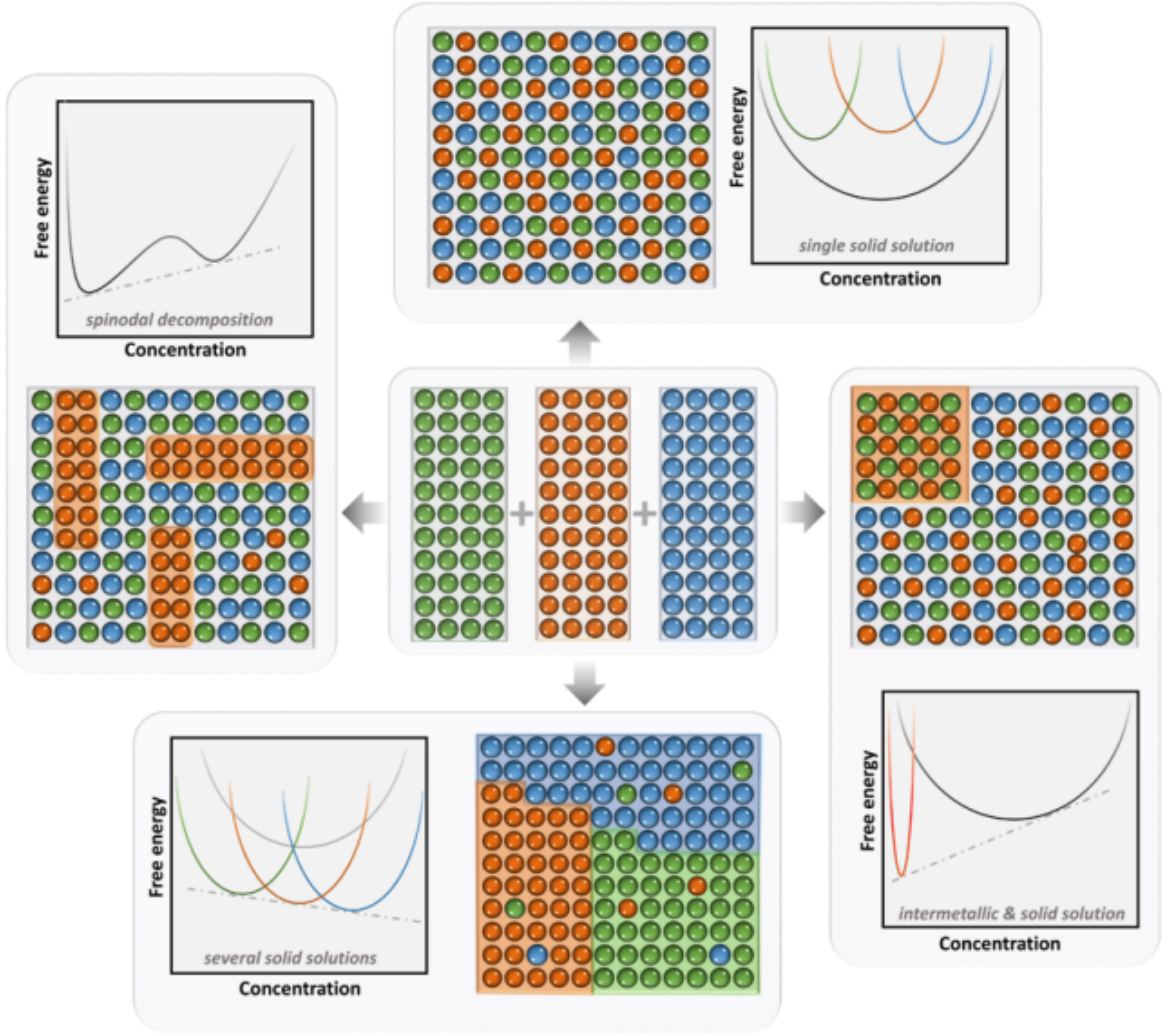
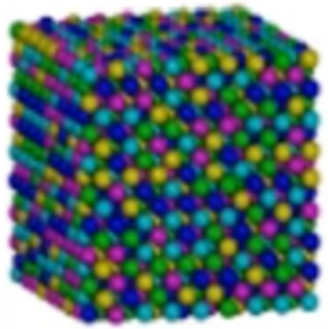
HIGH ENTROPY MATERIALS AND THE ‘COCKTAIL’ EFFECT



$$\Delta G = \Delta H - T\Delta S$$

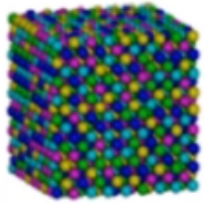


4,5+ components

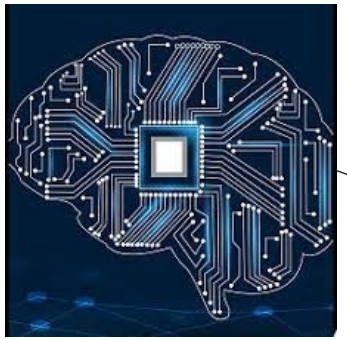
George et. al. *Nature Reviews Materials* (2019)

WIDE RANGING PERFORMANCE ENHANCEMENTS, FUNCTIONALITIES AND APPLICATIONS

entropy oxides

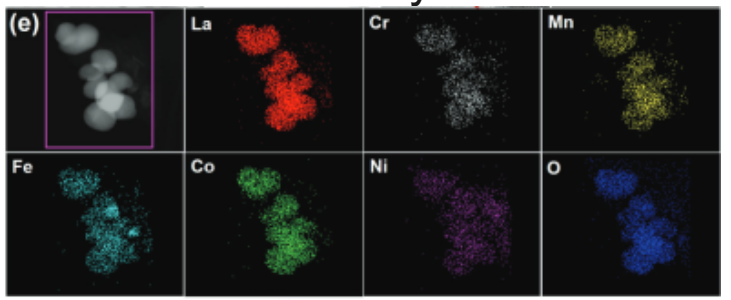


beyond Moore computing devices



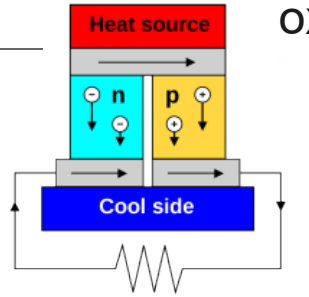
Ahn et. al. Adv. Elec. Mat. 2021

catalysts



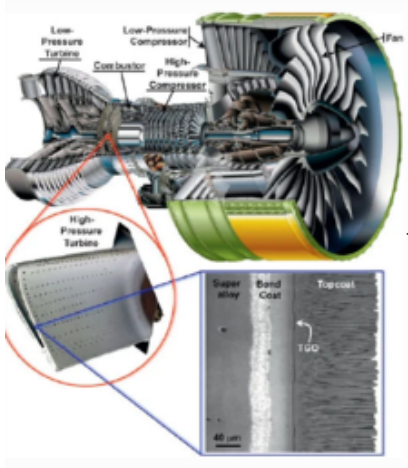
Nguyen et. al. Adv. Func. Mat. 2021

oxide thermoelectrics



Banerjee et. al. ACS Sust. Chem. Eng. 2020

thermal barrier coatings

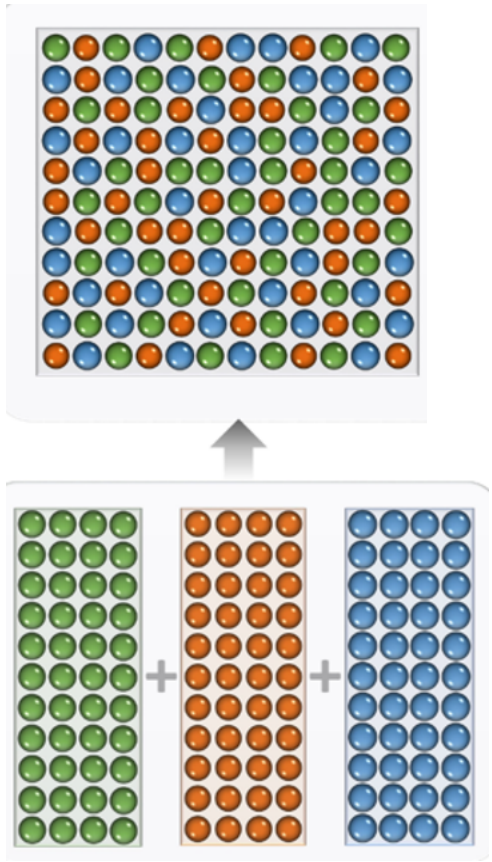


ceramic capacitors

Yang et. al. Nat. Mat. 2022

WHAT IS THE ROLE OF COMPOSITIONAL COMPLEXITY IN OXIDES?

$$X' = \frac{A+ \quad B+ \quad C+..}{N}$$



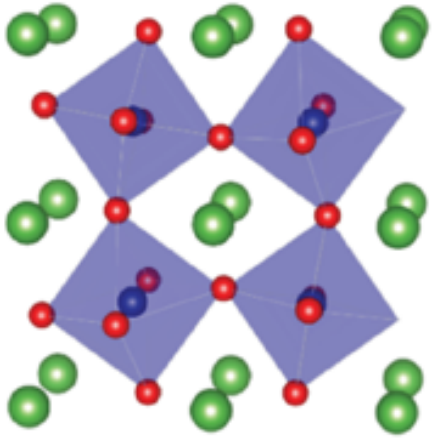
X = A B C…

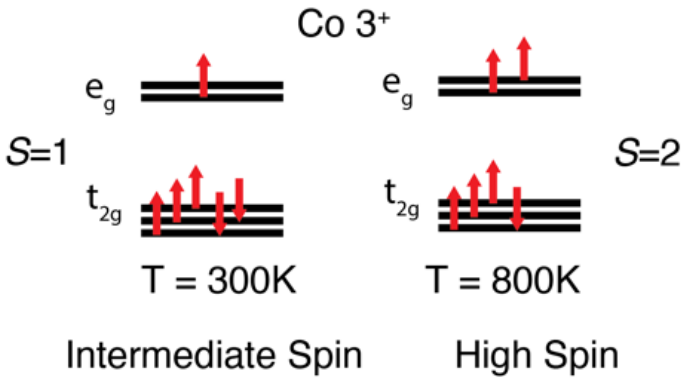
When does complexity play a role?

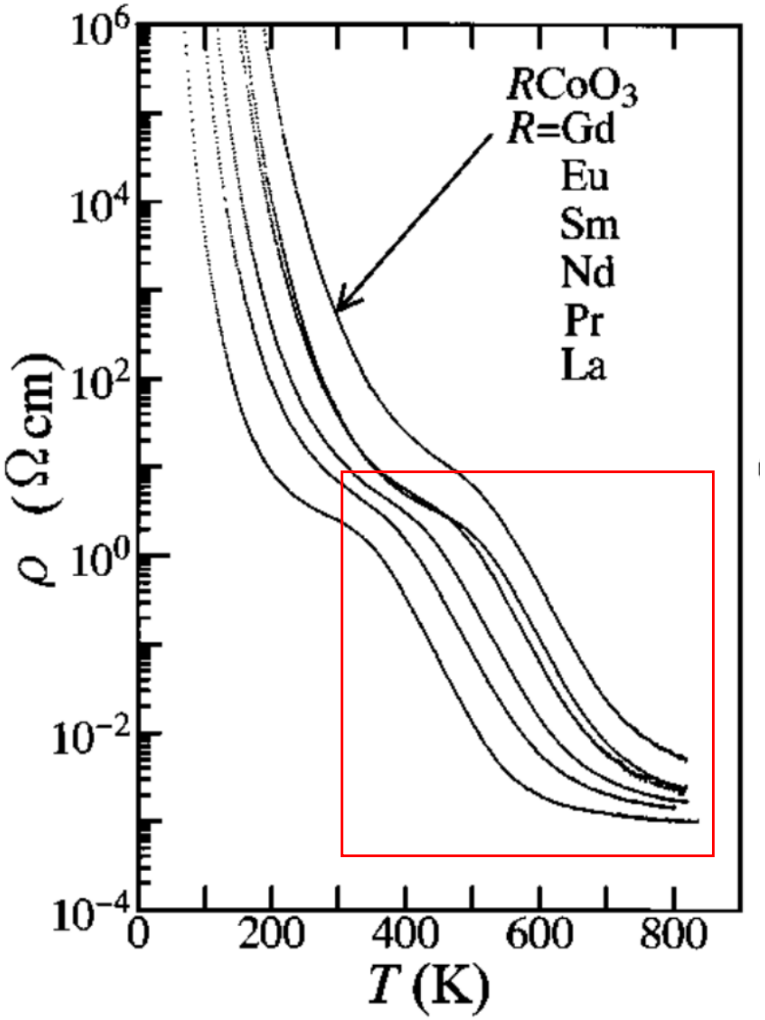
- Correlated effects mean exquisite sensitivity to small variations
- Functionality or performance is strongly affected by disorder
- Entropy stabilization effects occur, preferring order, solid solutions etc.
- Strong distortions lead to new electronic hybridization

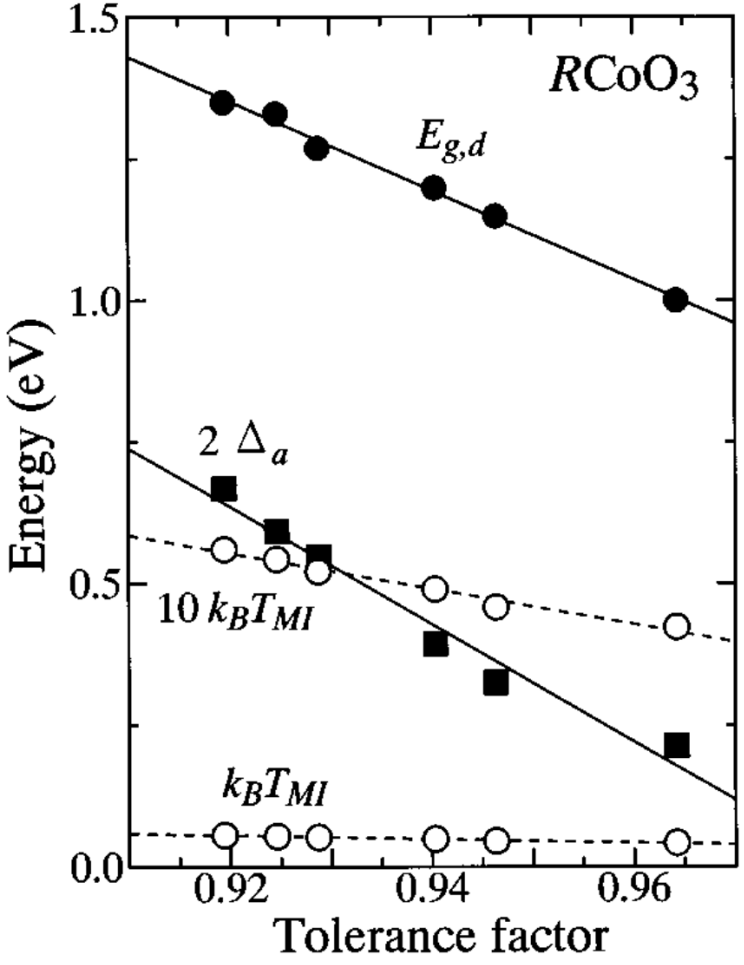
…. So when do these effects occur? What do they do? Rational design?

RARE EARTH COBALTATES – AN IDEAL SYSTEM TO STUDY COMPLEXITY



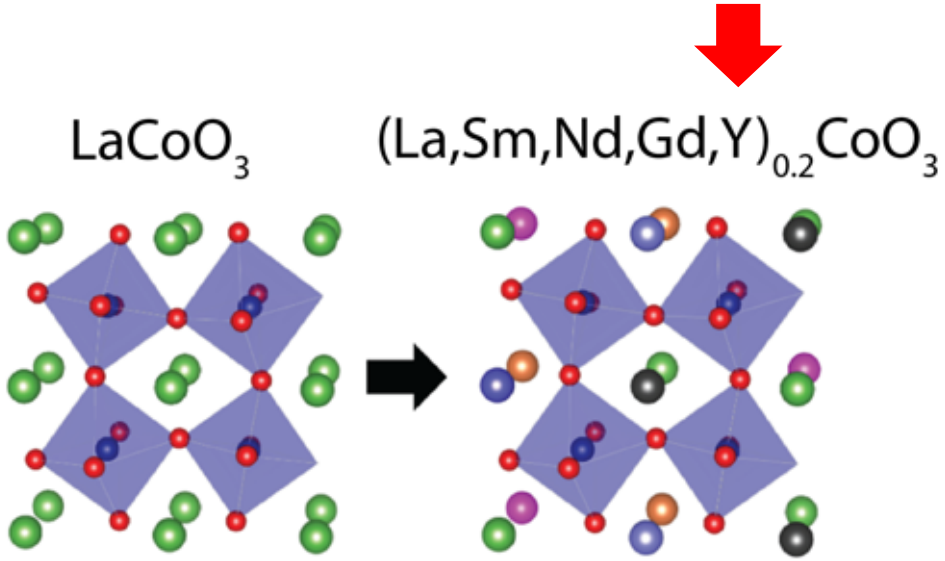




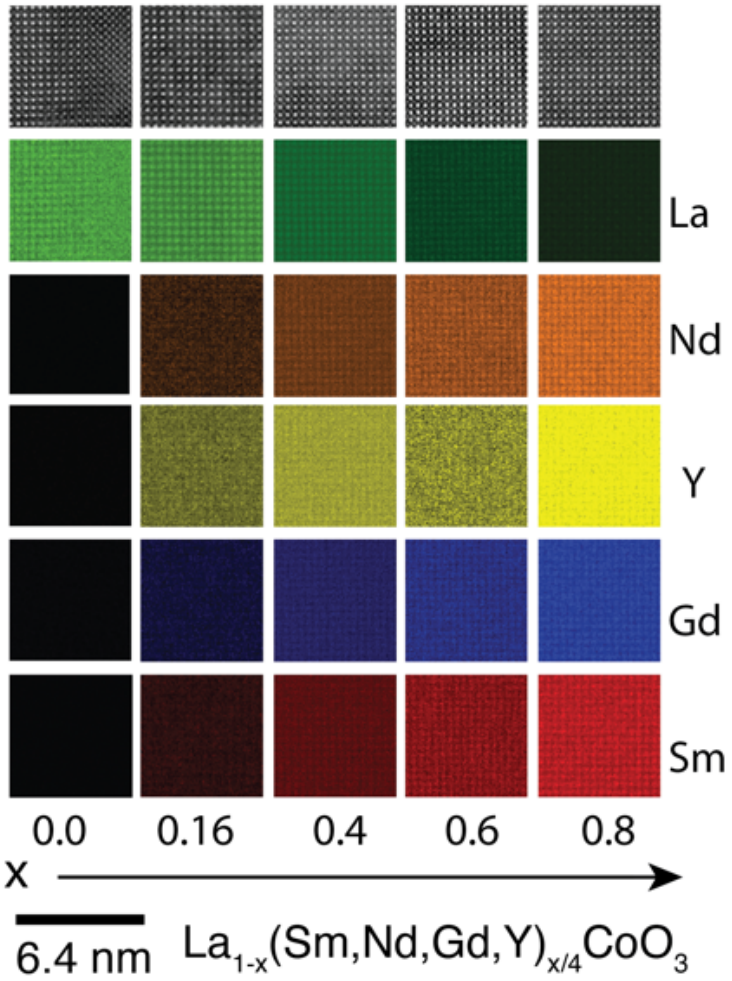


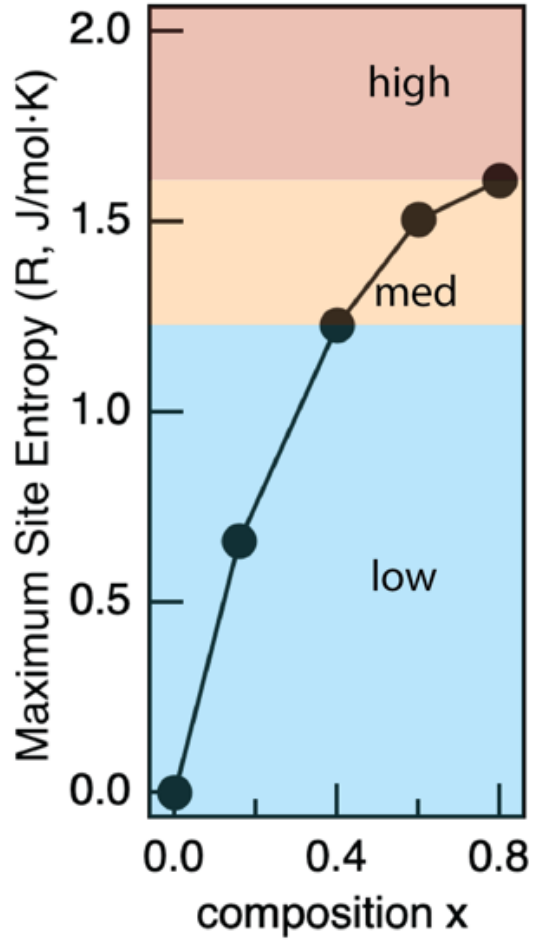
rare earth complexity can become a tunable parameter of the system

COMPLEXITY AS A TUNABLE PARAMETER IN THE COBALTATE SYSTEM



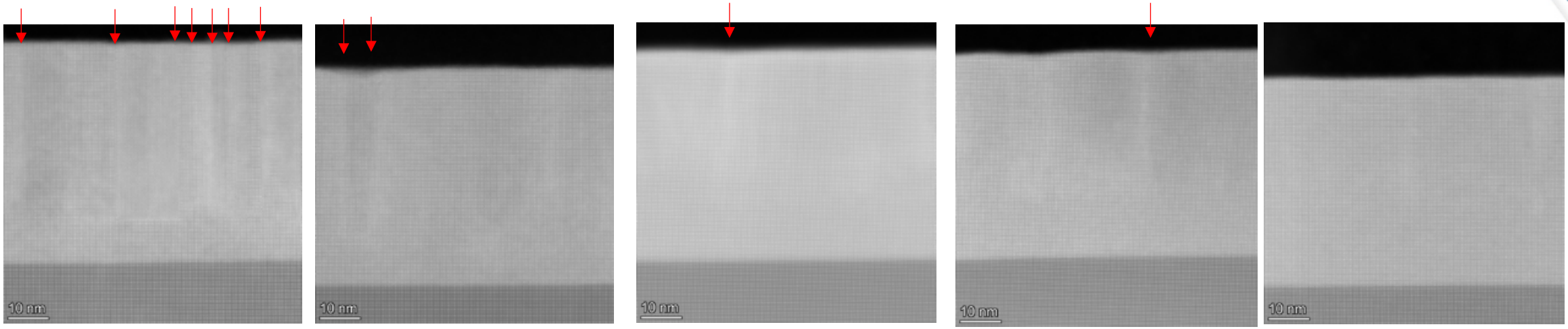
Strategy:
gradually increase the *population* of complex cations and watch the system evolve…

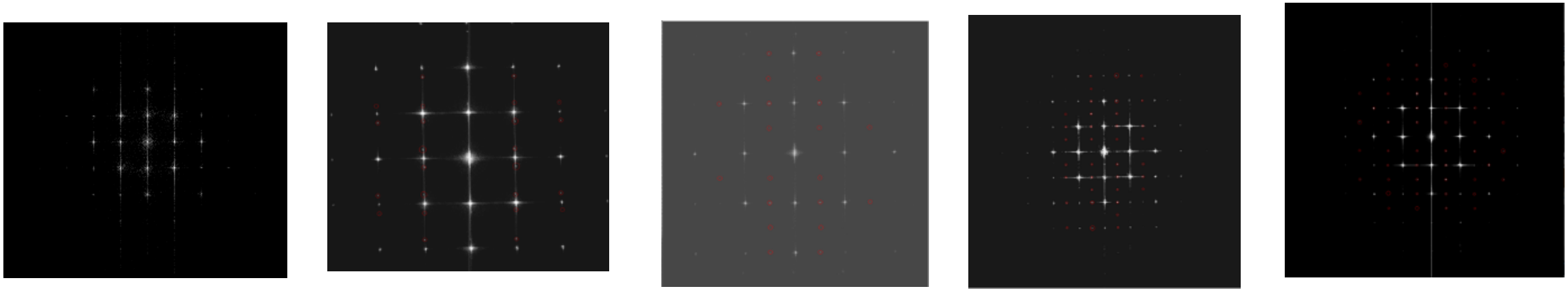




Zhang et. al., *in preparation*

STRUCTURAL ENHANCEMENT, EVEN AT DILUTE COMPLEXITY





x=0.00
rhombohedral

x=0.16
rhombohedral

x=0.40
orthorhombic

x=0.60
orthorhombic

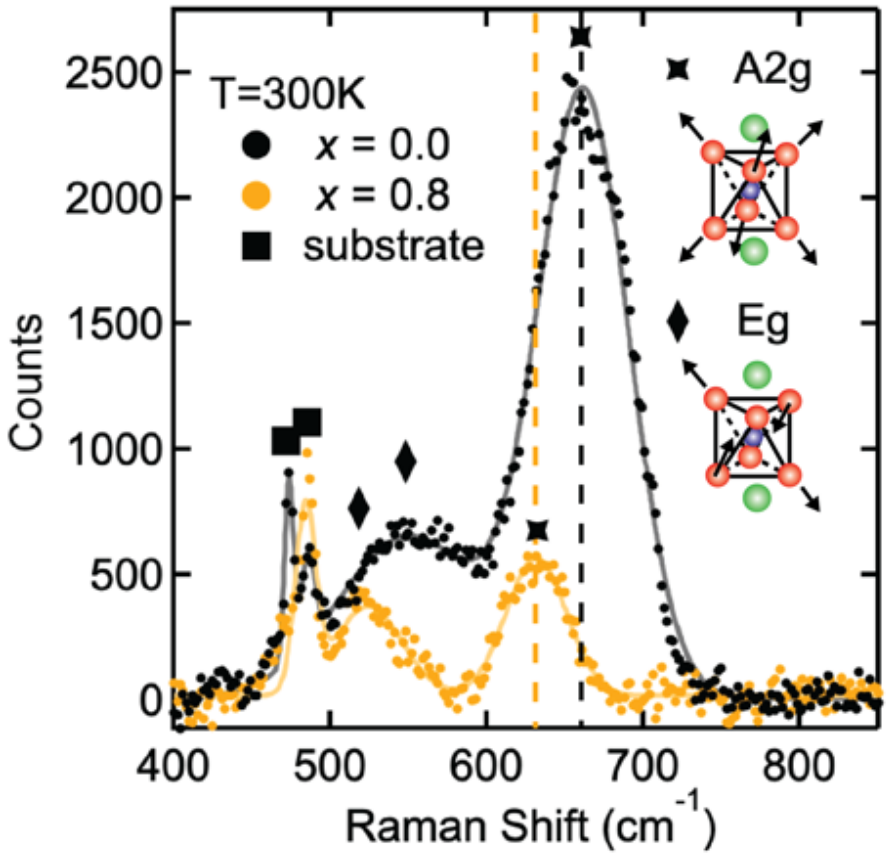
x=0.80
orthorhombic

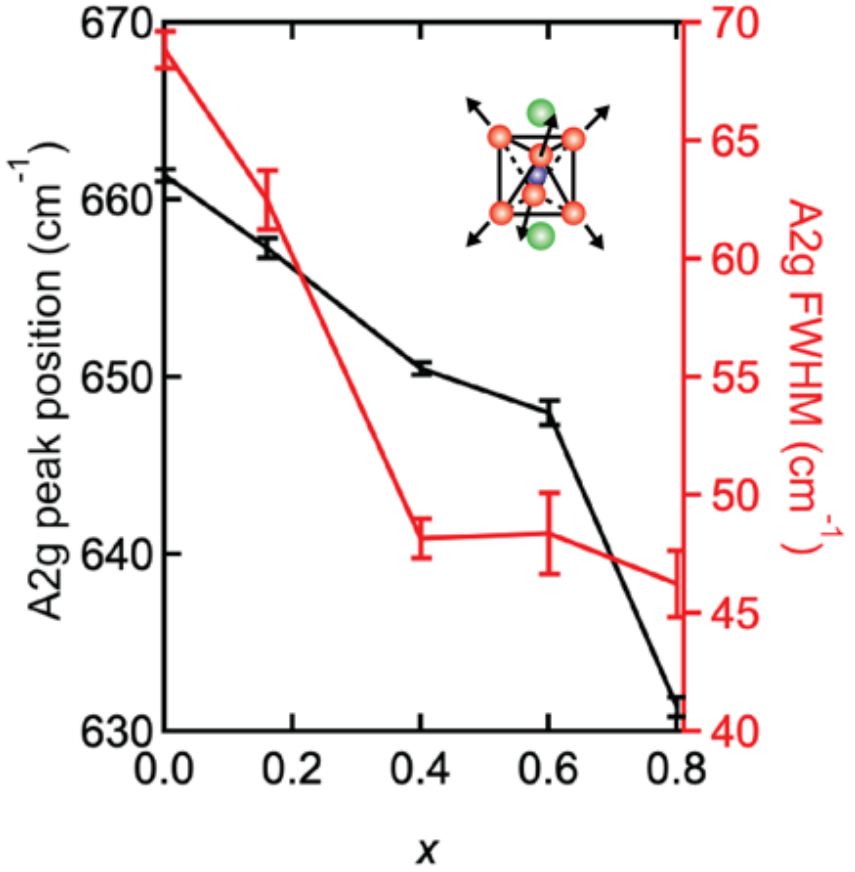
Even at low molar fractions, dilute complexity suppresses defects!

$$\Delta G = \Delta H - T\Delta S$$

Zhang et. al., *in preparation*

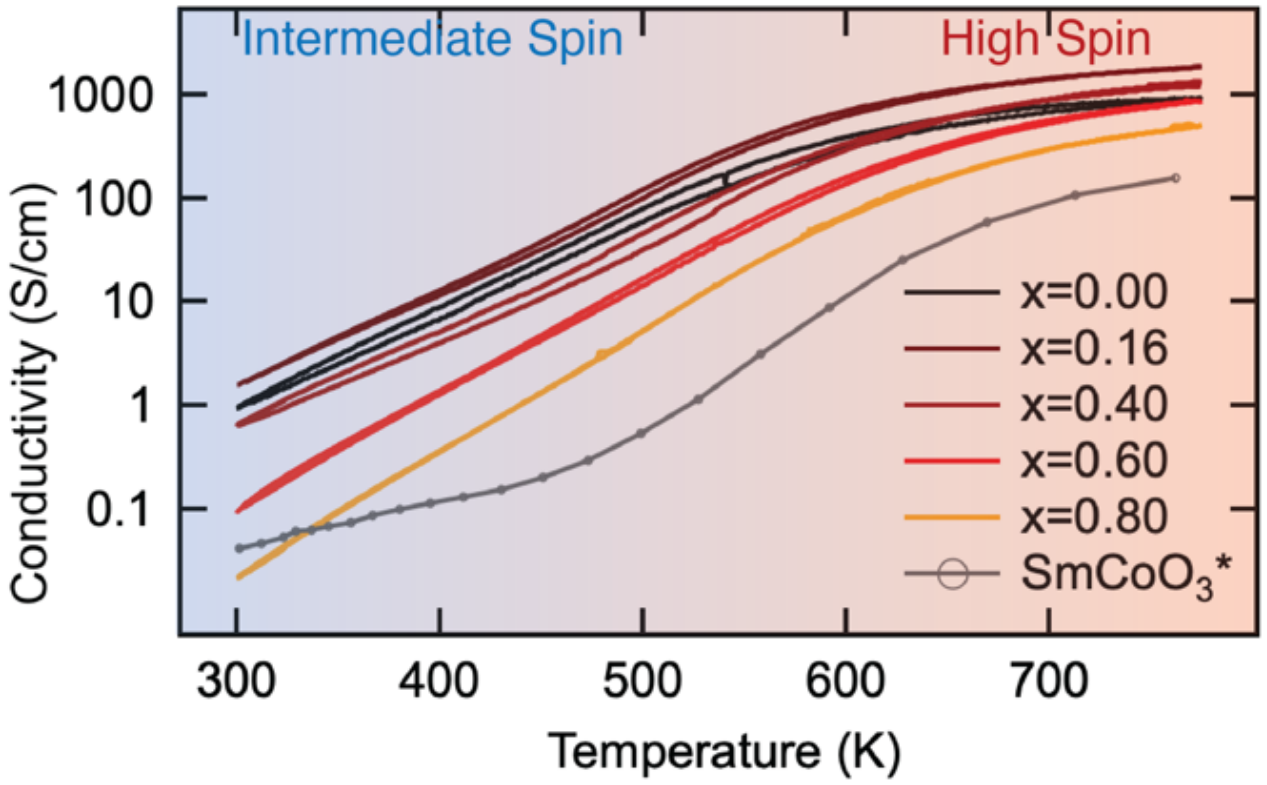
STRUCTURAL ENHANCEMENT ALSO OBSERVED IN RAMAN MODES

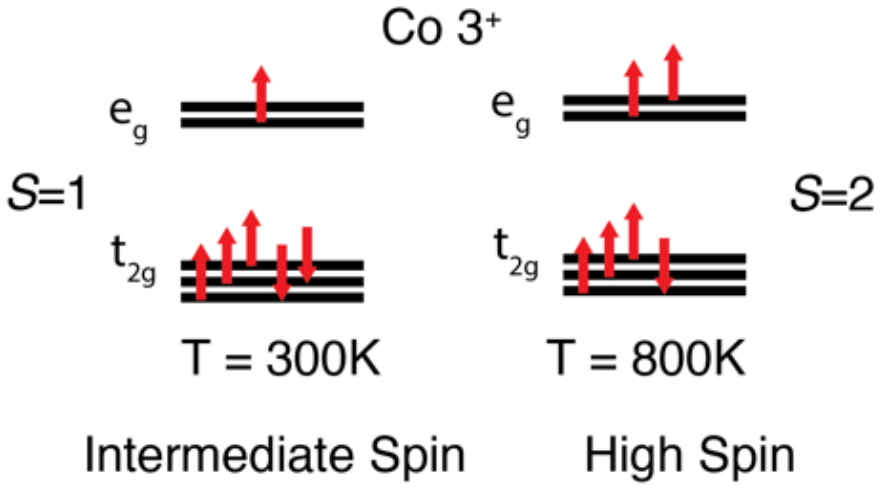




Zhang et. al., *in preparation*

CONTINUOUSLY TUNABLE SMT, BUT NOT SIMPLE ALLOYING



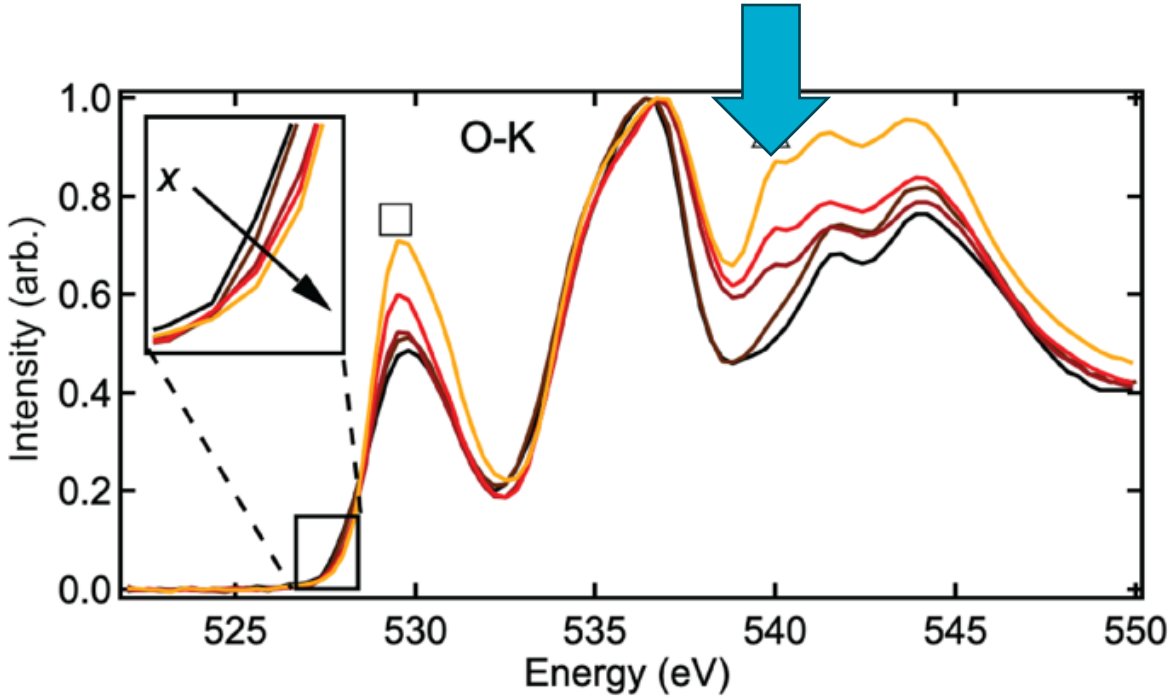


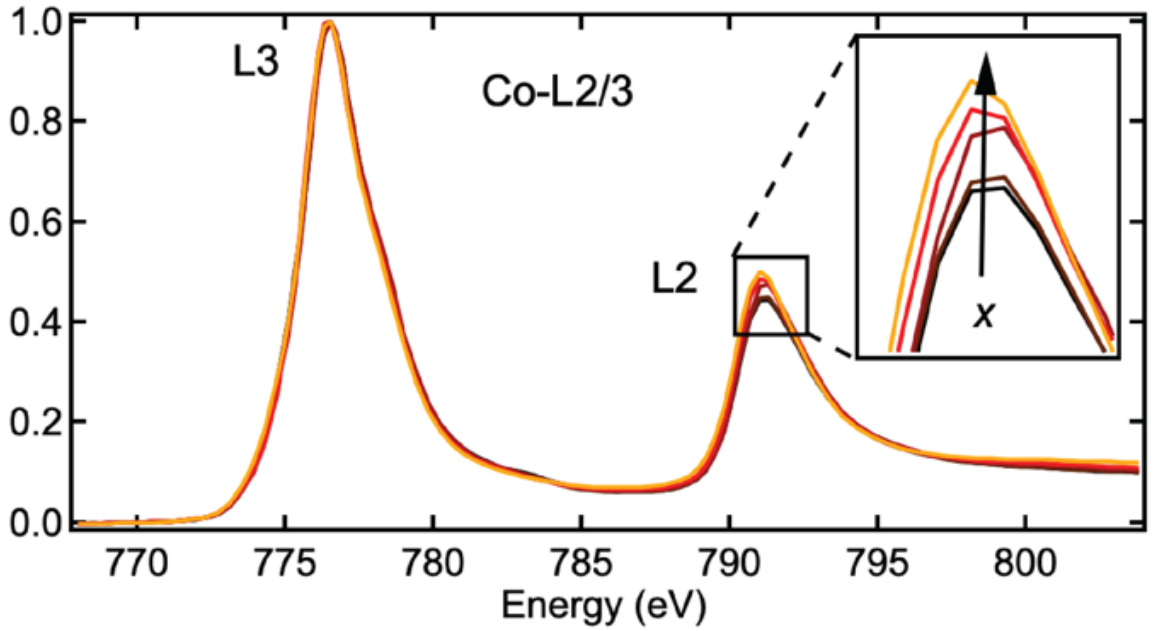
transition temperatures are not the same as simple alloys or their averages (based on tolerance factor)

Zhang et. al., *in preparation*

XAS SUGGESTS NEW HYBRIDIZATION DUE TO DISTORTIONS

Between La 5d and Co 4sp

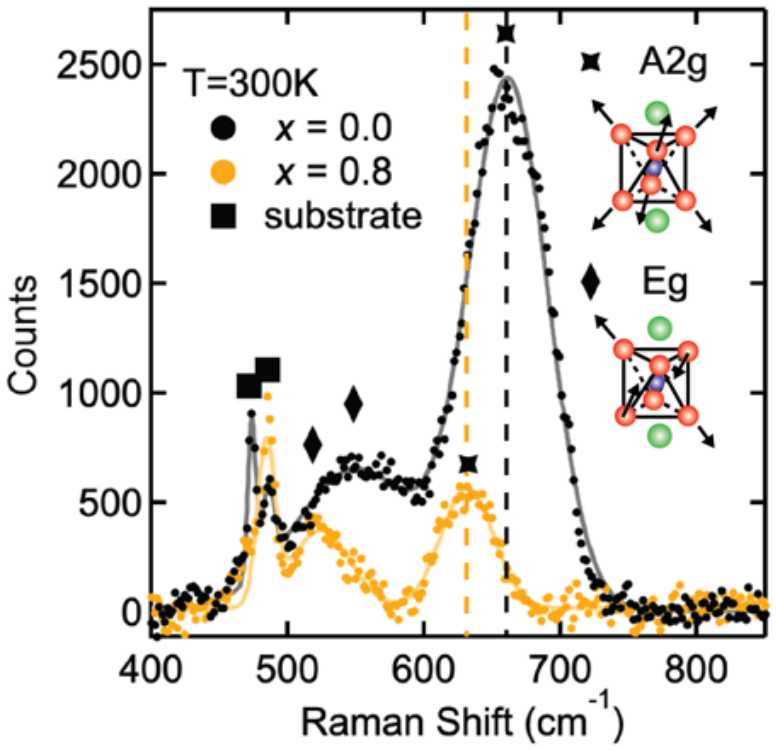


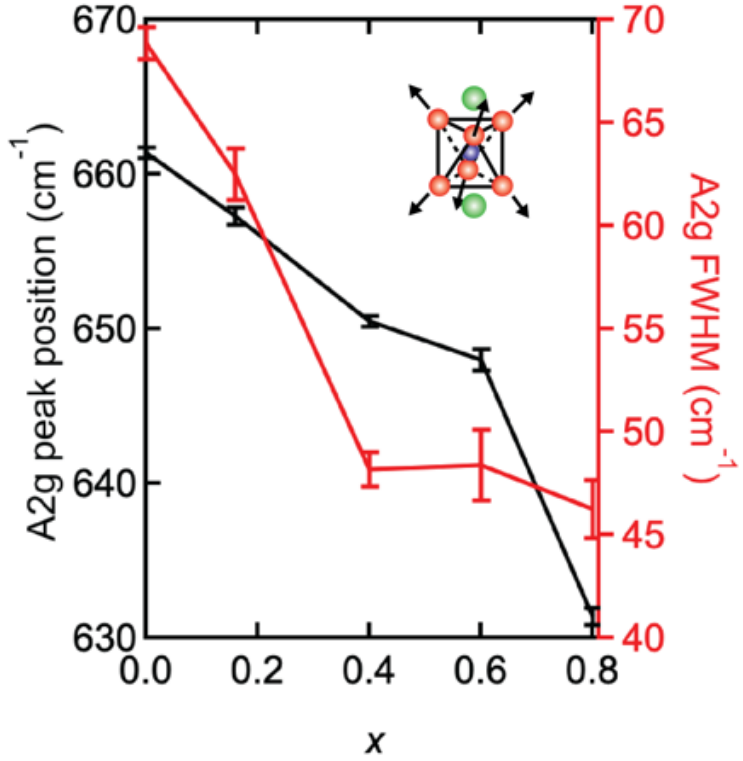


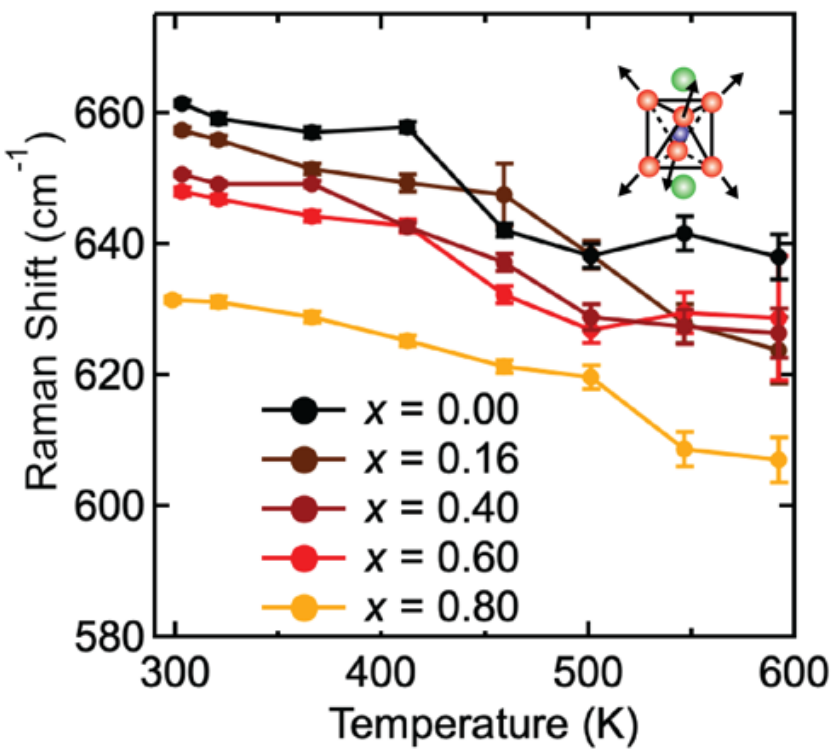
lattice distortions are strong enough to create new hybridizations of deep lying states

Zhang et. al., *in preparation*

STRUCTURAL COMPONENT OF SMT IS PRESERVED

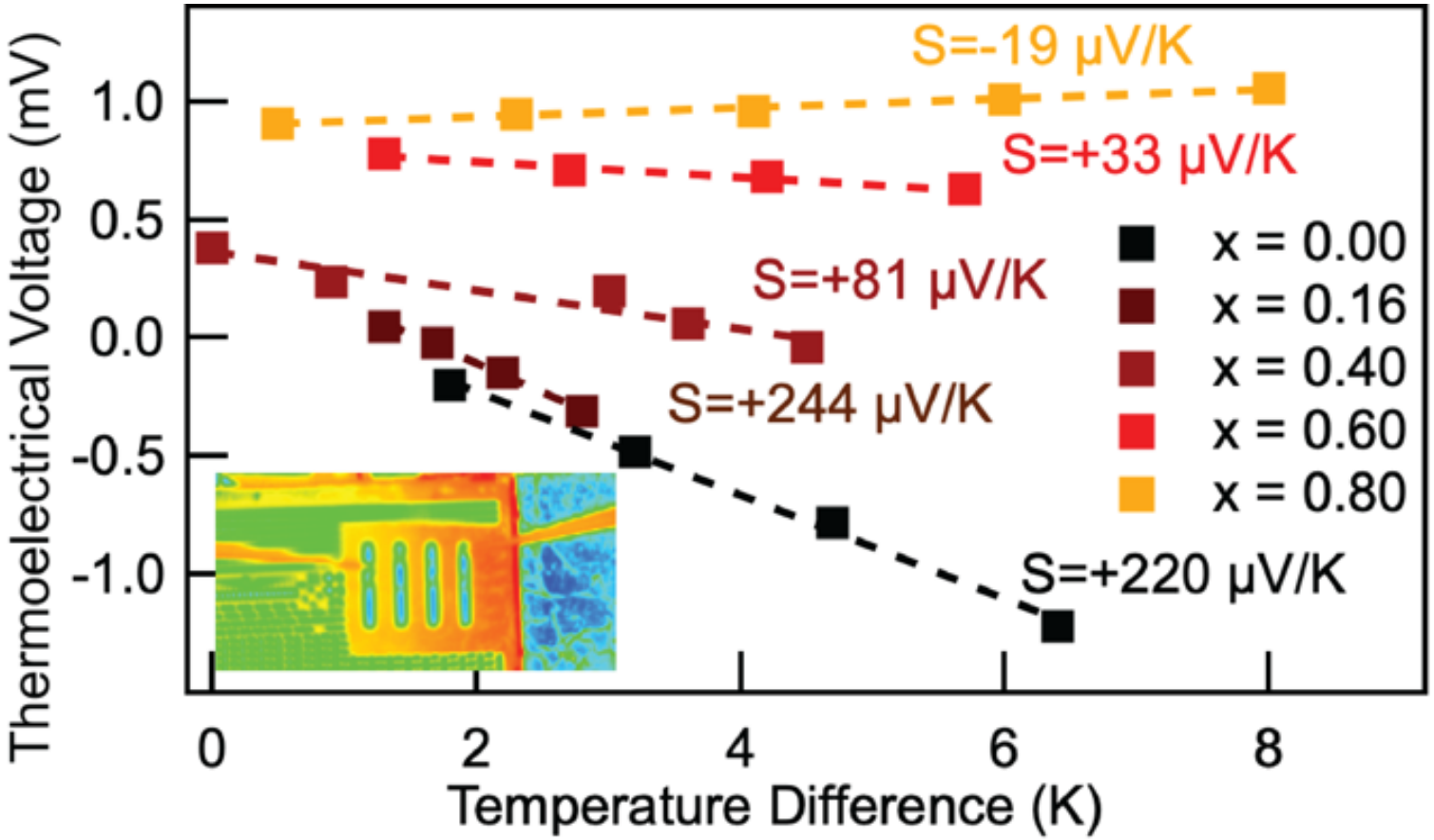






Zhang et. al., *in preparation*

TUNE CARRIER TYPE WITH COMPLEXITY

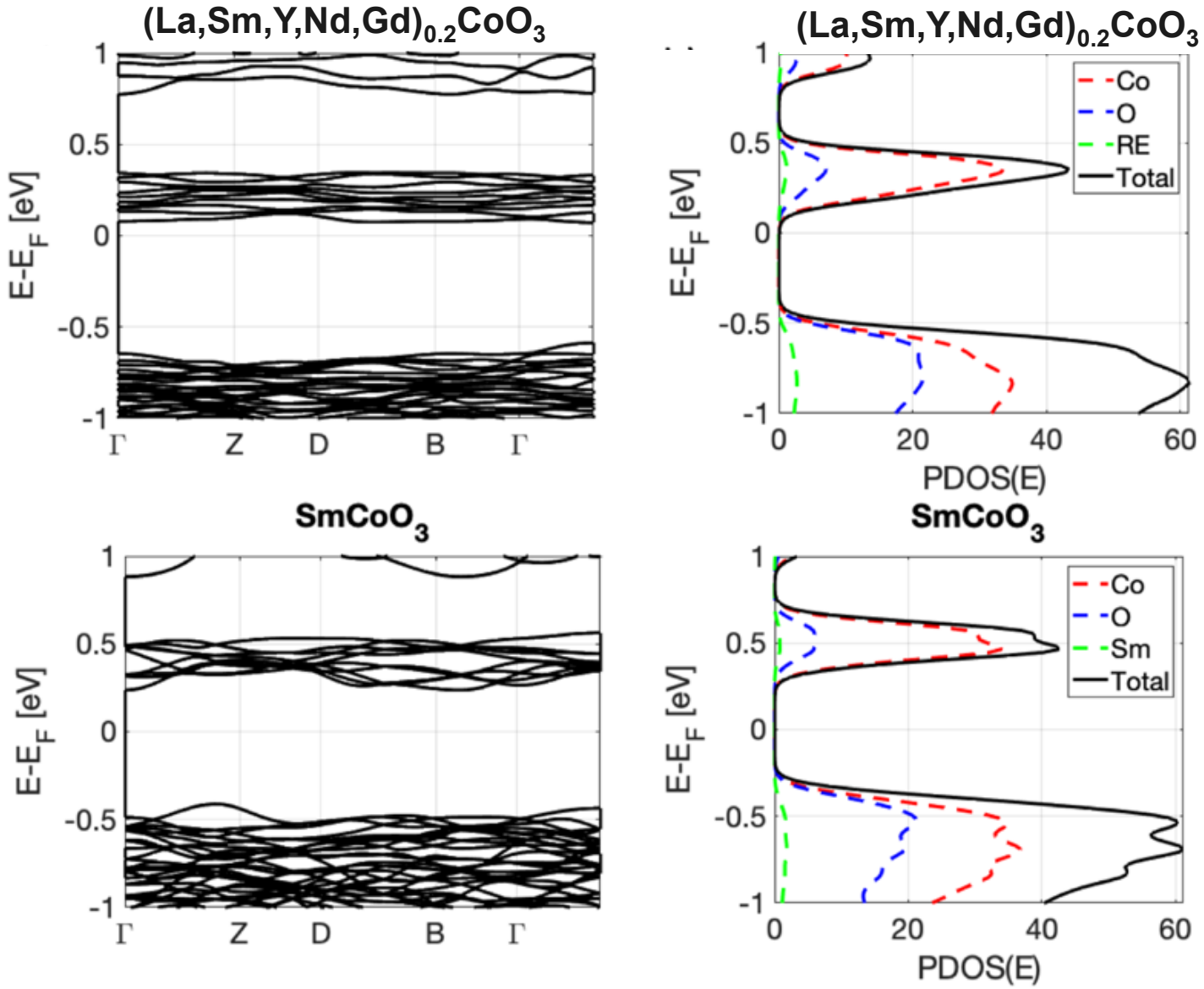


All simple alloys are p-type.

Why the carrier reversal?

Zhang et. al., *in preparation*

DFT: DISTORTIONS LEAD TO DISPROPORTIONATE HOLE LOCALIZATION



Zhang et. al., *in preparation*

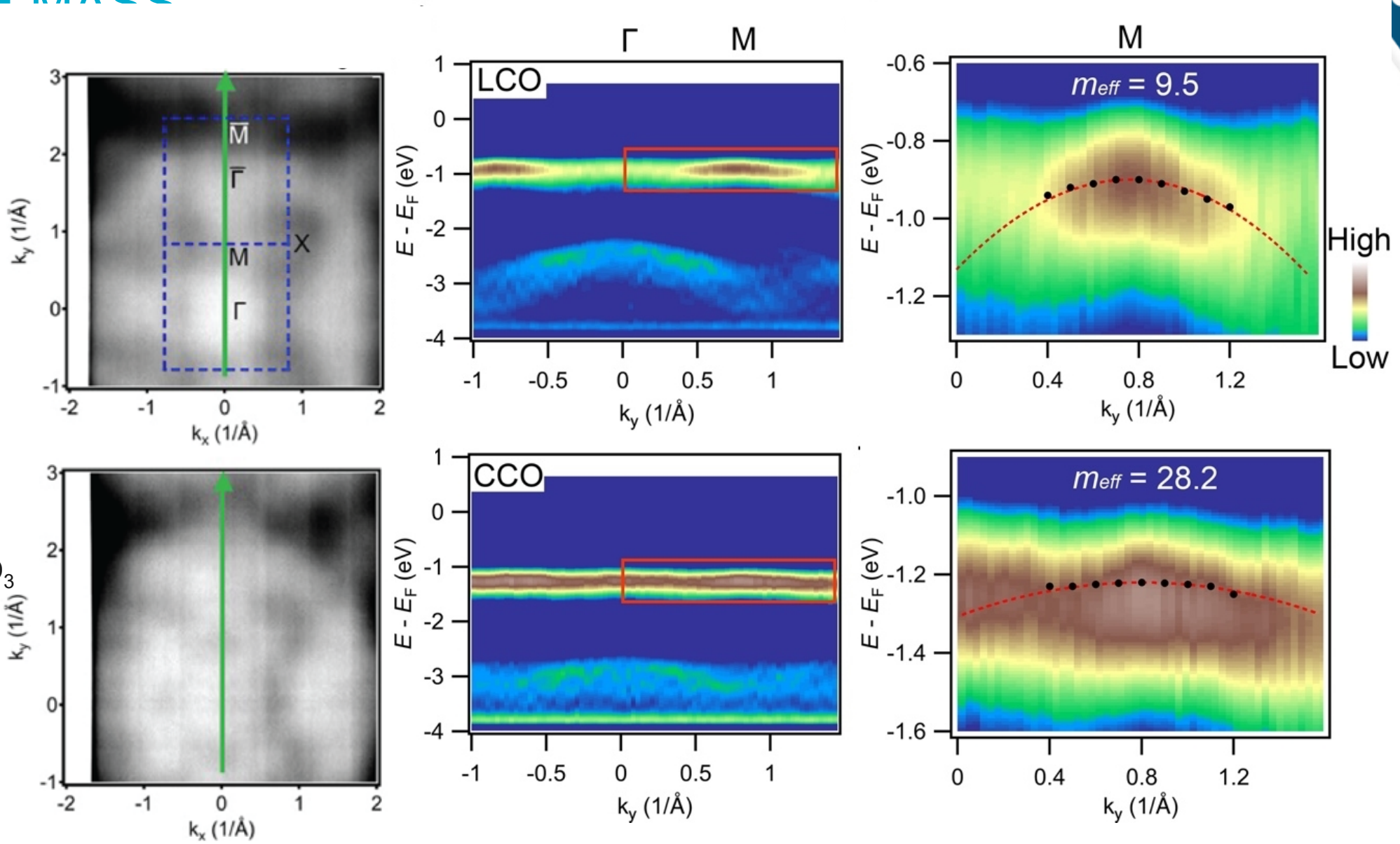
Selective localization:

- target the RE site
- RE has more contribution to the valence DOS,
- localize holes over electrons

ANGLE RESOLVED PHOTOEMISSION CONFIRMS INCREASED EFFECTIVE MASS

$LaCoO_3$

$(La,Sm,Y,Nd,Gd)_{0.2}CoO_3$

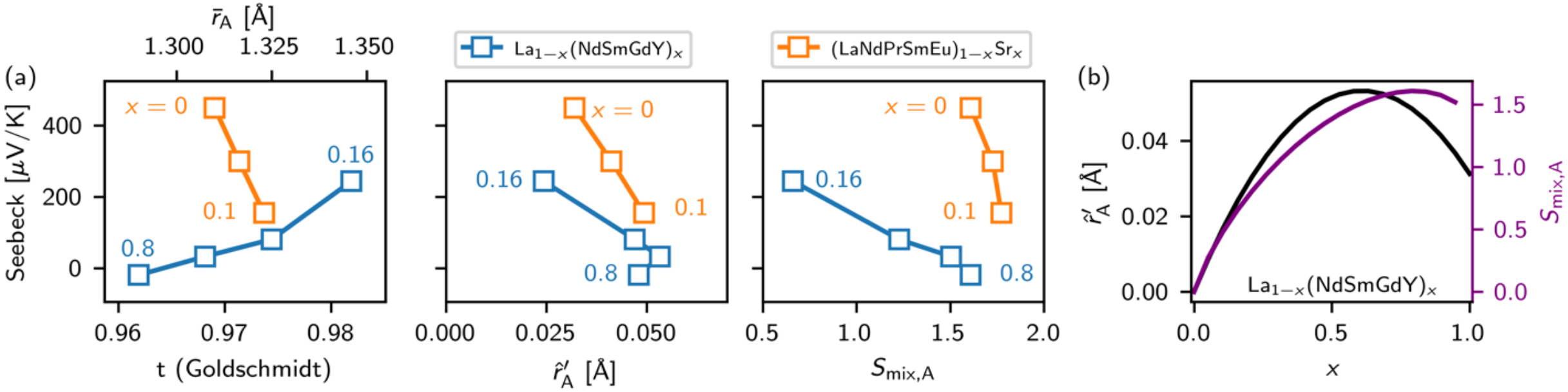


first ARPES,

HEO or LCO

Zhang et. al., *in preparation*

CAN WE CREATE GENERALIZED MATERIAL DESCRIPTORS?

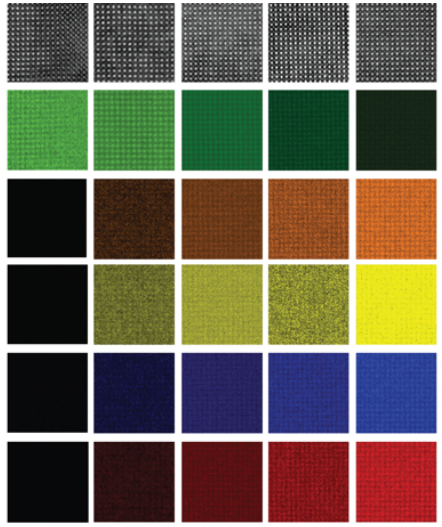


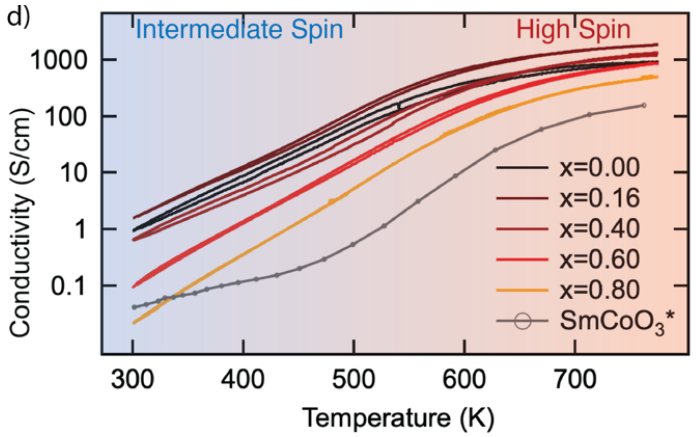
$(LaNdPrSmEu)_{1-x}Sr_xCoO_3$ Kumar et. al., J. *Materiomics* 2023

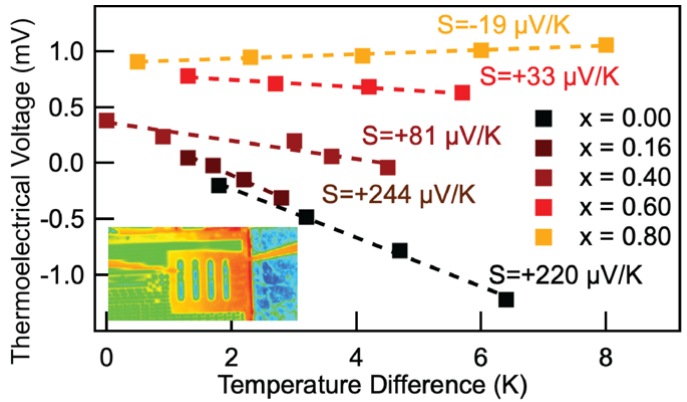
$La_{1-x}(NdSmGdY)_{x/4}CoO_3$ Zhang et. al., *in preparation*

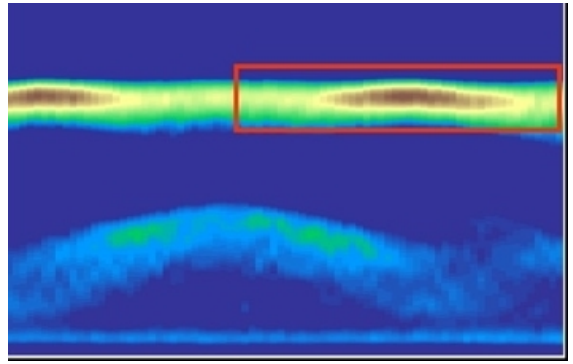
CONCLUSIONS

- **Tunable complexity allows us to distinguish the effects of simple alloying vs. complexity/entropy**
- Structural enhancements can occur even at dilute molar fractions of complexity
- Correlated transitions are continuously tunable with entropy, but properties distinct from conventional alloys
- Complexity can be targeted to specific lattice sites to tune carrier type in oxide semiconductors
- ARPES reveals the electronic structure of entropy oxides, localization can have dramatic effects!









Zhang et. al., *in preparation*

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