ACCELERATING THE DISCOVERY OF NEW FUNCTIONAL MATERIALS: THEORY ASSISTED SYNTHESIS

MEIGAN ARONSON

STEWART BLUSSON QUANTUM MATTER INSTITUTE DEPARTMENT OF PHYSICS AND ASTRONOMY UNIVERSITY OF BRITISH COLUMBIA



The Materials Development Pyramid



Tier 4: Materials for real technologies and societal benefit Material incorporated into devices and systems

> Tier 3: Materials for Technology and Science Improved synthesis for optimized properties

Tier 2: Materials of Interest Material has special property (i.e. superconductivity)

> Tier 1: New Materials Generally, only structure is known

Steps for taking materials up the pyramid (R. J. Cava, Physics **4**, 7 (2011))

- 1. Identify problem that material addresses: *Find a higher temperature superconductor.*
- 2. Which Tier 1 materials are likely candidates? Identify a structural theme.
- 3. Synthesize materials, assemble team to characterize, establish theoretical context.

Seek high superconducting onset temperature, high critical field.

4. Can materials be made in form desired for application? *Ductility, chemical stability, cost.*

Guided Discovery of New Superconductors: Materials by Design

"New computational tools have the potential to accelerate materials development at all stages of the continuum. For example, software could guide the experimental discovery of new materials by screening a large set of compounds and isolating those with desired properties. Further downstream, virtual testing via computer-aided analysis could replace some of the expensive and time-consuming physical tests currently required for validation and certification of new materials. "

--- from the Materials Genome Initiative for Global Competiveness

How to use theory, esp. electronic structure calculations, to predict new superconductors?

1. We have no theory that predicts conditions for superconductivity in specific terms.

2. Electronic structure calculations increasingly realistic, but no marker such as `Cooper pair susceptibility' to identify potential superconductors.

3. Require a phenomenological approach: we know experimentally that superconductivity is associated with other phenomena that are successfully captured by electronic structure calculations, such as magnitudes of the charge gap and magnetic moment.

A Possible Scheme for Theory Assisted Synthesis of Functional Materials

Validation Phase:

Can electronic structure calculations accurately determine properties of known compound using only crystal structure information as input, especially when correlations are strong?



Square net Mn compounds



LaMnPO: electronic gap Δ ~1 eV, 3.2 μ_B /Mn

LaMnPO: Antiferromagnetic Correlation Gap Insulator

- 1. DFT: metallic (Δ =0) LaMnPO is thus a correlation gap insulator.
- 2. DFT + U=10 eV: still no gap. LaMnPO is not a simple Mott system.
- 3. DFT+DMFT: U=8 eV, J_{Hunds} =0.9 eV Gap is present in PM state (T>T_N).

4. DFT+DMFT: U=8 eV, J_{Hunds} =0.9 eV, J_{Heis} ~0.1 eV Gap enhanced for T<T_N



G. Kotliar, Z. P. Yin, M. Pezzoli (Rutgers)



DMFT Captures Experimental Collapse of Optical Gap Δ at P=25 GPa



Kirk Post + Dimitri Basov (UCSD)



Alexandre Goncharov Carnegie Institute



G. Kotliar (Rutgers)





Post 2016



Z. P. Yin, M. Pezzoli (Rutgers)

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Validation Phase:

Can electronic structure calculations accurately determine properties of known compound using only crystal structure information as input, especially when correlations are strong?



Discovery Phase:

Propose a new approach `Articulated Synthesis' that combines in-situ powder x-ray diffraction with electronic structure calculations.

- Carry out powder x-ray diffraction in melt, use structural information as input for electronic structure calculations. DMFT calculations can provide basis for go/no go decisions.
- Reserve effort to grow large crystals and carry out physical characterization only when system seems sufficiently promising.

Synthesis is Rate Limiting Step: How to Reduce Opportunity Costs?















Flux Growth and Solid State Synthesis:

- Weighed amounts of elements/compounds are sealed in quartz ampoule.
- Reactants are heated to ~1200 C, then slowly cooled. If flux is used, it is decanted while liquid, revealing crystals.

Current synthesis approach is very resource intensive:

- May take several months to produce crystals of new system big enough for physical measurements.
- Can't make decision about how promising the material is until full characterization is complete.
- Takes as much time to reach decision point for both promising and unpromising materials.

If a synthesis is not successful, generally don't really know why: need to examine the synthesis process as it occurs.

- High temperature in-situ xray diffraction provides this insight
- Can greatly reduce time needed to produce high quality single crystals of desired compounds

In situ XRD: XPD Beamline NSLS-II and Beamline 6-ID-C at APS



- Syntheses carried out in silica or alumina tubes using quadrupolar focused lamp furnace for T<1400 C.
- Powder Diffraction measured in transmission on 2-dimensional detector.
- Experiments carried out while temperature drifts up or down. Exposure time< 1 minute
- Takes several weeks in conventional synthesis lab to achieve what we can do in 1 day at synchrotron.

-determine limits of solubility of dopant in flux, flux melting point.

-determine dopability limits of compound via changes in melting points and lattice constants.

-identify new compounds, possibly metastable.

-track reactions: breakdown of reactants, formation of high temperature phases, determine solidification temperatures.

Ca_3P_2 – a newly identified 3D Dirac semimetal

- Hexagonal Mn_5Si_3 type, charge balance is achieved by Ca vacancy Ca²⁺ P³⁻
- Calculation: 3D Dirac semimetal with an unusual ring of Dirac nodes at the Fermi level
- Synthesized from elements Ca:P=5:3 in Ta tube, heated at 1200 C for 2h with induction furnace. By products include Ca_5P_3H , Ca_4P_2O , Ca_xTaO_3



APL MATERIALS 3, 083602 (2015)

In-situ XRD measurements speed synthesis of large single crystals for experiments from flux

- Find the best fluxes
- Perhaps find new Ca-P binary phases?
- Possible new routes for charge balance via ternary formation?

AM115 Ca₃P₂ in KCl flux: Possible



Ca₃P₂ dissolves in KCl flux below 800 C, and recrystallized on cooling.

AM114 Ca₃P₂ in NaCl flux: No Good



- Decomposition of Ca_3P_2 peaks above 650 °C, formation of CaP.
- Ca₃P₂ didn't dissolve in NaCl; instead, it converts from one solid form to another.

AM102 Ca₃P₂ in In flux: No Good



- Ca_3P_2 dissolved into In flux ~650 °C, forming homogeneous melt.
- Caln₂ formed below 300 °C on cooling (not Ca₃P₂)

AM103 Ca₃P₂ in Bi flux: No Good



- Decomposition of Ca₃P₂ peaks above 650 °C, formation of CaP.
- Ca₃P₂ didn't dissolve into Bi; instead, it converts from one solid form to another.
- CaBi₂ forms on cooling the melt.

AM104 Ca₃P₂ in Sn flux: No Good



- Ca₃P₂ dissolved into Sn flux ~850 C, forming ~ homogeneous melt.
- CaSn₃ formed on cooling melt.

Tuning the charge transfer energy for T_{C,max}: sulfur-doped La₂CuO₄

Contrasting theories about the $T_{c,max}$

- Reducing the charge-transfer energy $\varepsilon_d - \varepsilon_p$ enhances $T_{c,max}$

- Reducing the admixture of the Cu $3d_z^2$ orbital with $3d_x^2 - y^2$ orbital may enhance $T_{c,max}$

C. Yee and G. Kotliar have proposed theoretical compounds R_2CuSO_3 and $R_2CuS_2O_2$ (R=La, Sc, Y, Lu) and their synthetic routes.

Can these theoretically proposed compounds be synthesized ?

ΔE	ΔV	Synthesis pathway	
141	- 7.3	$La_2O_2S + CuS$	\rightarrow La ₂ CuO ₂ S ₂
223	- 3.4	$Y_2O_2S + CuS$	$\rightarrow Y_2CuO_2S_2$
267	- 5.0	$Lu_2O_2S + CuS$	$\rightarrow Lu_2CuO_2S_2$
356	- 3.0	$Sc_2O_2S + CuS$	\rightarrow Sc ₂ CuO ₂ S ₂
101	- 4.9	$La_2O_2S_2 + Cu$	$\rightarrow La_2CuO_2S_2$
148	- 3.3	$La_2O_3 + CuS$	\rightarrow La ₂ CuO ₃ S
454	- 0.7	$Sc_2O_3 + CuS$	\rightarrow Sc ₂ CuO ₃ S
97	- 4.9	$La_2O_2S + CuO$	→ La ₂ CuO ₃ S
269	2.8	$Sc_2O_2S + CuO$	\rightarrow Sc ₂ CuO ₃ S
28	- 5.1	La ₂ O ₃ + CuO	$\rightarrow La_2CuO_4$



Yee, C.-H. and Kotliar G. PRB 2014

Warmup Experiment: In situ XRD and the synthesis of La₂CuO₄

Starting materials: La_2O_3+CuO However, XRD at room temperature indicated that $La(OH)_3$ was starting material

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460-580°C: La(OH)_3 = 3 LaOOH + H_20 (g)
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640-760°C: 2 LaOOH = $La_2O_3 + H_2O(g)$

900°C: $La_2O_3 + CuO = La_2CuO_4$

Theory Proposed Synthesis Pathway #1: La₂O₂S + CuO = La₂CuO₃S

In situ XRD experiments:

Step 1 (760-1000 °C): $La_2O_2S + 8 CuO = 4 Cu_2O + (LaO)_2SO_4$ Step 2 (~1100 °C): $2 La_2O_2S + Cu_2O = 2 LaCuSO + La_2O_3$

Total Effective Reaction:

 $La_2O_2S + CuO = 7/8 LaCuSO + 7/16 La_2O_3 + 1/8 (LaO)_2SO_4 + 1/16 Cu_2O_3$

Theory Proposed Synthesis Pathway #2: La₂O₃ + CuS = La₂CuO₃S

Step 1 (500 °C): 8 CuS + 4 La₂O₃ = 4 Cu₂S + 3 La₂O₂S + La₂O₂SO₄

Step 2 (900 °C): $La_2O_2S + Cu_2S = 2 LaCuSO$

```
Total Effective Reaction:

La_2O_3 + CuS = 1/8 La_2O_2SO_4 + 1/8 Cu_2S + \frac{3}{4} LaCuSO + \frac{1}{2} La_2O_3
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A A The The Materials Project

Harnessing the power of supercomputing and state of the art electronic structure methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools to inspire and design novel materials.

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Warmup Experiment: In situ XRD and the synthesis of La₂CuO₄

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La₂CuO₄ grows directly from La₂O₃ + CuO above 900 C, although computed ΔE =+48 meV/atom

Theory Proposed Synthesis Pathway #1: La₂O₂S + CuO = La₂CuO₃S

Theory Proposed Reaction: $La_2O_2S+CuO = La_2CuO_3S$

In situ XRD experiments: Step 1 (760-1000 °C): $La_2O_2S + 8 CuO = 4 Cu_2O + (LaO)_2SO_4$ (-197 meV/atom) -222 meV/atom Step 2 (~1100 °C): 2 La_2O_2S + Cu_2O = 2 LaCuSO + La_2O_3 (-64 meV/atom)

Total Effective Reaction: Energetically Favored, esp by CuO \rightarrow Cu₂O formation La₂O₂S + CuO = 7/8 LaCuSO + 7/16 La₂O₃ + 1/8 (LaO)₂SO₄ + 1/16 Cu₂O (-136 meV/atom)

Theory Proposed Synthesis Pathway: La₂O₃ + CuS = La₂CuO₃S

Theory Proposed Reaction: $La_2O_3+CuS = La_2CuO_3S$

(266 meV/atom)

In situ XRD experiments:

Step 1 (500 °C): 8 CuS + 4 La2O3 = 4 Cu2S + 3 La2O2S + La2O2SO4-43 meV/atomStep 2 (900 °C): La2O2S + Cu2S = 2 LaCuSO-22 meV/atom

Total Effective Reaction: $La_2O_3 + CuS = 1/8 La_2O_2SO_4 + 1/8 Cu_2S + \frac{3}{4} LaCuSO + \frac{1}{2} La_2O_3$ -37 meV/atom

Compositional phase diagram of $LaCuS_xO_{4-x}$ (0 \le x \le 3)

- The redox reaction happens at temperature below the formation of La₂CuO₄ $Cu^{2+} + S^{2-} \rightarrow Cu^{1+} + SO_4^{2-}$
- Once Cu²⁺ is reduced to Cu¹⁺, LaCuSO prevails at the high temperature range.

Can theory/calculation explain the experimental reaction pathways?

Thermodynamic stability: convex hull construction

Energy above hull: quantify a compound's thermodynamic instability

Energy below hull: quantify a compound's thermodynamic stability

The thermodynamic instability/stability of a compound can be evaluated using energy above/below hull, the energy difference between a compound and the set of the most stable compounds with the same average chemical composition.

Convex hull of the La-Cu-O-S quaternary system

The theoretical compounds are formidably unstable:

 $La_{2}CuO_{2}S_{2} = La_{2}SO_{2} + CuS \qquad (\Delta E = -469 \text{ meV/atom})$ $La_{2}CuO_{3}S = \frac{3}{4}La_{2}SO_{2} + Cu + \frac{1}{4}La_{2}O_{2}SO_{4} \qquad (\Delta E = -464 \text{ meV/atom})$

In-situ Studies of Synthesis Pathways: New Mott Insulator BaCoSO

Powder diffraction experiments carried out on Beamline XPD (NSLS-II) and Beamline 6-ID-B (APS) using specially designed 4-lamp furnace (T<1200 C).

Above 500 °C BaO + CoS_{1+x} = BaCoSO + x S²⁻ Ba· · · O + S²⁻ = BaS + O²⁻

Between 700-900 °C $Co_9S_8 \rightarrow Co_{1+x}S$ $Ba \cdots O + CoS = BaCoSO$

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Doping a Mott Insulator: $BaCoSO \rightarrow BaCoS_2$?

Previously unreported AF-Insulator T_N = 220 K Δ = 0.25 eV Known Mott system AF-Insulator T_N = 305 K Δ =3.5 eV

Our Team

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Jack Simonson

Daniel McNally

Shelby Zellman

Jed Kistner-Morris

Gabi Kotliar

Maria Pezzoli

Chuck Yee

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Zhiping Yin

Gabi Kotliar (Rutgers)

Maria Pezzoli

Hao Tjeng Max Planck Institut Dresden

Jim Allen U. Michigan

Andrea Severing University of Koln

Igor Zaliznyak

Brookhaven

Jeff Lynn NIST

Steve Nagler Oak RIdge

Collin Broholm Johns Hopkins

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