PARADIM

AN NSF MATERIALS INNOVATION PLATFORM

Lecture #5—

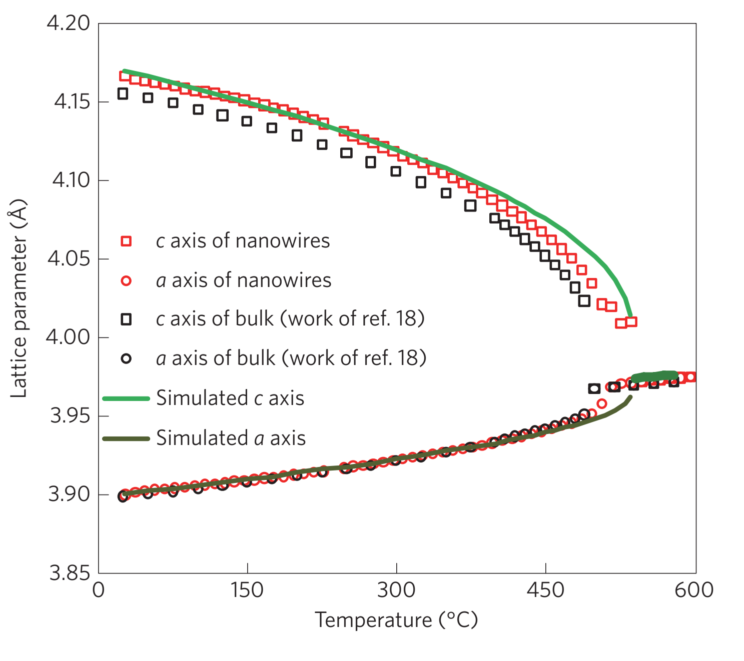
Detailed Examples of Oxide MBE:

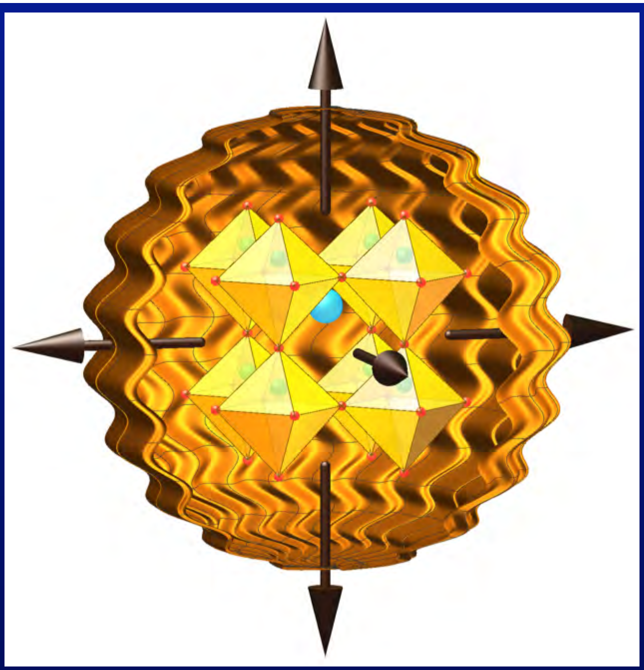
Growth of Ruthenates ($CaRuO_3$, $SrRuO_3$, Ca_2RuO_4, Sr_2RuO_4)

Darrell G. Schlom

Negative-pressure-induced enhancement in a freestanding ferroelectric

enhancement of the tetragonality, Curie temperature and spontaneous polarization in freestanding $PbTiO_3$ nanowires, driven by stress that develops during transformation of the material from a lower-density crystal structure to the perovskite phase. This study suggests a simple route to obtain



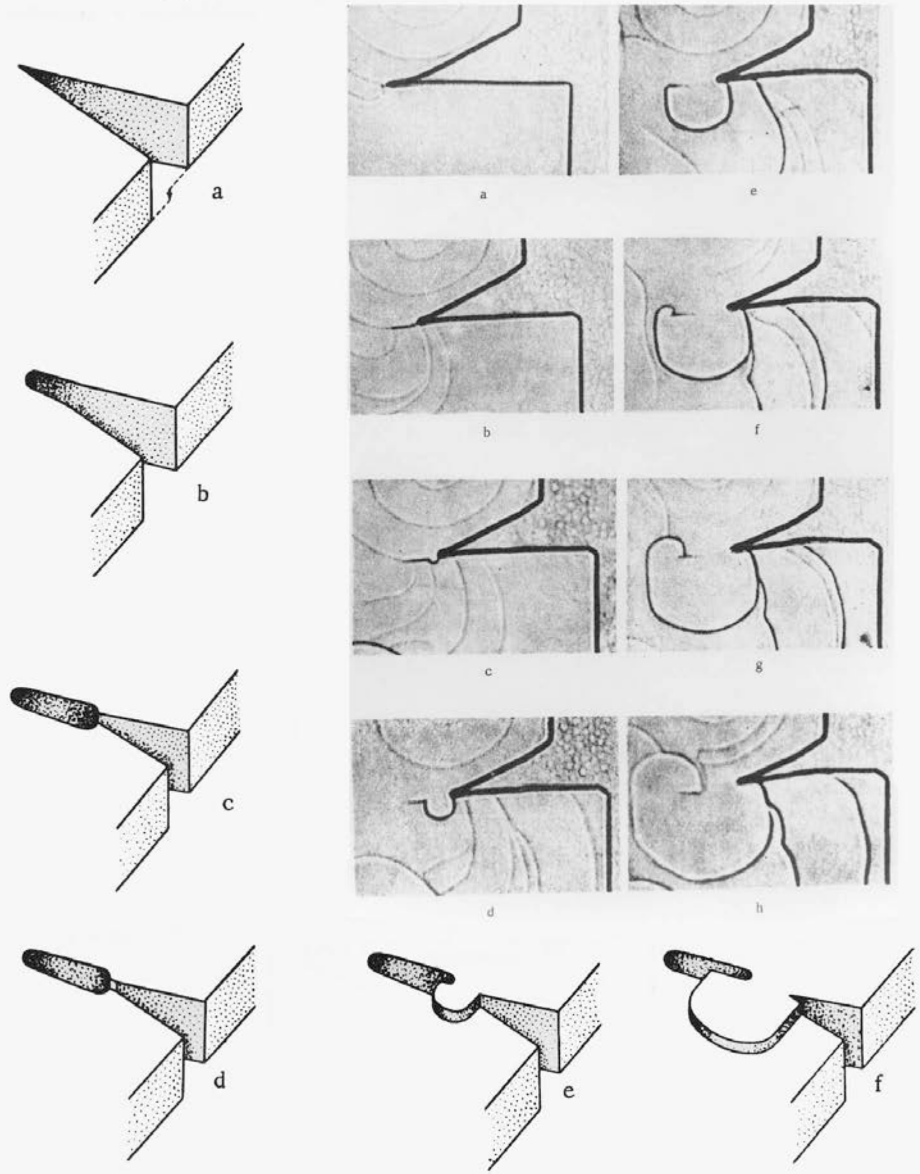


$PbTiO_3$ transformed from lower density PX metastable polymorph of $PbTiO_3$

J. Wang, B. Wylie-van Eerd, T. Sluka, C. Sandu, M. Cantoni, X.-K. Wei, A. Kvasov, L. J. McGilly, P. Gemeiner, B. Dkhil, A. Tagantsev, J. Trodahl, and N. Setter, "Negative-Pressure-Induced Enhancement in a Freestanding Ferroelectric," *Nature Materials* **14** (2015) 985–990.

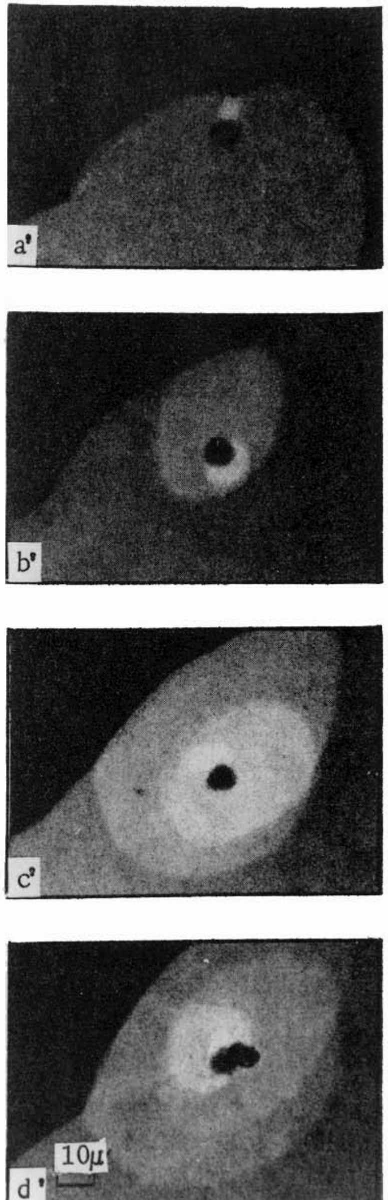
A. Kvasov, L. J. McGilly, J. Wang, Z. Shi, C. S. Sandu, T. Sluka, A. K. Tagantsev, and N. Setter, "Piezoelectric Enhancement under Negative Pressure," *Nature Communications* **7** (2016) 12136.

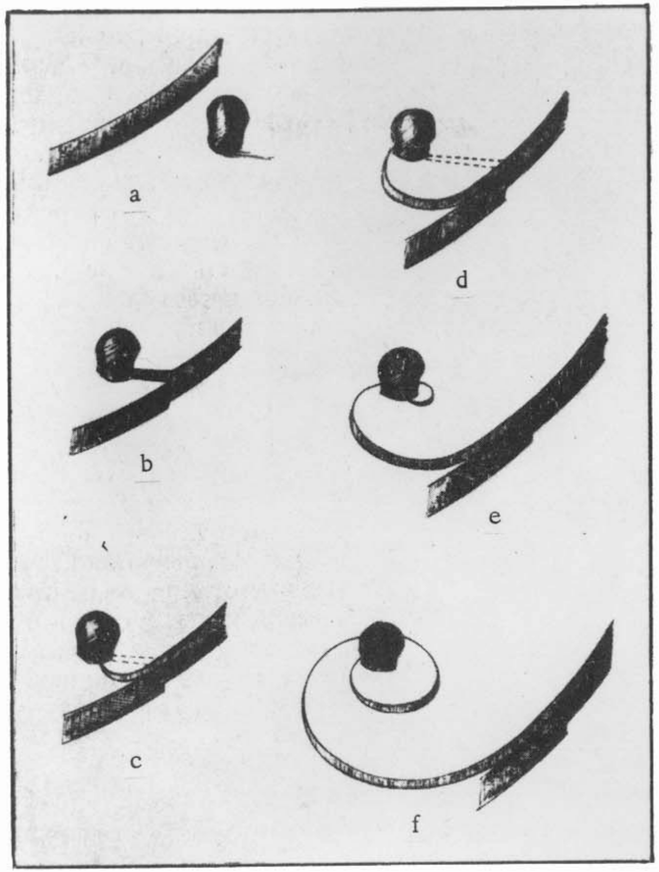
Coalescence of Non-parallel Growth Fronts

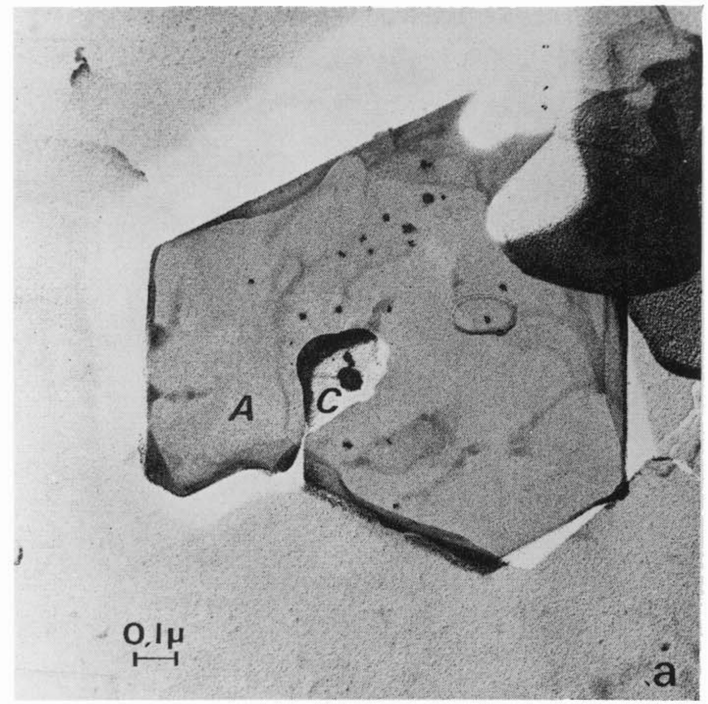


p-Toluidine
G.G. Lemmlein and E.D. Dukova,
Sov. Phys. Crystallogr. **1**, 269 (1956).

Recombination of Two Offset Branches of a Single Growth Front



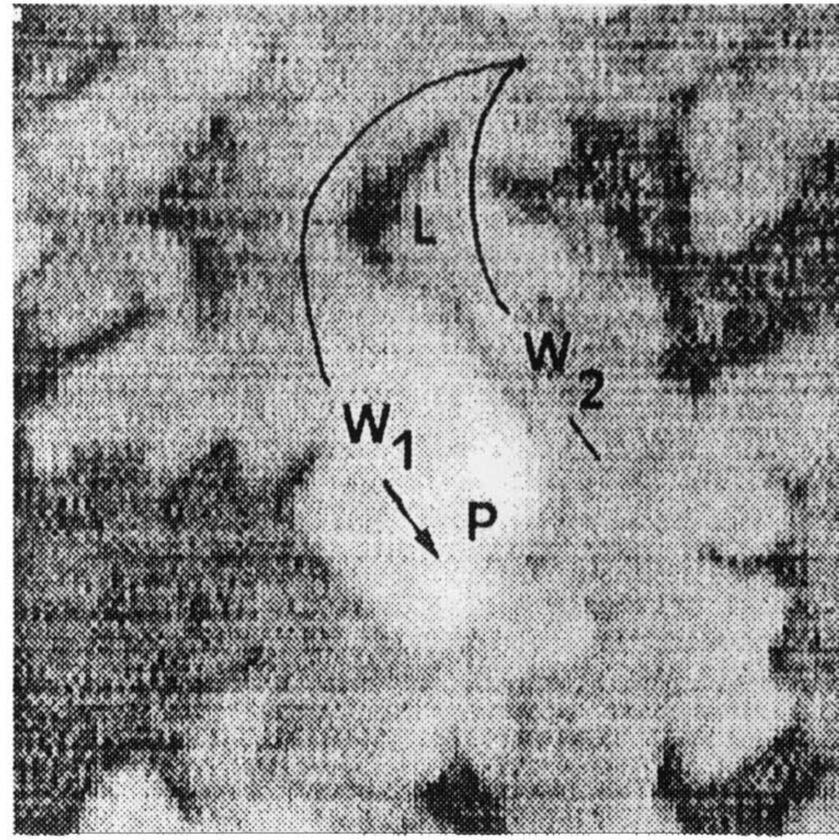




β-methylnaphthalene (001)
M.I. Kozlovskii,
Sov. Phys. Crystallogr. **3**, 206 (1958).

Muscovite Mica
A. Baronnet,
J. Cryst. Growth **19**, 193 (1973).

Coalescence of Growth Fronts



200 nm

Sputtered $YBa_2Cu_3O_{7-\delta}$, $SrTiO_3$ {100}

$t \approx 12$ nm

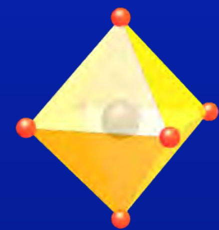
J. Burger, Ph. D. Thesis, University of Erlangen (1992).

Sputtered $DyBa_2Cu_3O_{7-\delta}$
$t \approx 20$ nm

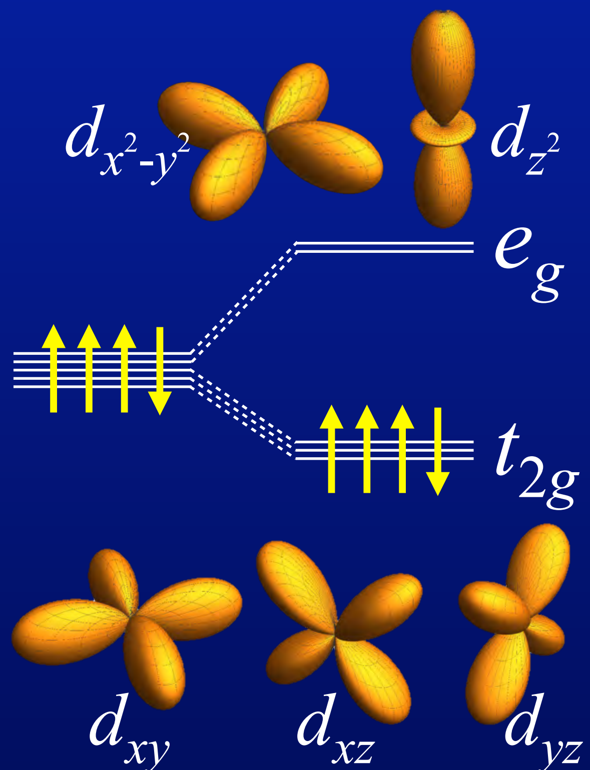
I. Maggio-Aprile,
University of Geneva

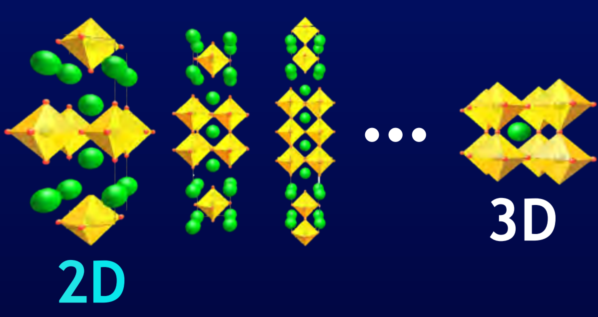
Ruthenates are Hyper-Sensitive

Ru^{4+} : $4d^4$



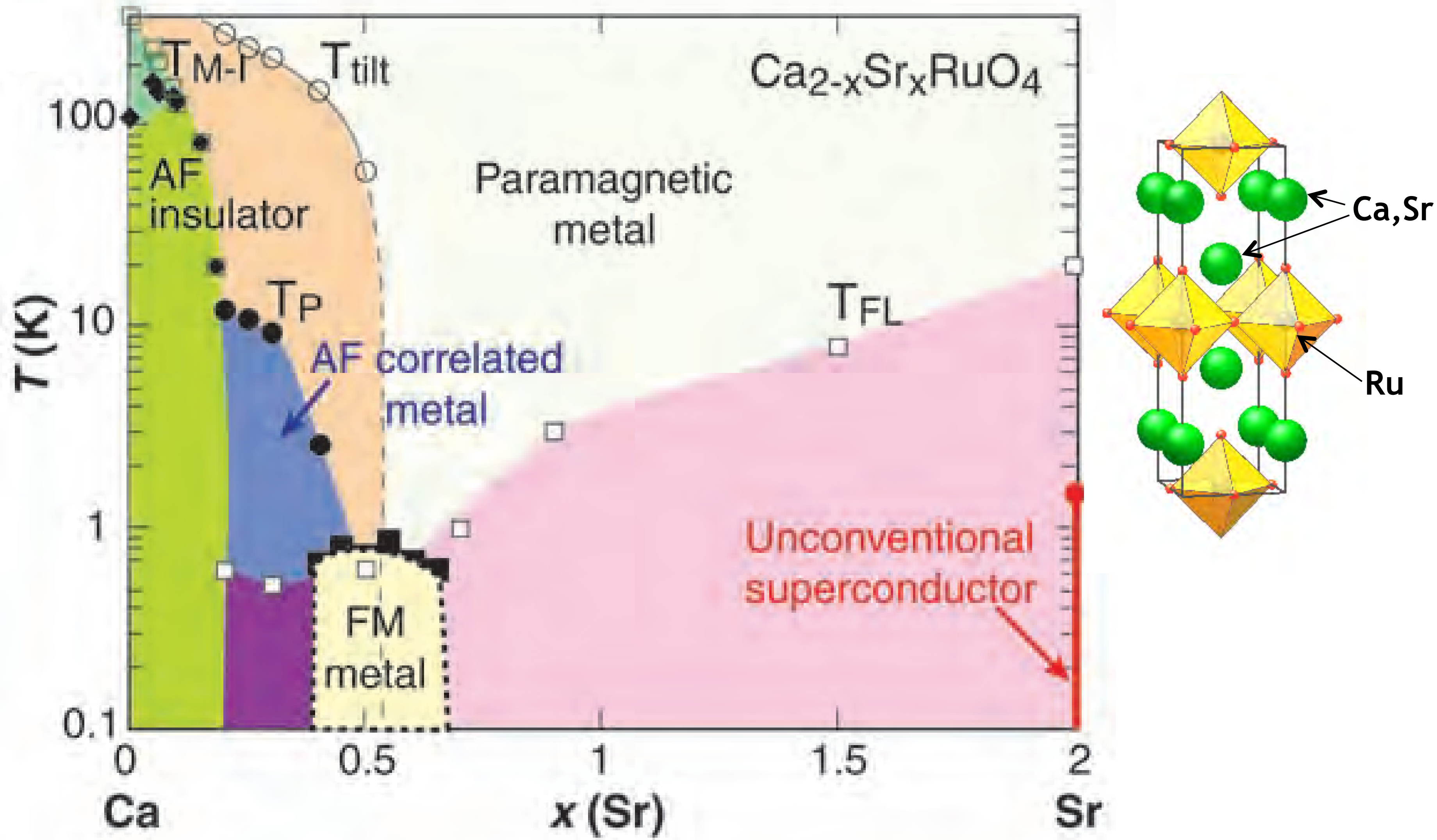
Ruthenates exhibit large changes in properties with rather minor changes in structure





Compound	Dimensionality	Cation	Ground State
$CaRuO_3$	3D	Ca^{2+}	Paramagnetic non-Fermi liquid metal?
Ca_2RuO_4	2D	Ca^{2+}	antiferromagnetic Mott insulator
$SrRuO_3$	3D	Sr^{2+}	ferromagnetic metal
Sr_2RuO_4	2D	Sr^{2+}	odd-parity superconductor
$BaRuO_3$	3D	Ba^{2+}	ferromagnetic metal
Ba_2RuO_4	2D	Ba^{2+}	paramagnetic metal?

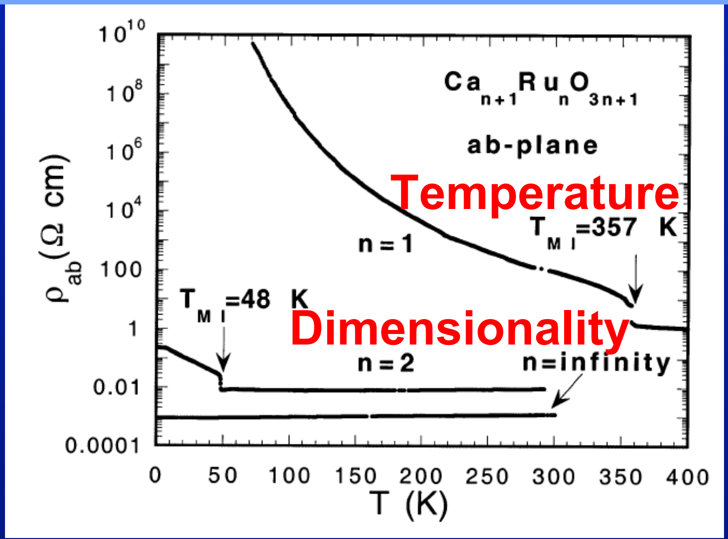
Bulk Approach to Tune Ruthenates



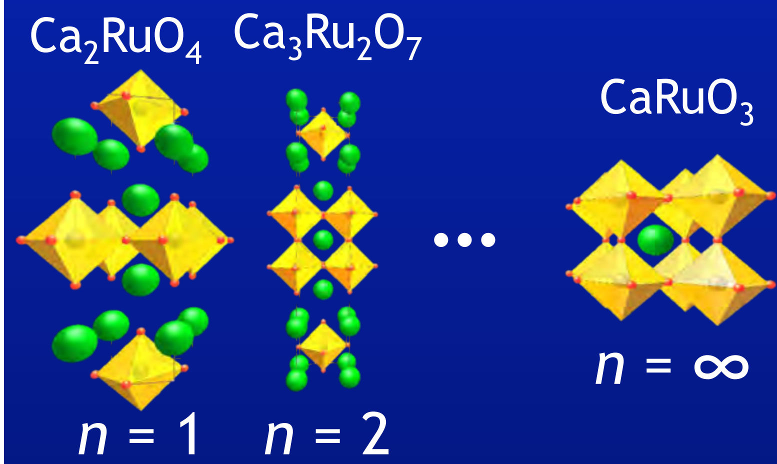
Similar energy scales lead to many competing phases

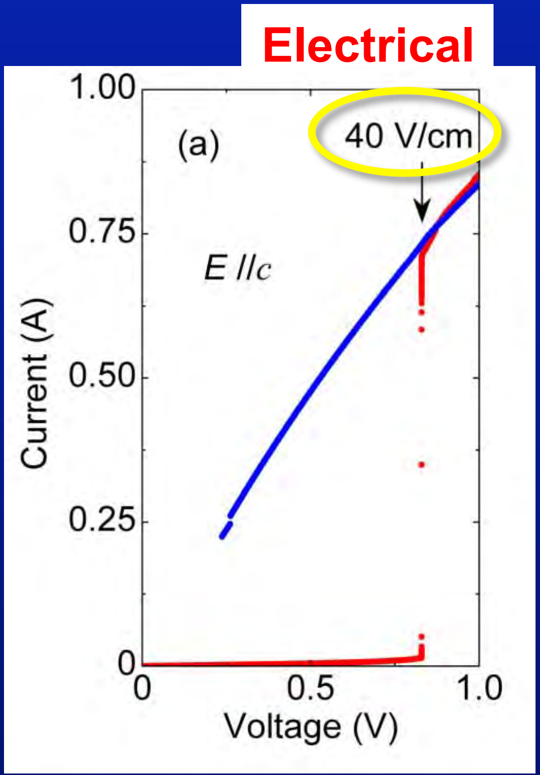
E. Dagotto
Science **309** (2005) 257–262.

Ca_2RuO_4—a very Tunable System



G. Cao, C.S. Alexander, S. McCall, and J.E. Crow, *Mater. Sci. Eng., B* **63** (1999) 76–82.

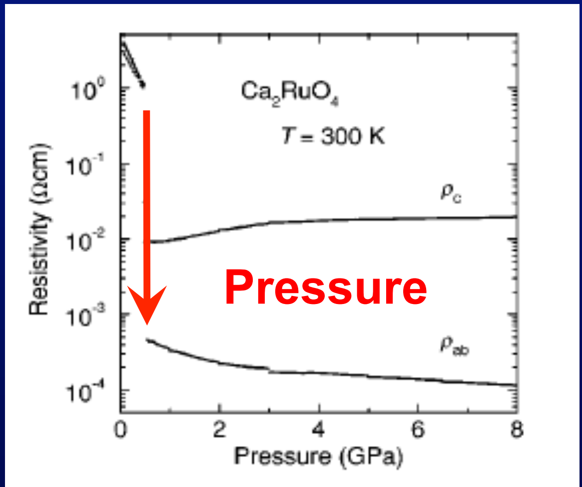




F. Nakamura, M. Sakaki, Y. Yamanaka, S. Tamaru, T. Suzuki, and Y. Maeno, *Sci. Rep.* **3** (2013) 1–6.

Metal-Insulator Transition in Ca_2RuO_4 Triggered by

- Temperature
- Dimensionality
- Pressure
- Voltage/current



F. Nakamura, T. Goko, M. Ito, T. Fujita, S. Nakatsuji, H. Fukazawa, Y. Maeno, P. Alireza, D. Forsythe, and S. R. Julian *Phys. Rev. B* **65**, (2002) 220402.

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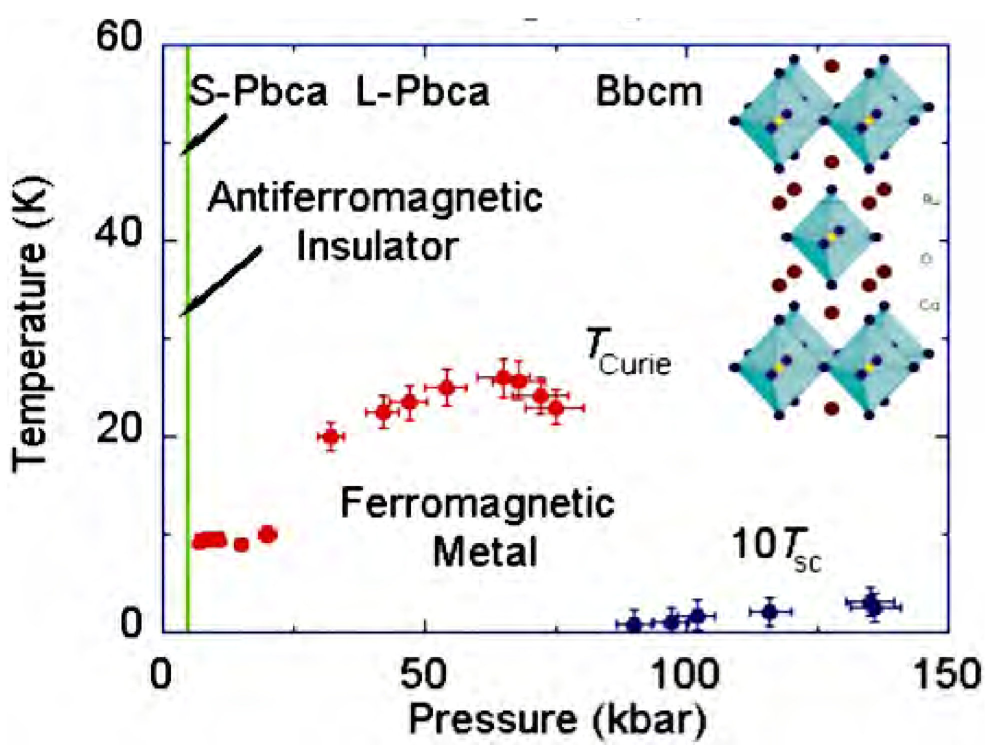
Ca_2RuO_4 under Hydrostatic Pressure



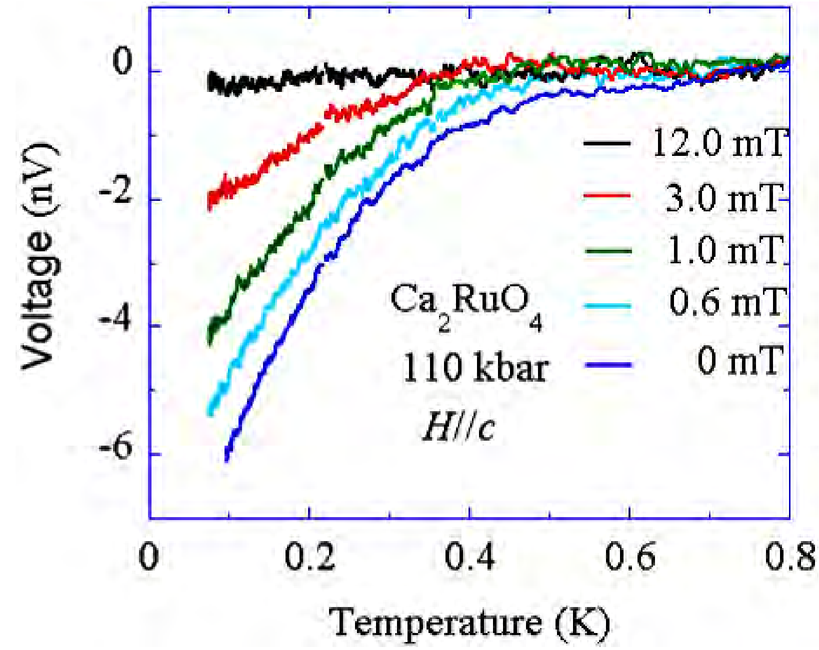


Figure 3. Evidence of superconductivity in the ac susceptibility. The collapse of the ac susceptibility with decreasing temperature relative to 0.8 K at different magnetic fields as seen in the change in the pick-up voltage in a susceptometer at approximately 110 kbar. The

superconducting T_c ~ 0.4 K at 140 kbar

P.L. Alireza, F. Nakamura, S.K. Goh, Y. Maeno, S. Nakatsuji, Y.T.C. Ko, M. Sutherland, S. Julian, and G.G. Lonzarich, *J. Phys.: Condens. Matter* **22**, 052202 (2010).

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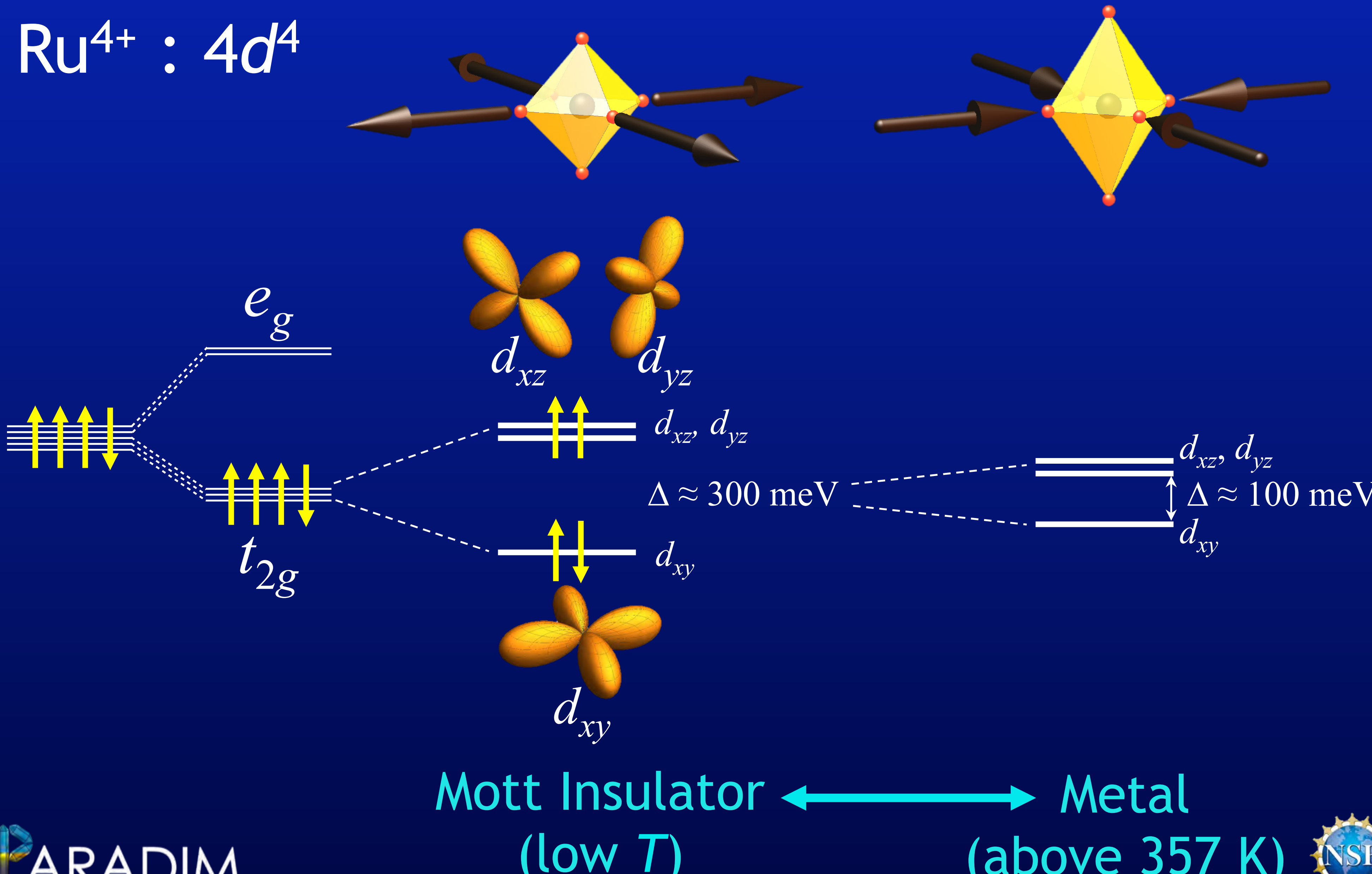
Understanding Ca_2RuO_4

Ru^{4+} : $4d^4$



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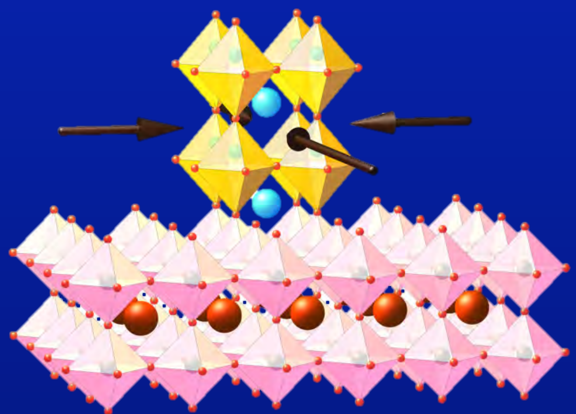
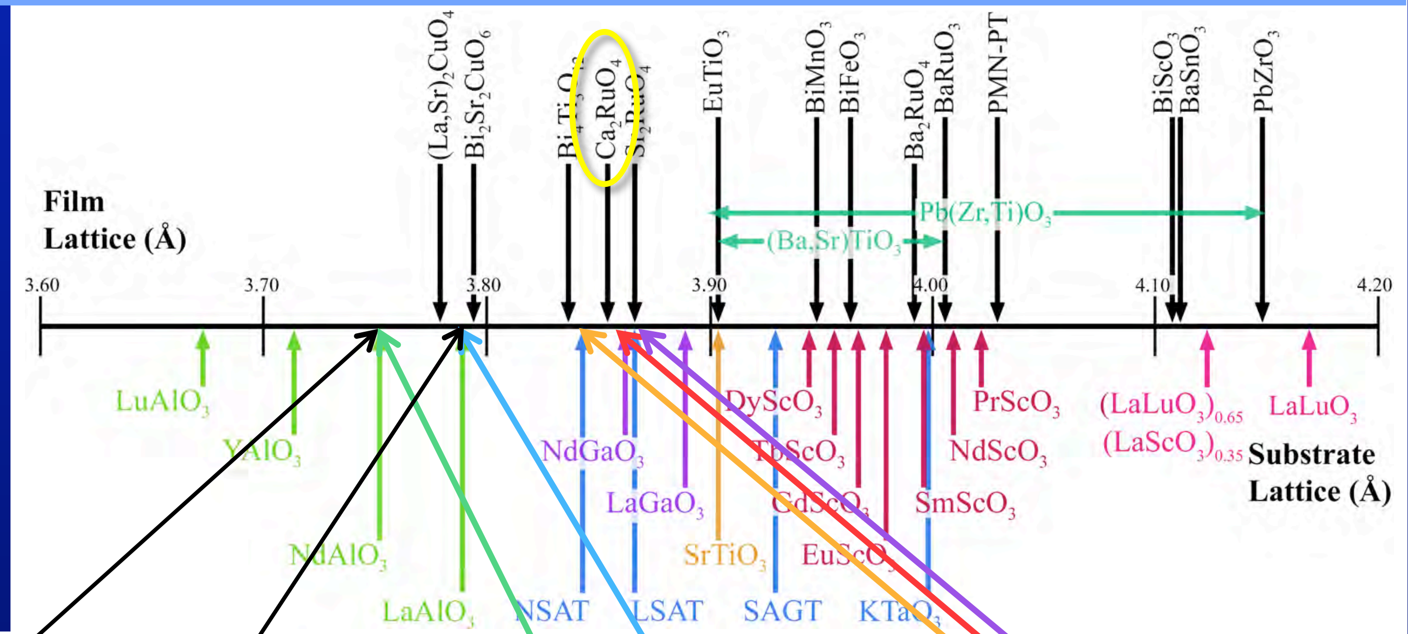
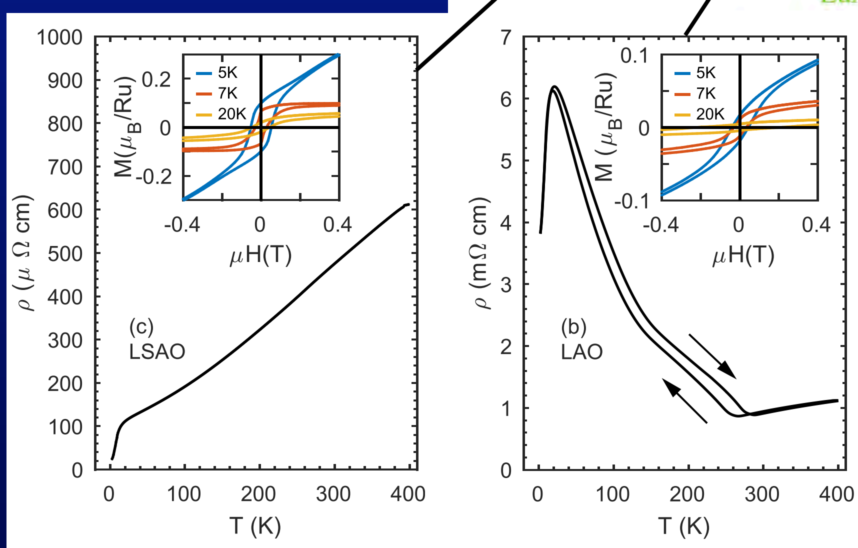
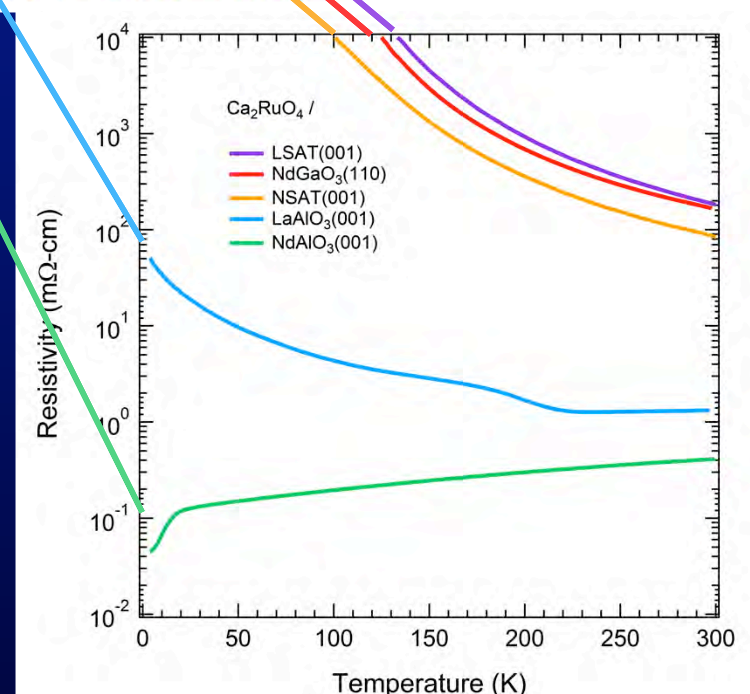
Thin-Film Approach to Tune Ruthenates



Strain Engineering







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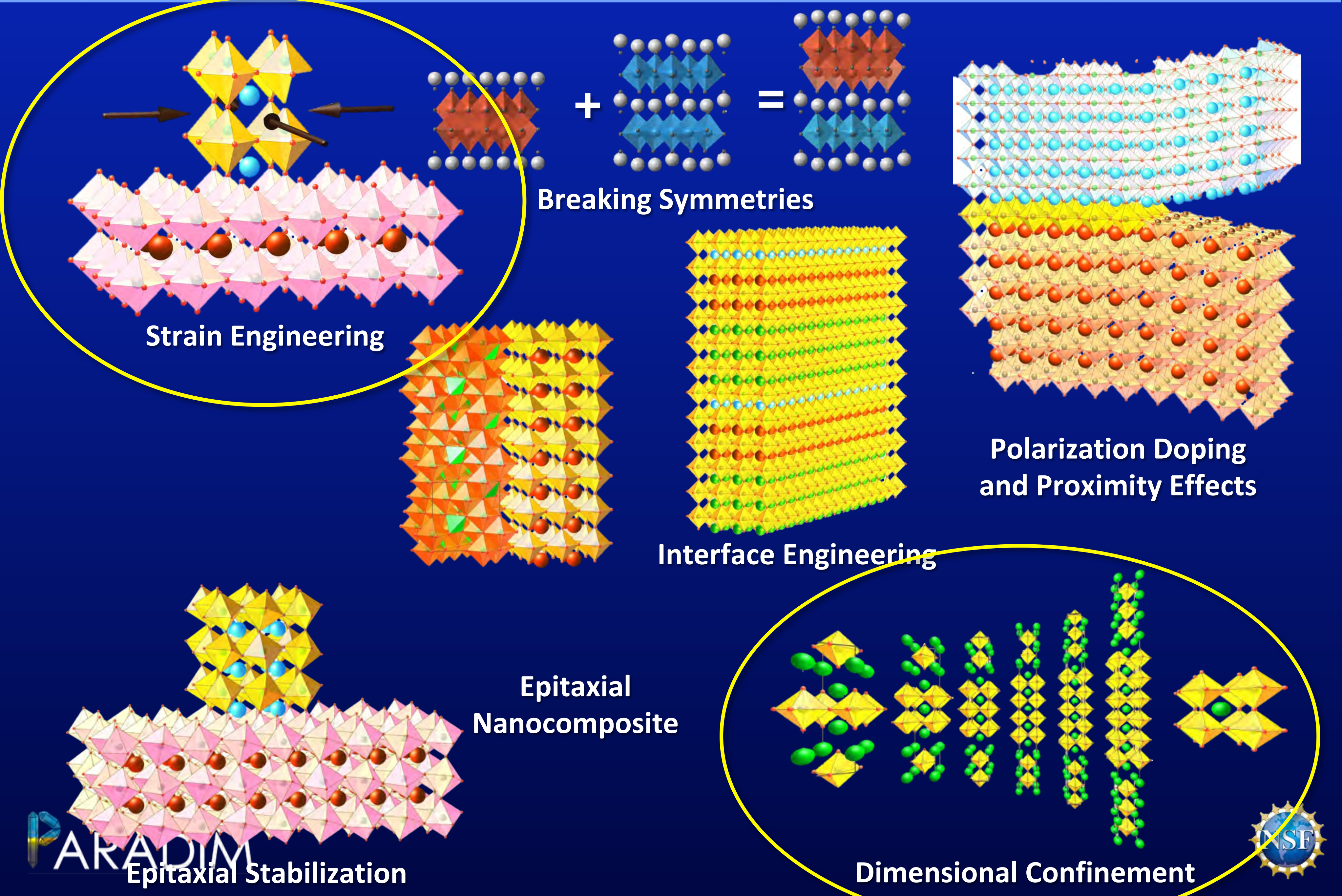
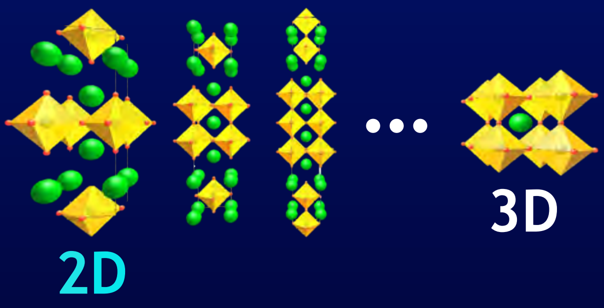
C. Dietl, S.K. Sinha, G. Christiani, Y. Khaydukov, T. Keller, D. Putzky, S. Ibrahimkutty, P. Wochner, G. Logvenov, P.A. van Aken, B.J. Kim, and B. Keimer, *Appl. Phys. Lett.* **112** (2018) 031902.

Epitaxial Routes to Engineer Properties

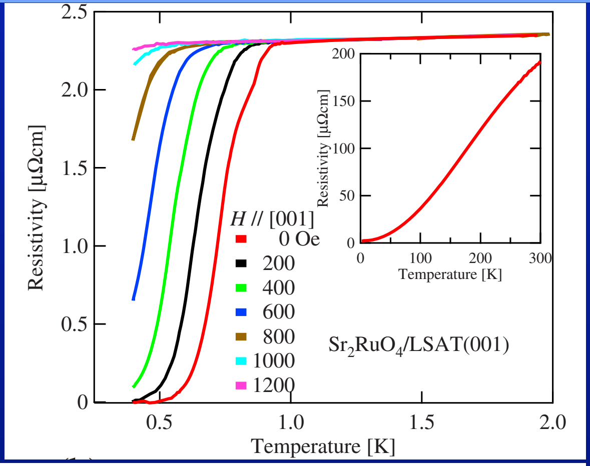


My Interest in Ruthenates—Odd Parity Topological Superconductor

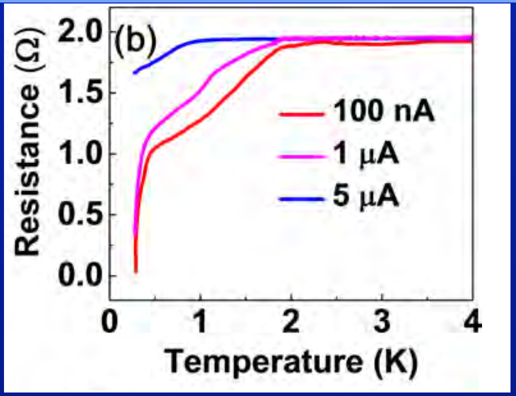
Compound	Dimensionality	Cation	Ground State
$CaRuO_3$	3D	Ca^{2+}	Paramagnetic non-Fermi liquid metal?
Ca_2RuO_4	2D	Ca^{2+}	antiferromagnetic Mott insulator
$SrRuO_3$	3D	Sr^{2+}	ferromagnetic metal
Sr_2RuO_4	2D	Sr^{2+}	odd-parity superconductor
$BaRuO_3$	3D	Ba^{2+}	ferromagnetic metal
Ba_2RuO_4	2D	Ba^{2+}	paramagnetic metal?



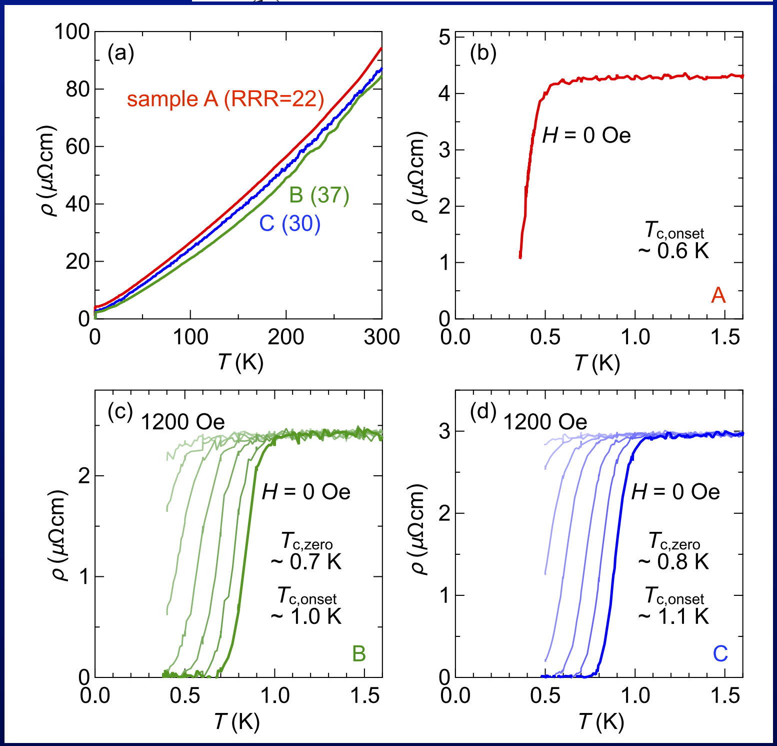
Superconducting Sr_2RuO_4 Films



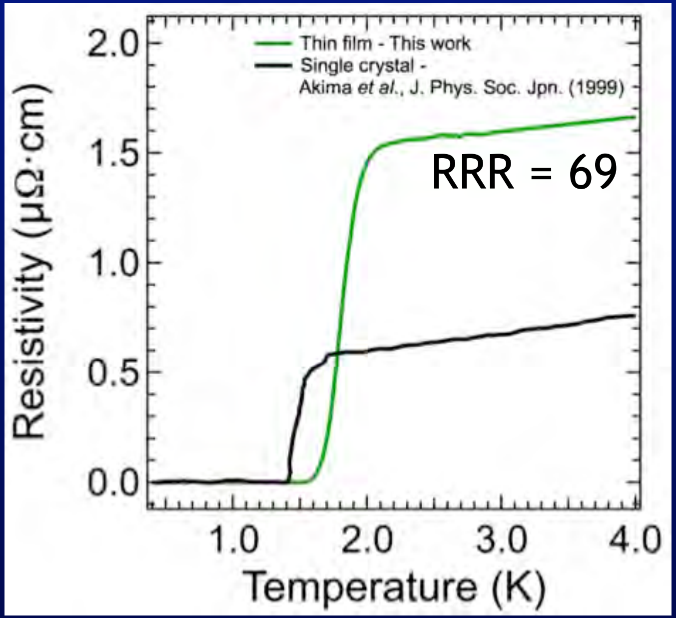
Y. Krockenberger, M. Uchida, K. S. Takahashi, M. Nakamura, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* **97** (2010) 082502.



J. Cao, D. Massarotti, M. E. Vickers, A. Kursumovic, A. Di Bernardo, J. W. A. Robinson, F. Tafuri, J. L. MacManus-Driscoll, and M. G. Blamire, *Supercond. Sci. Technol.* **29** (2016) 095005.

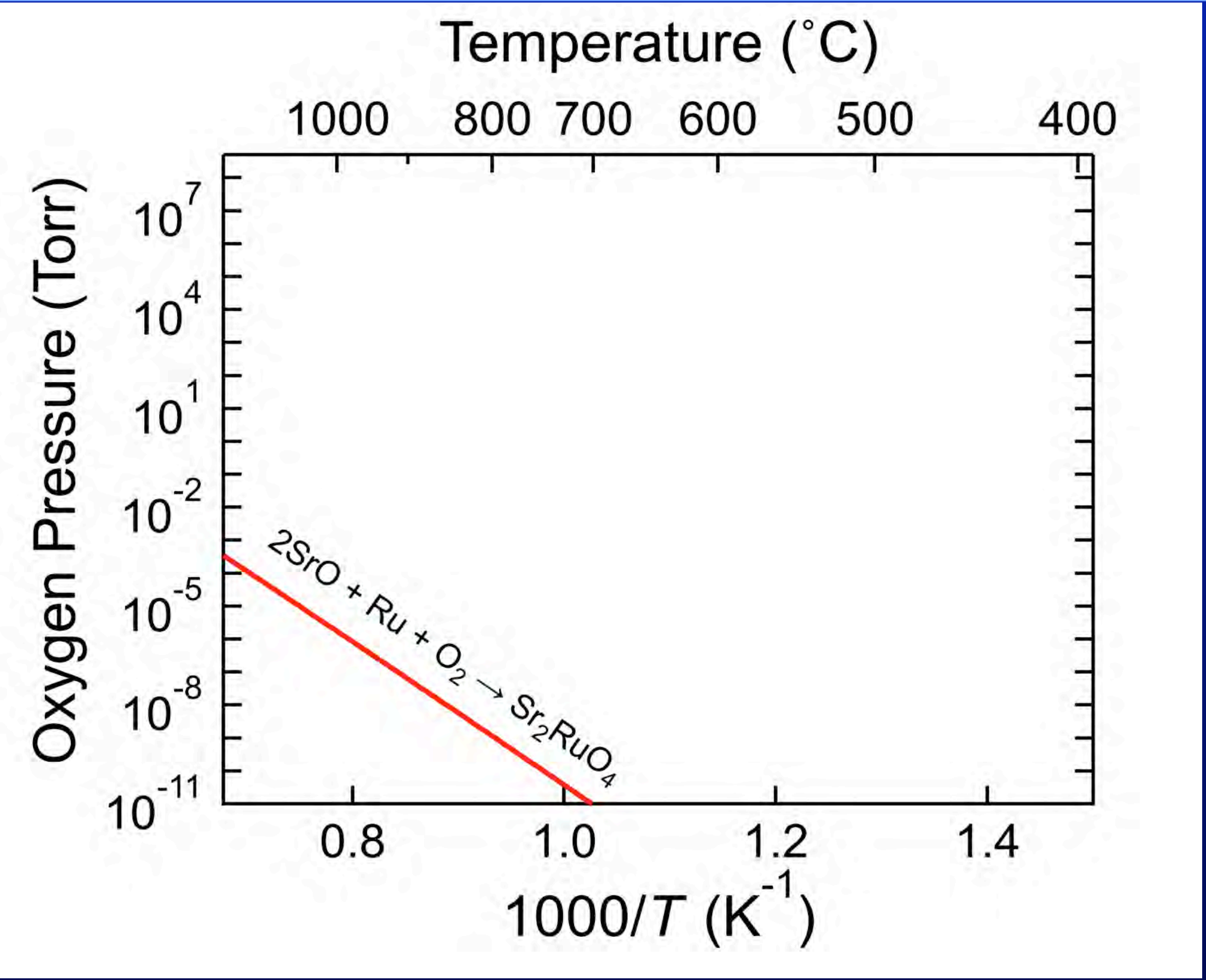


M. Uchida, M. Ide, H. Watanabe, K. S. Takahashi, Y. Tokura, and M. Kawasaki, *APL Mater.* **5** (2017) 106108.



H.P. Nair, J.P. Ruf, N.J. Schreiber, L. Miao, M.L. Grandon, D.J. Baek, B.H. Goodge, J.P.C. Ruff, L.F. Kourkoutis, K.M. Shen, and D.G. Schlom, *APL Mater.* **6** (2018) 101108.

Thermo of Sr_2RuO_4 by MBE



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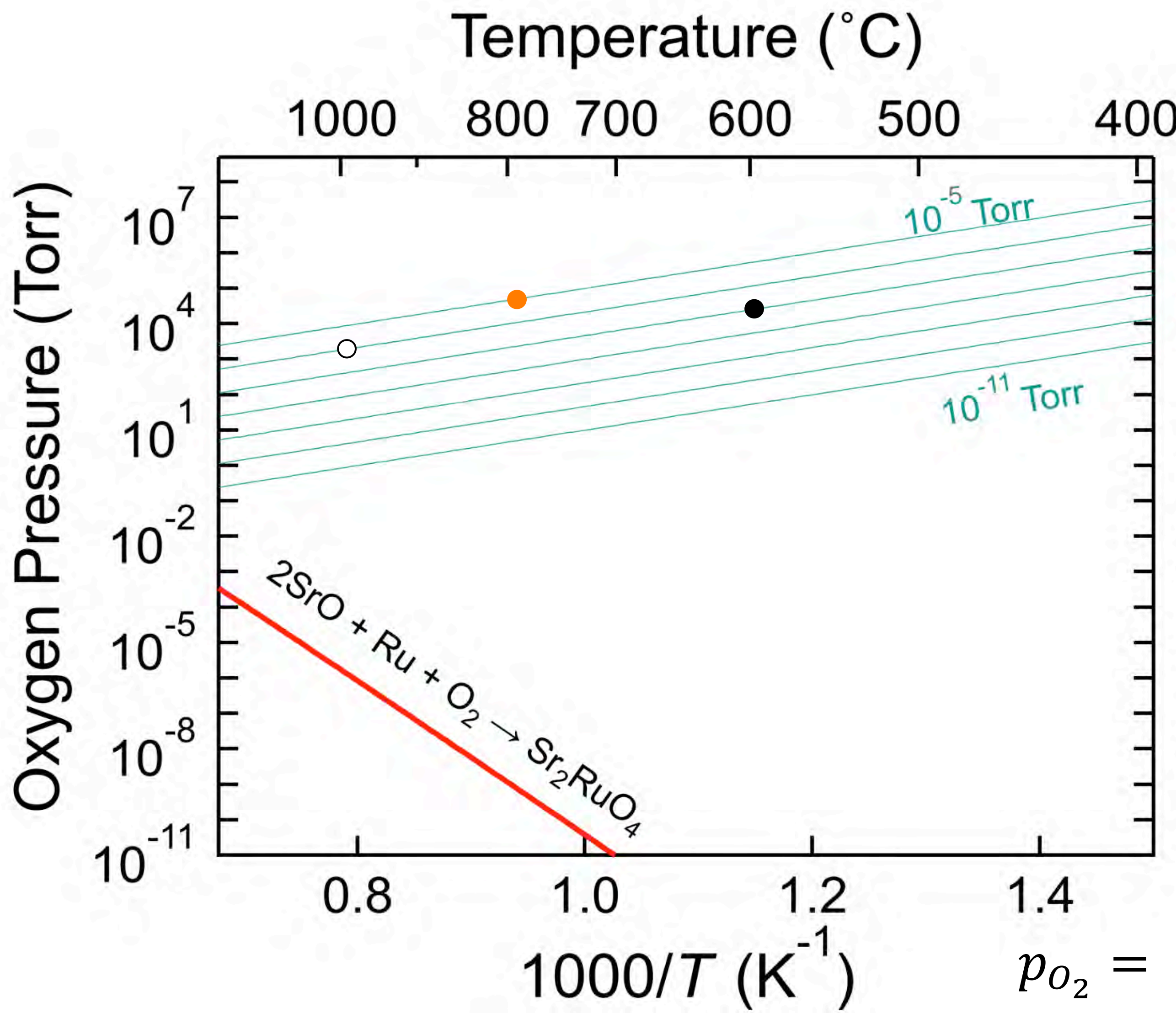
Thermodynamic data from: K.T. Jacob, K.T. Lwin, and Y. Waseda,
J. Mater. Sci. Eng., B **103** (2003) 152–161.

Thermo of Sr_2RuO_4 by MBE



- T_s = 600 ˚C, p_{O_3} = 10^{-7} Torr
- T_s = 1000 ˚C, p_{O_3} = 10^{-6} Torr
- T_s = 800 ˚C, p_{O_3} = 10^{-5} Torr

$$O_2 \xrightarrow{\Delta G^\circ} \frac{2}{3} O_3$$

$$p_{O_2} = p_{O_3}{}^{2/3} \exp\left[\frac{\Delta G_0}{RT_s}\right]$$

Ozone decomposition thermodynamic calculation:
Y. Krockenberger, J. Kurian, A. Winkler, A. Tsukada, M. Naito, and L. Alff, *Phys. Rev. B* **77** (2008) 060505.

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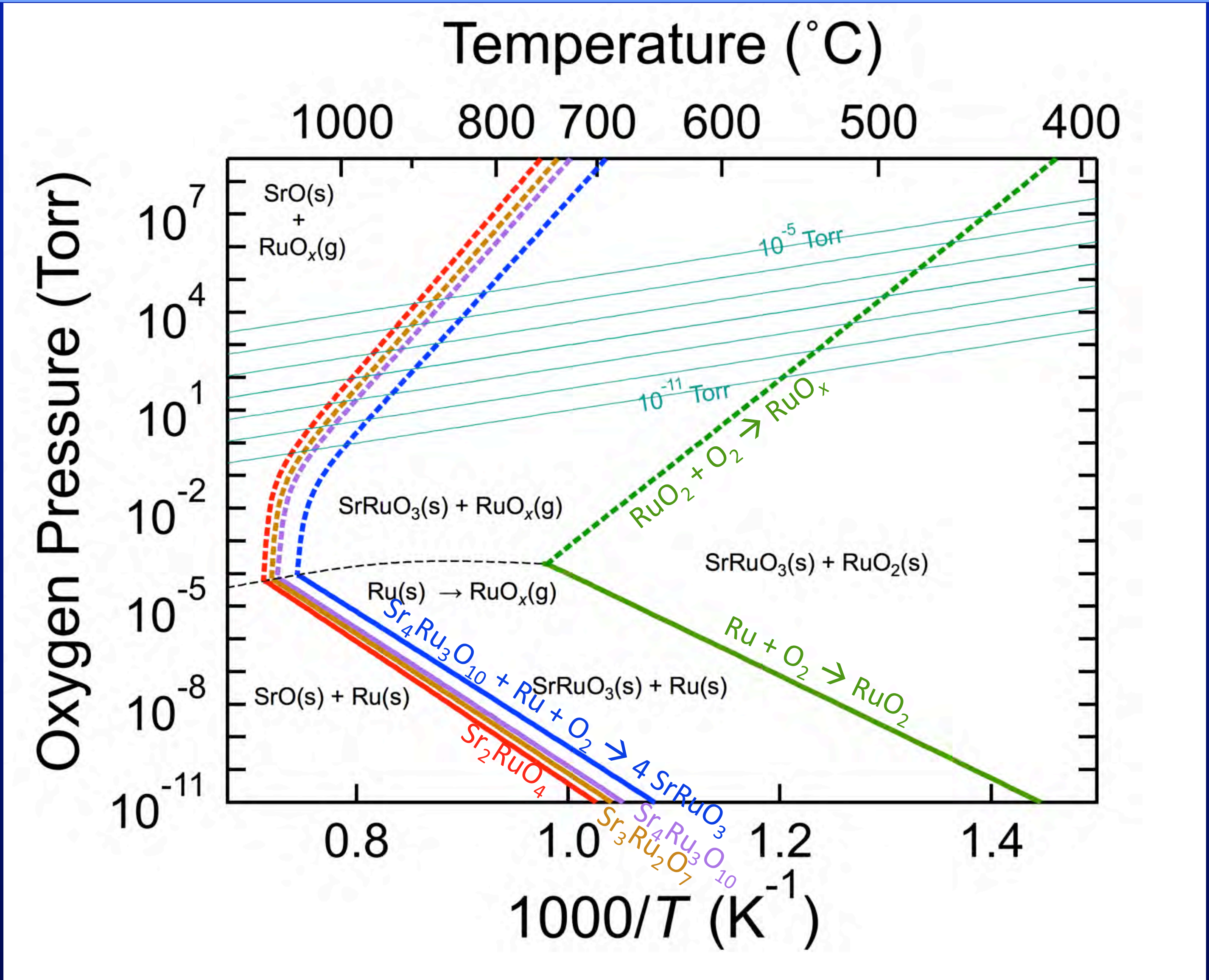
Thermo of $Sr_{n+1}Ru_nO_{3n+1}$ by MBE



H.P. Nair, Y. Liu, J.P. Ruf, N.J. Schreiber, S-L. Shang, D.J. Baek, B.H. Goodge, L.F. Kourkoutis, Z.K. Liu, K.M. Shen, and D.G. Schlom, *APL Materials* **6** (2018) 046101.

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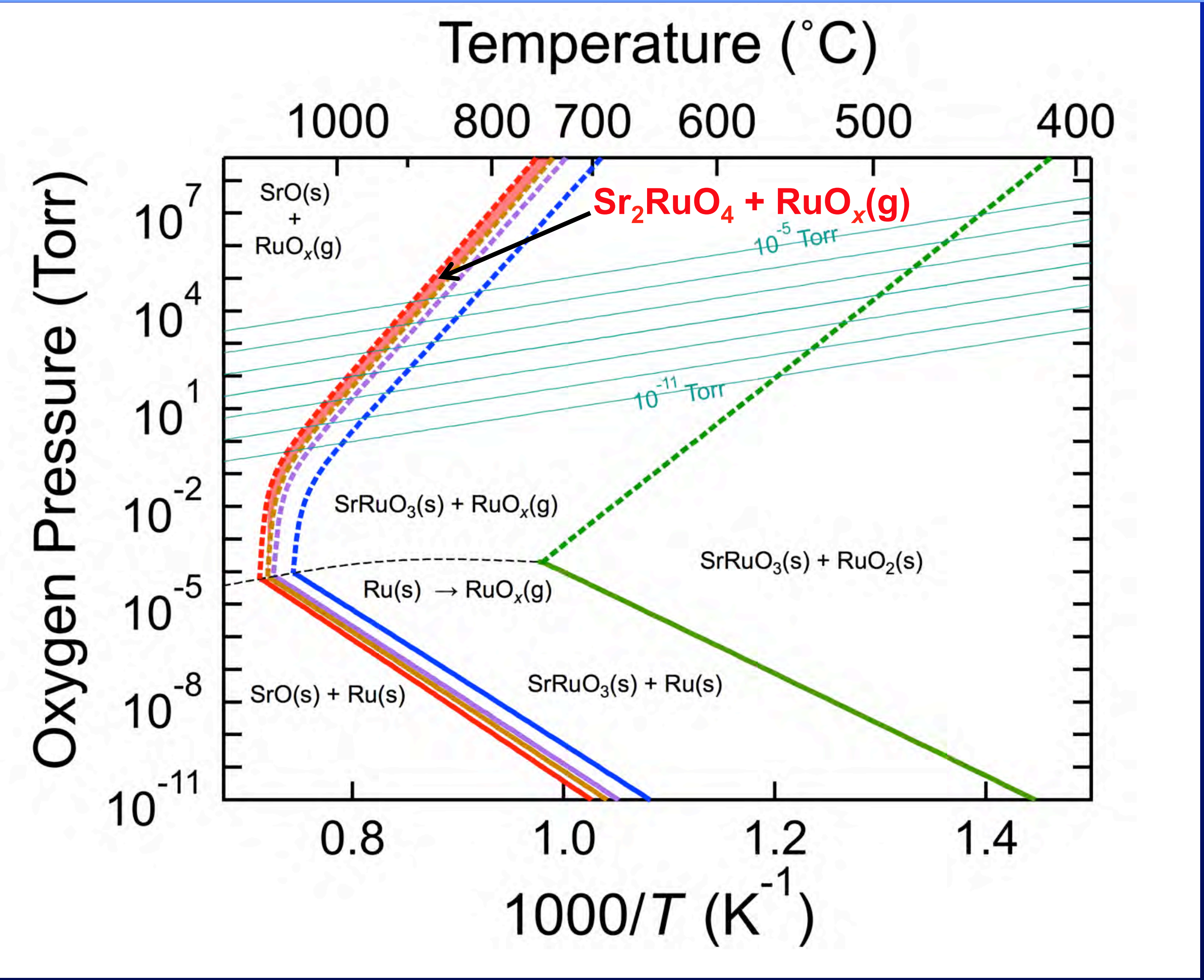
Thermo of $Sr_{n+1}Ru_nO_{3n+1}$ by MBE



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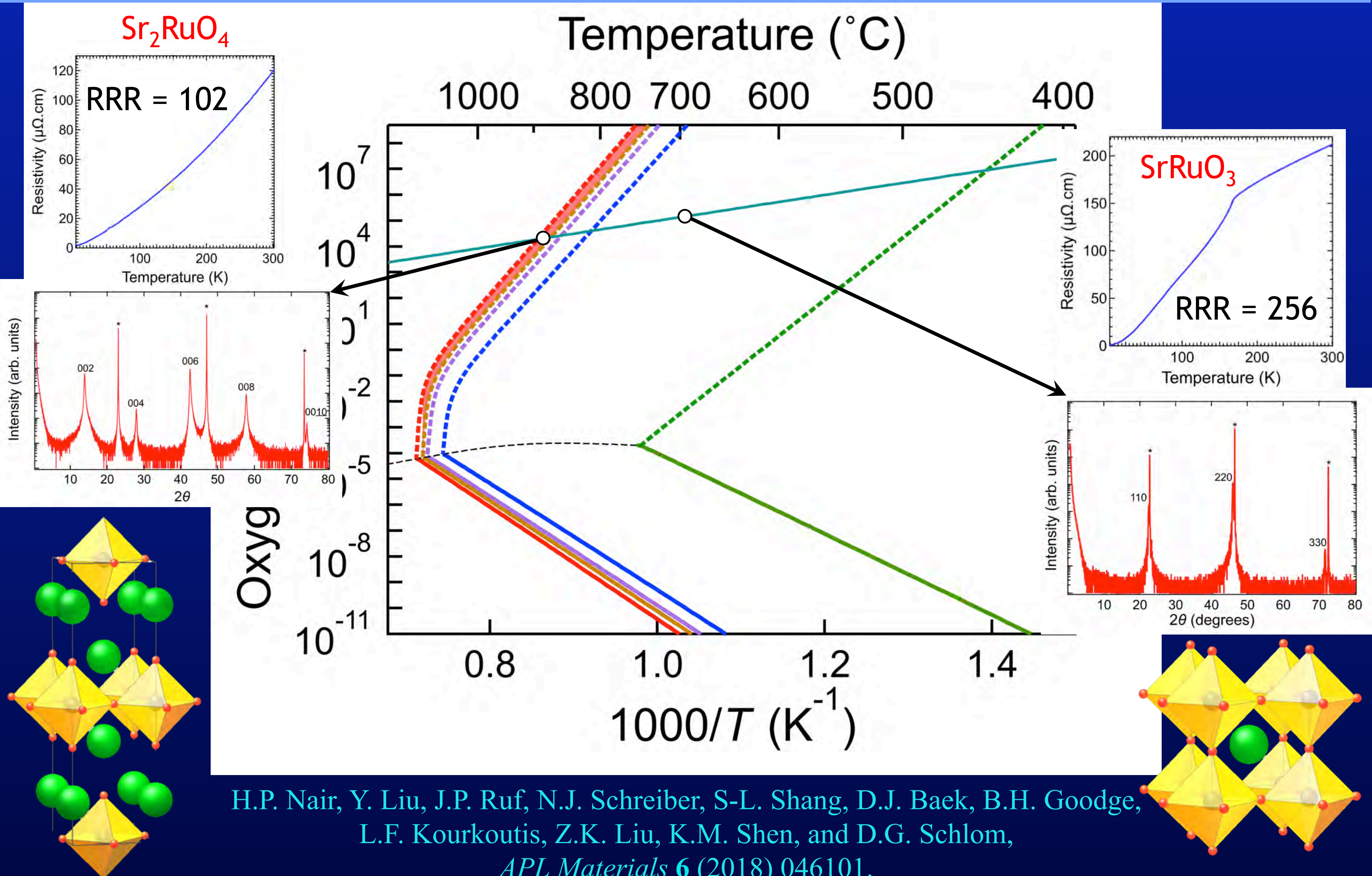
Thermo of $Sr_{n+1}Ru_nO_{3n+1}$ by MBE



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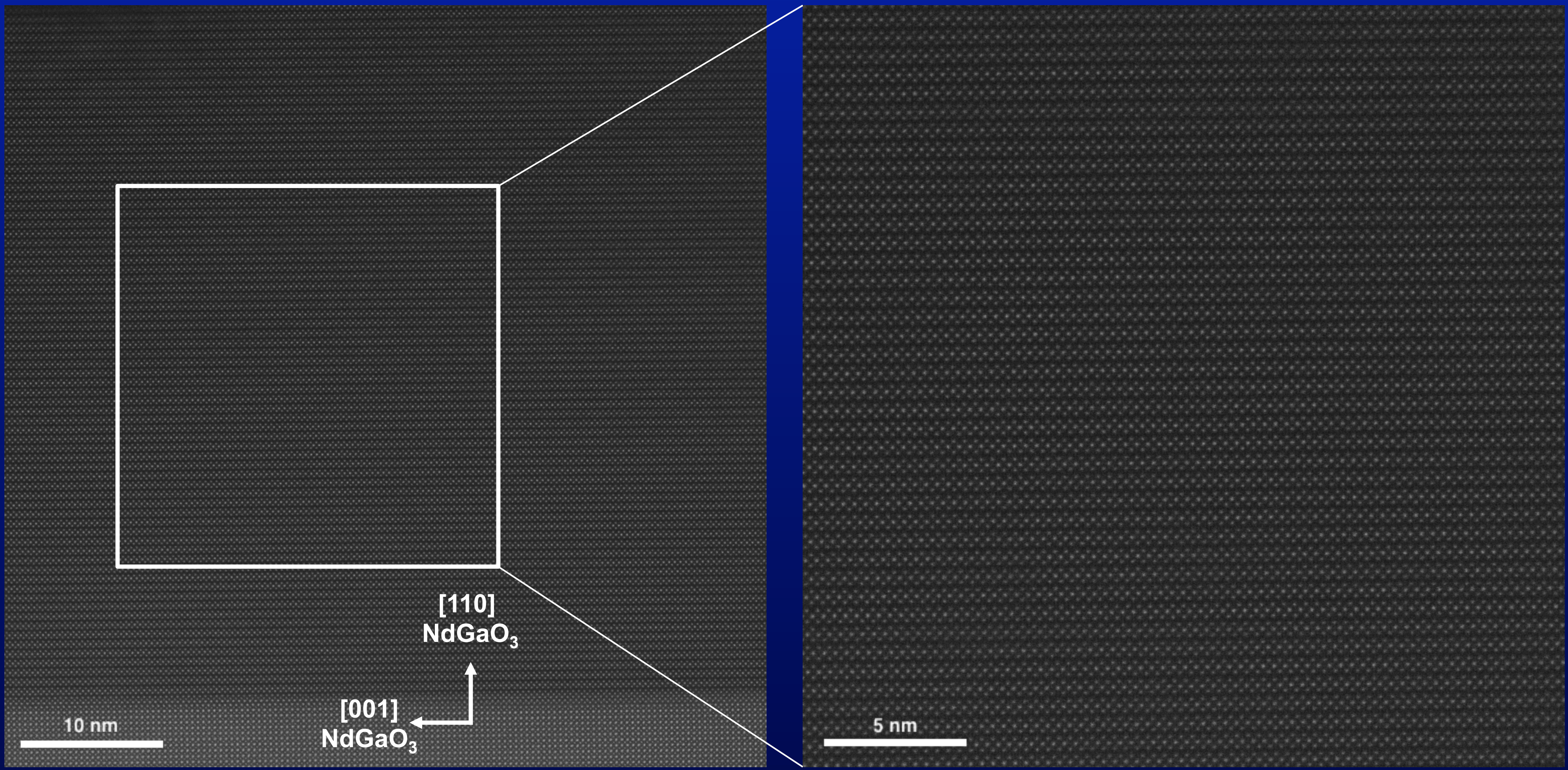
Superconducting Sr_2RuO_4 Films

55 nm thick Sr_2RuO_4 on (110) $NdGaO_3$



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STEM: Berit Goodge and Prof. Lena Kourkoutis (Cornell U.)

If you *increase* the Ru flux, how do you expect the growth window for Sr_2RuO_4 to shift?

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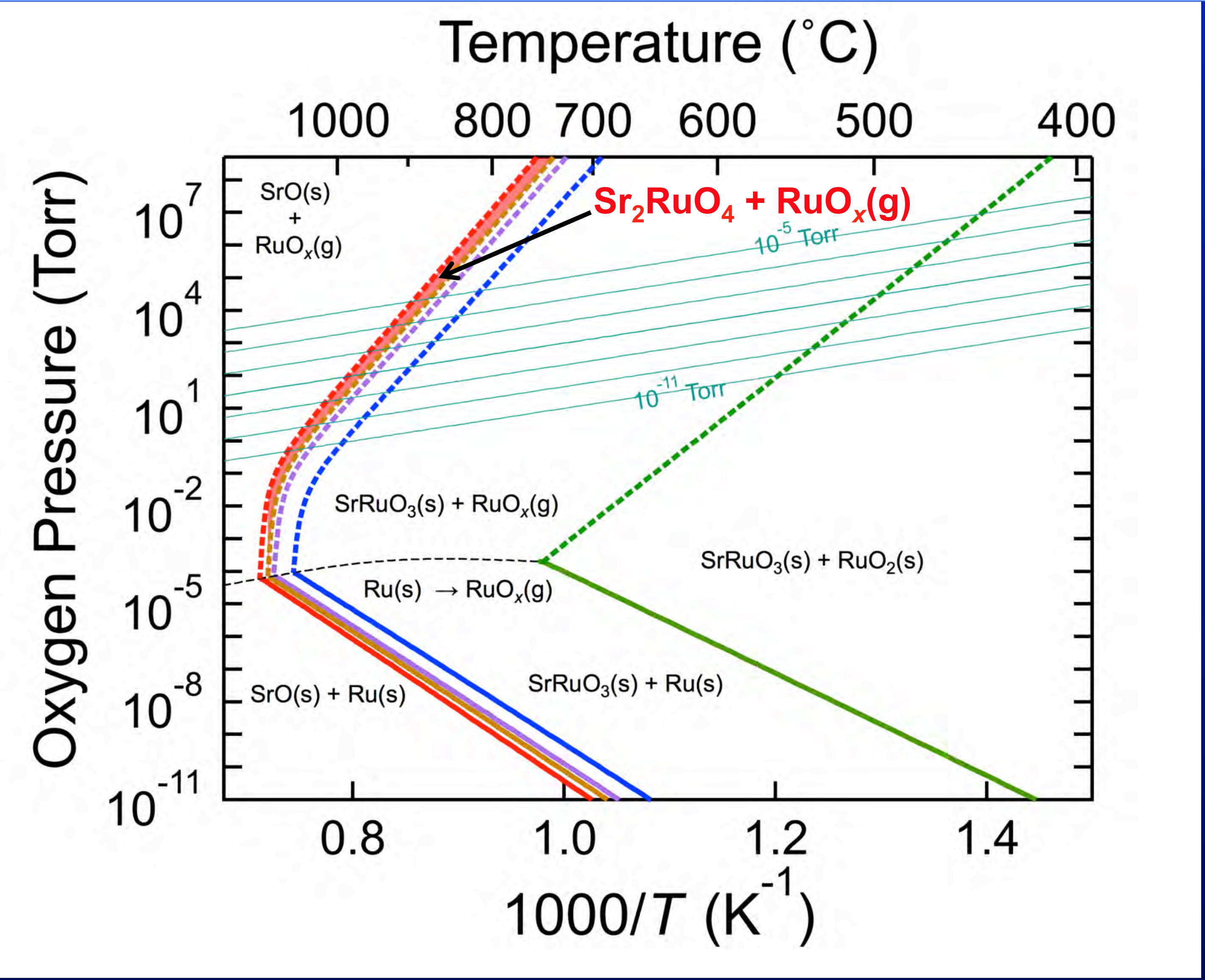
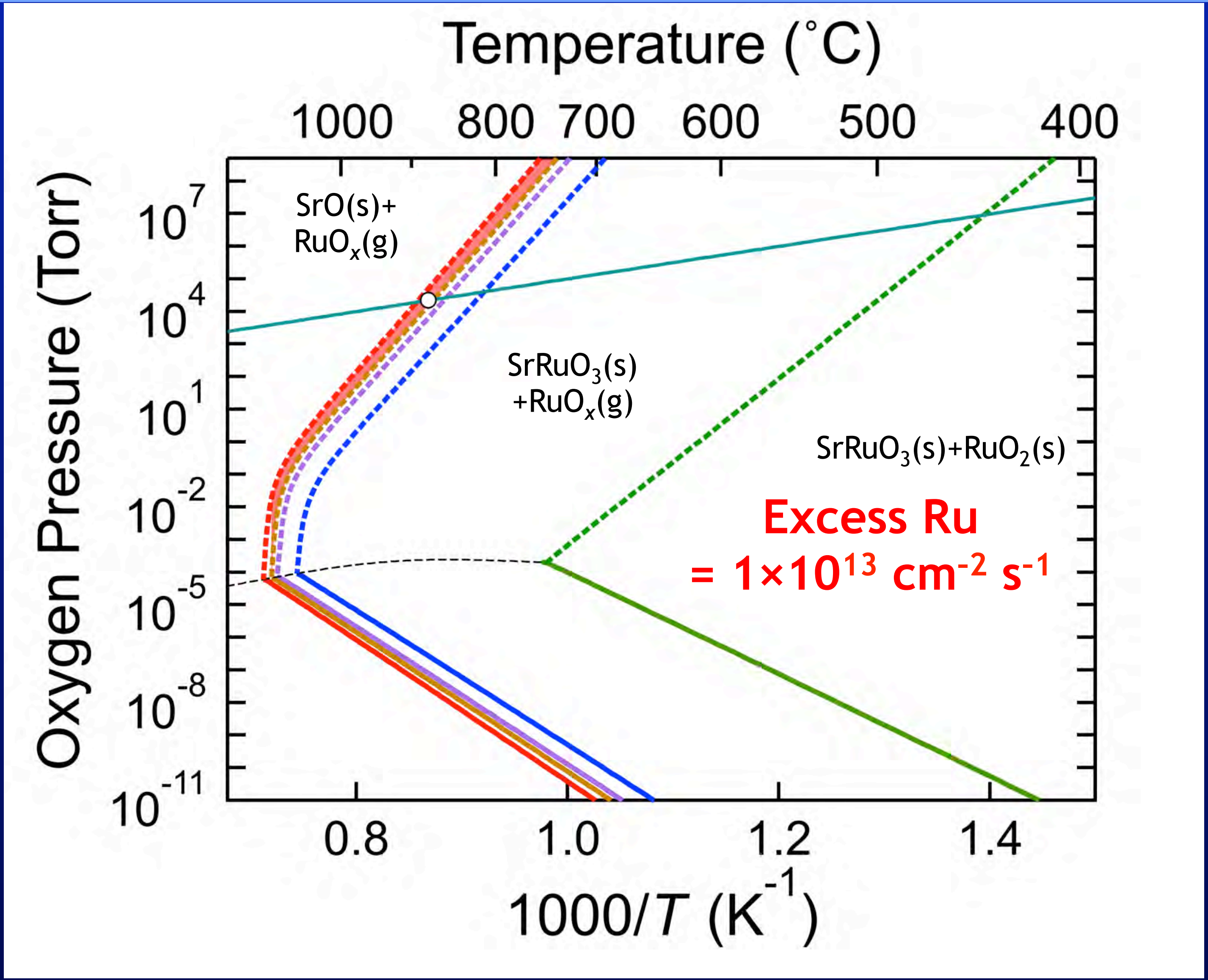
Thermo of $Sr_{n+1}Ru_nO_{3n+1}$ by MBE



H.P. Nair, Y. Liu, J.P. Ruf, N.J. Schreiber, S-L. Shang, D.J. Baek, B.H. Goodge, L.F. Kourkoutis, Z.K. Liu, K.M. Shen, and D.G. Schlom, *APL Materials* **6** (2018) 046101.

Effect of Increased Ru Flux



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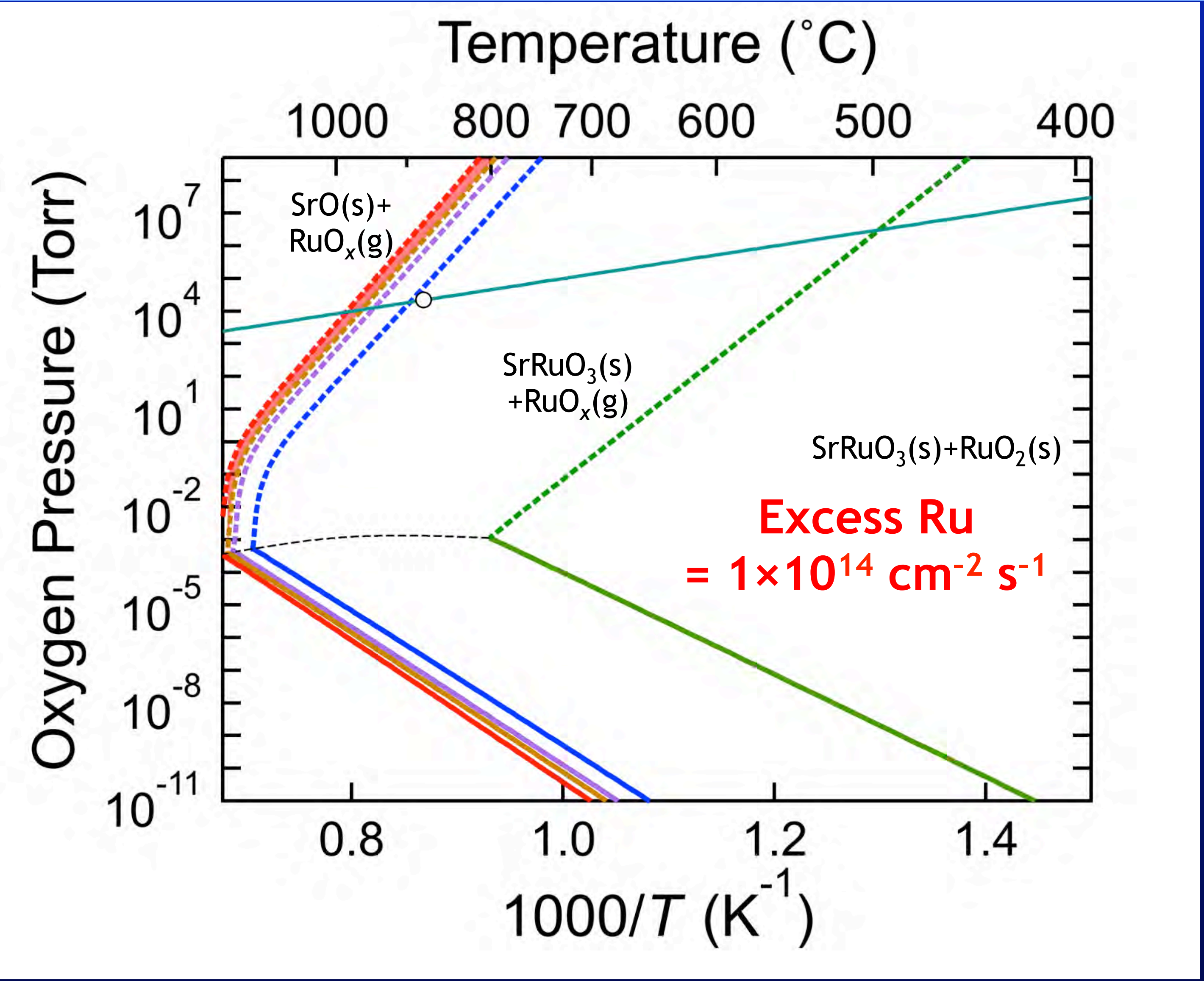
Effect of Increased Ru Flux



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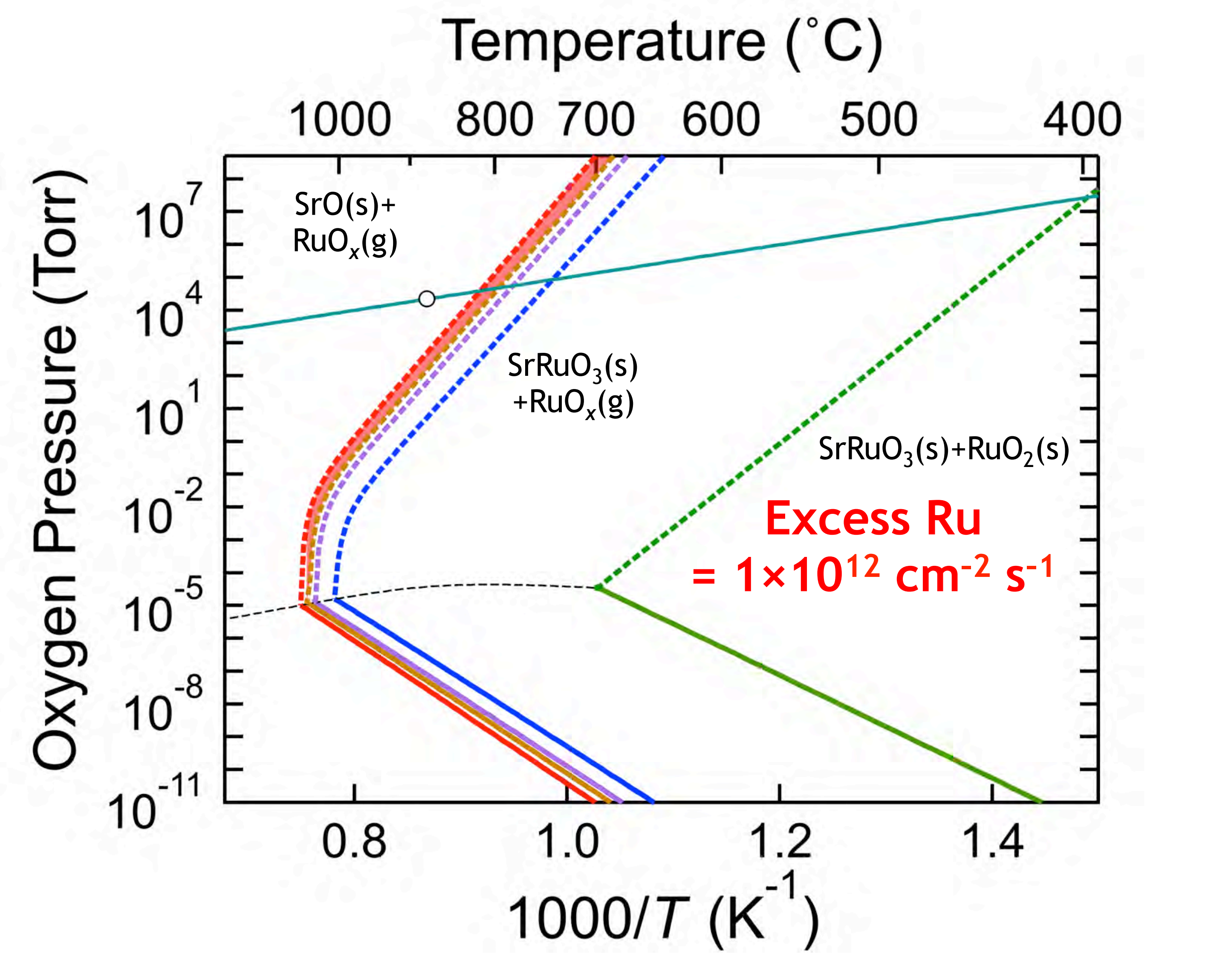
Effect of Increased Ru Flux



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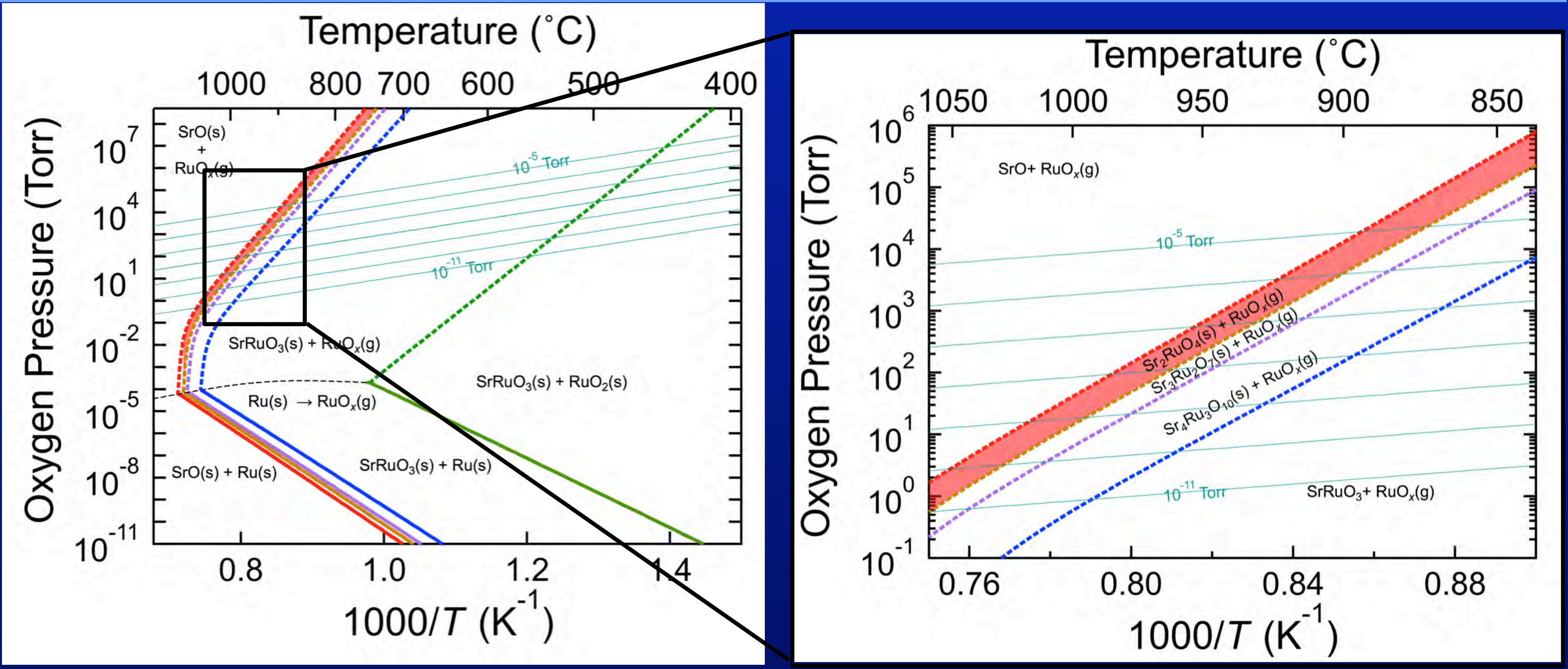
Narrow Growth Window



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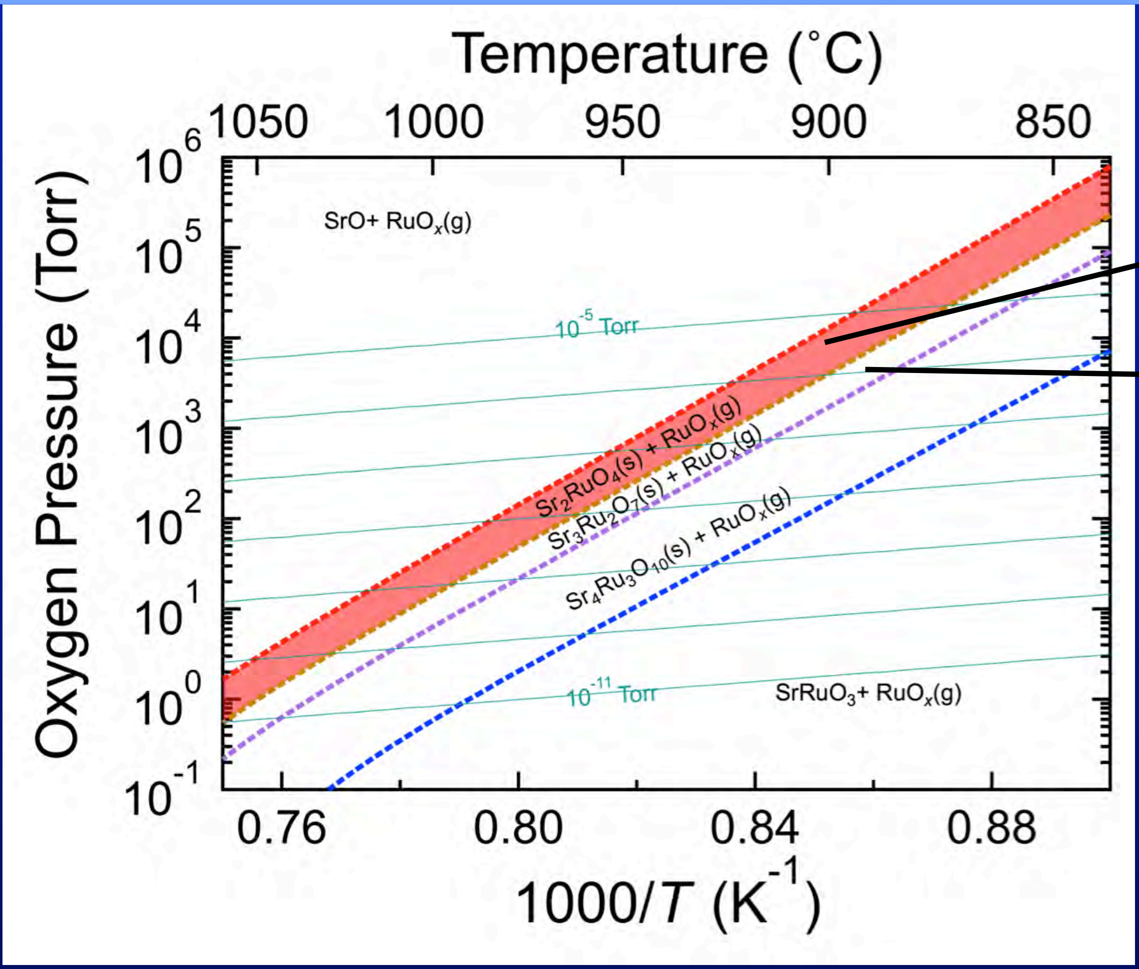
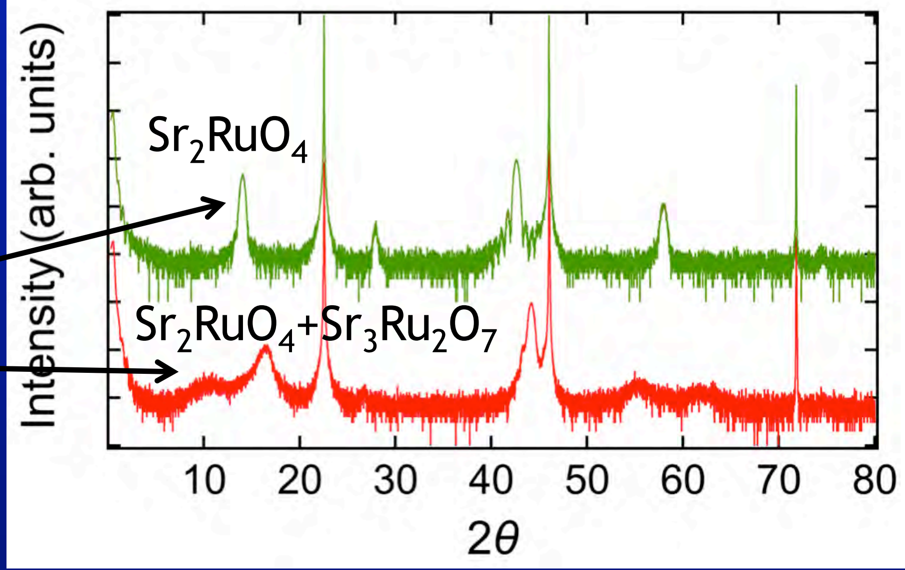
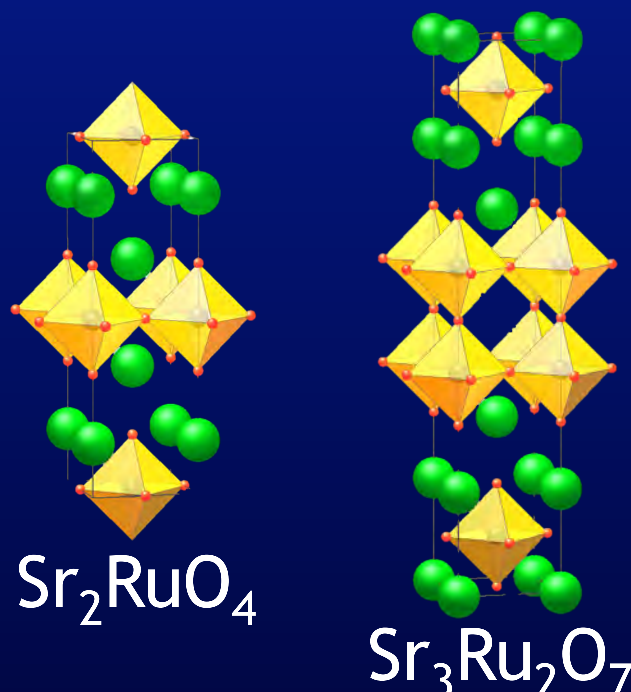
Narrow Growth Window







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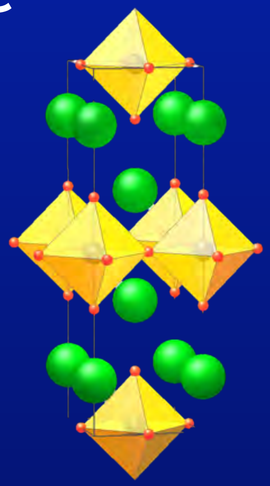
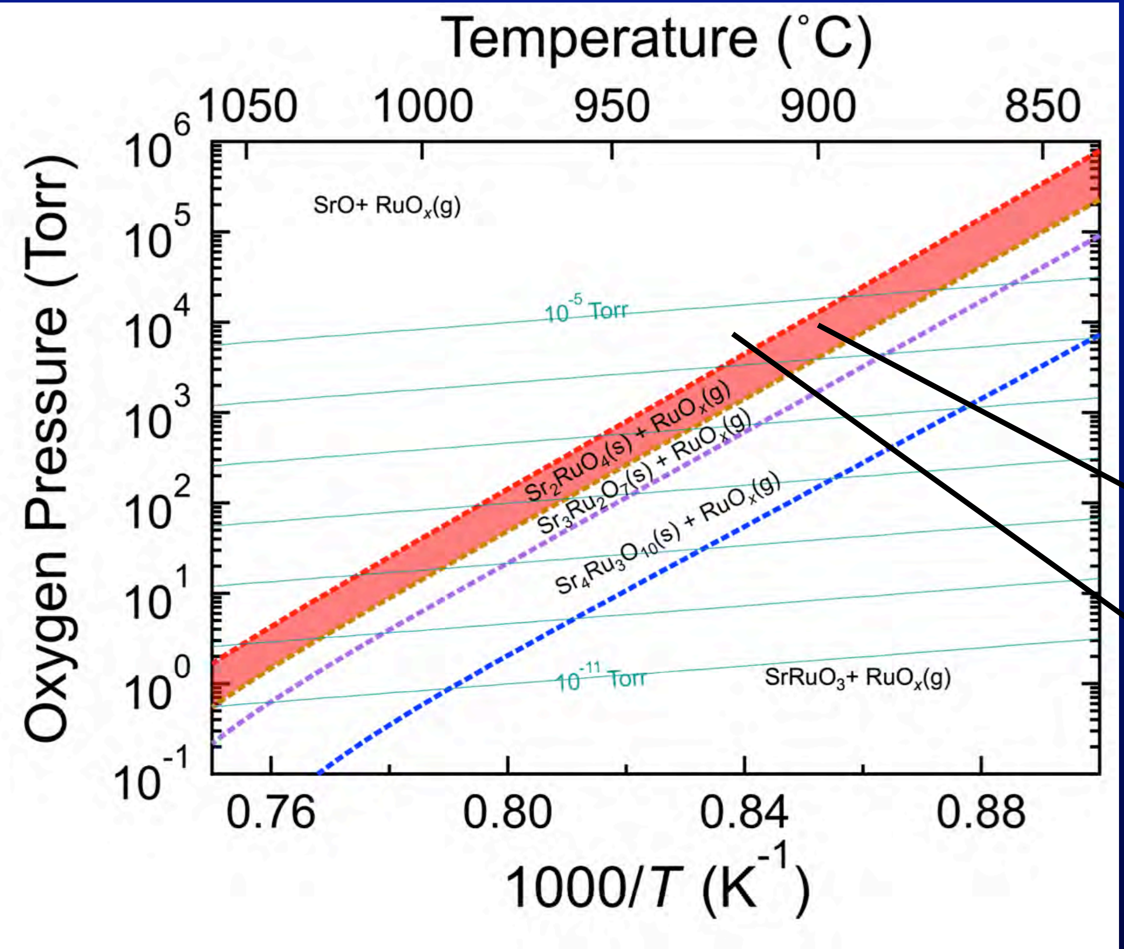
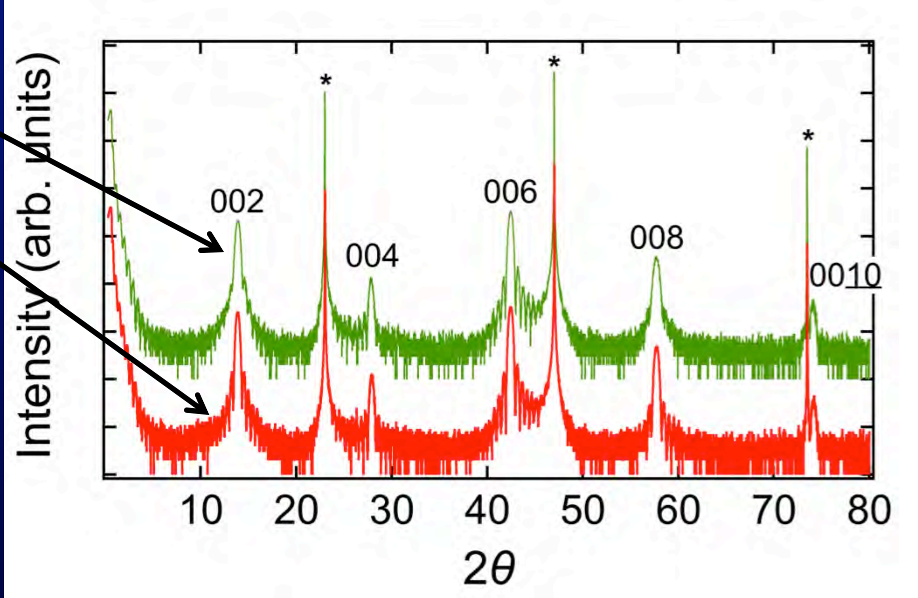
Which Sample Superconducts?

Both films are the correct phase

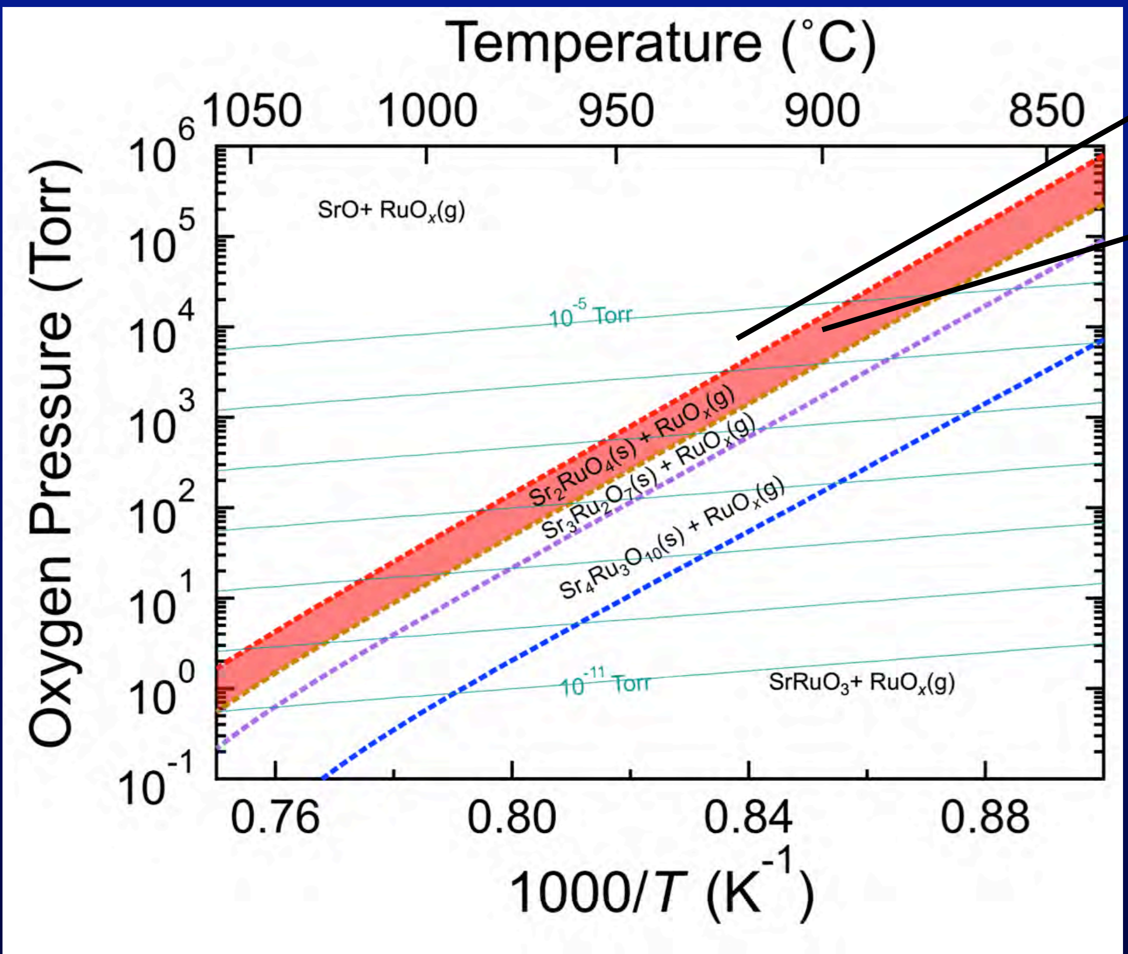


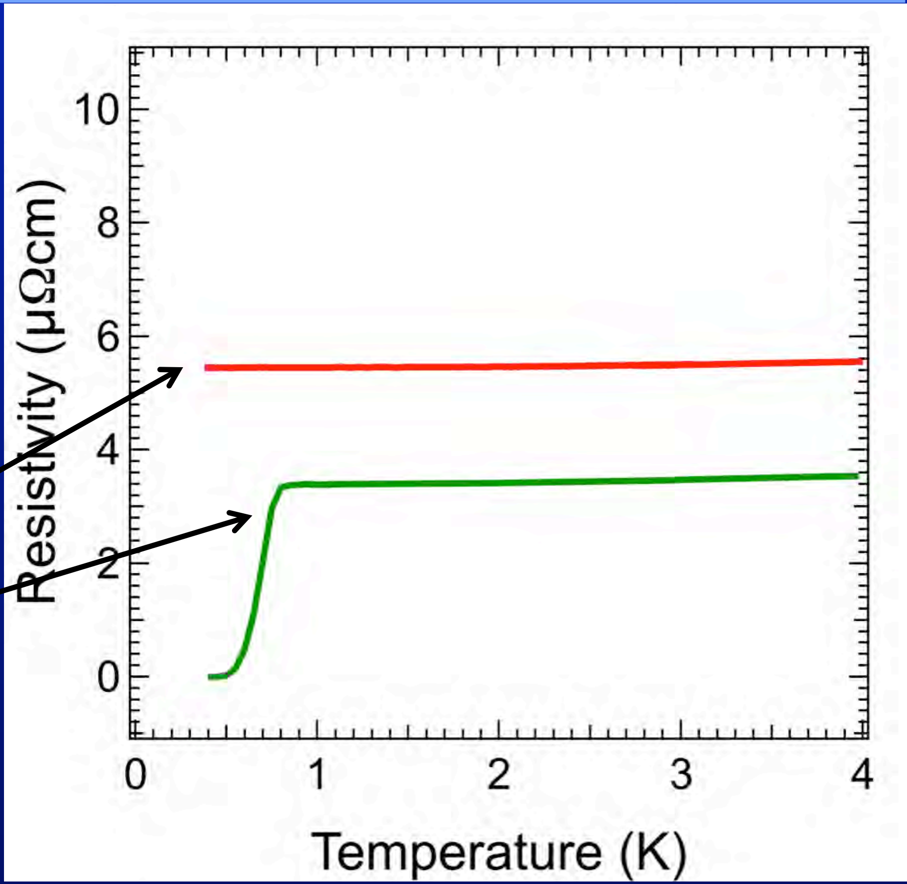




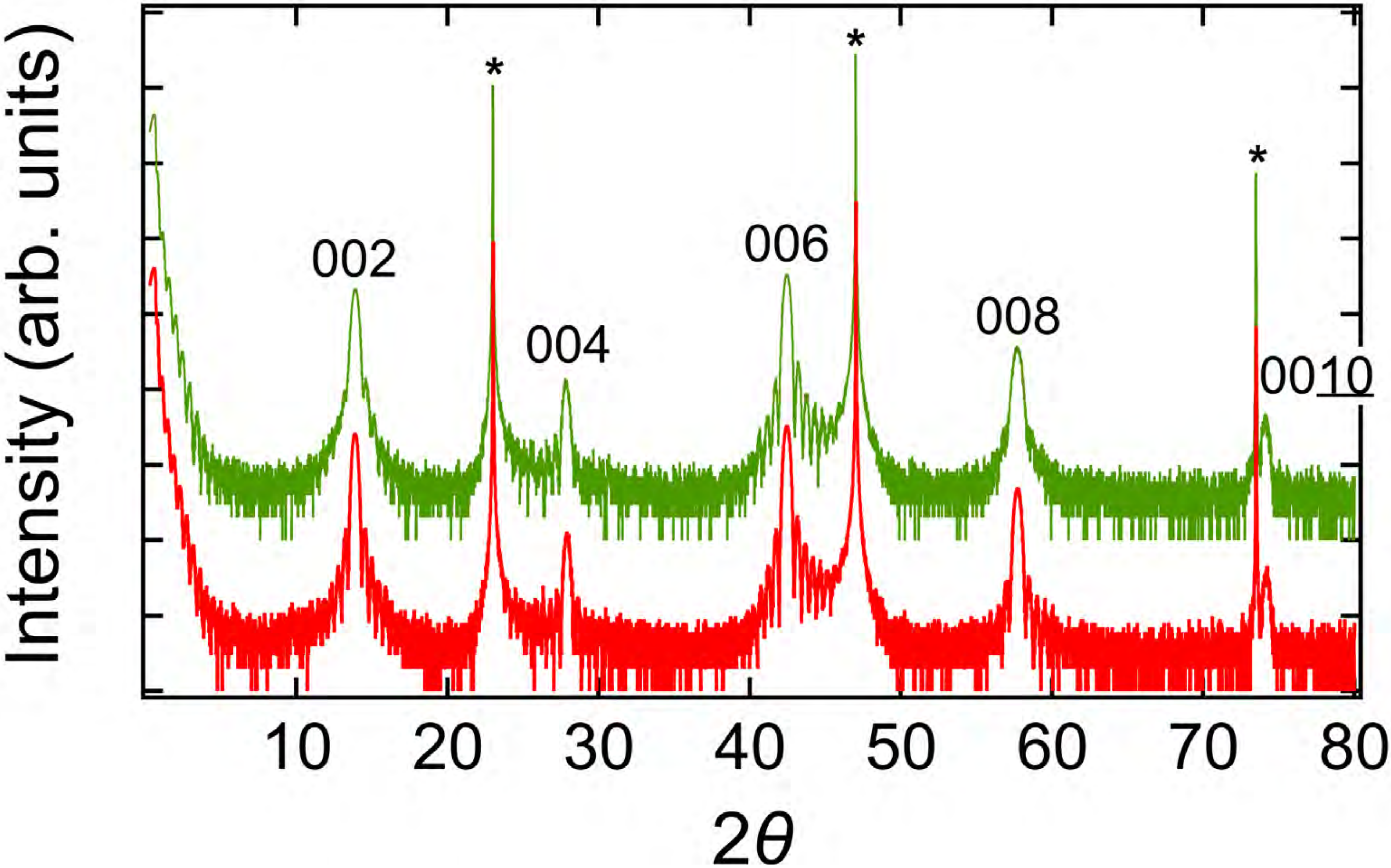
Which Sample Superconducts?

but only one of them superconducts!

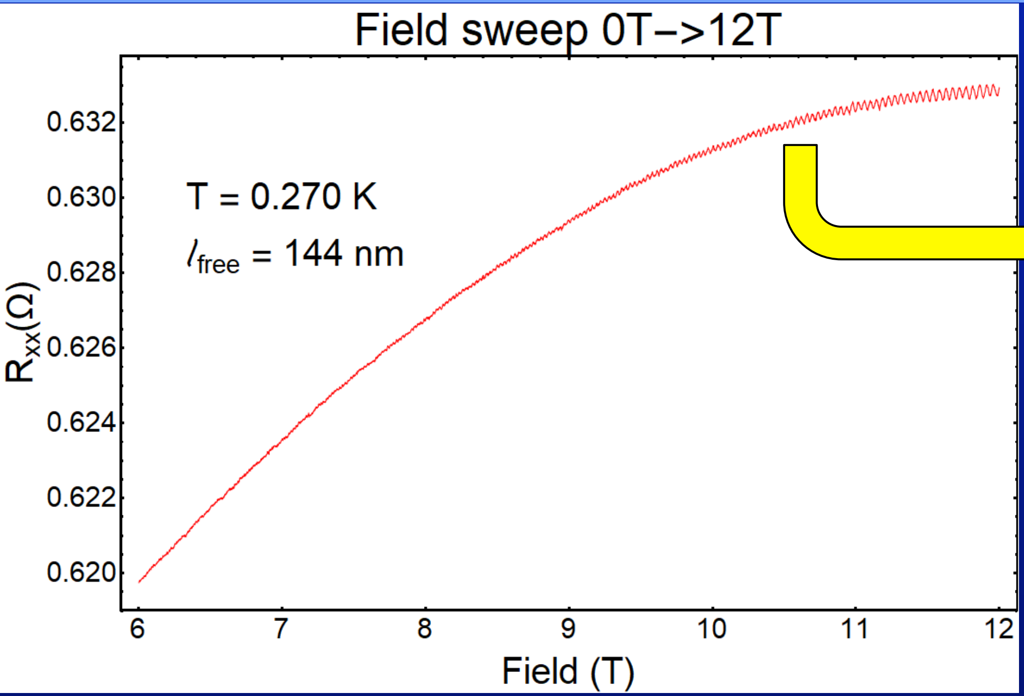


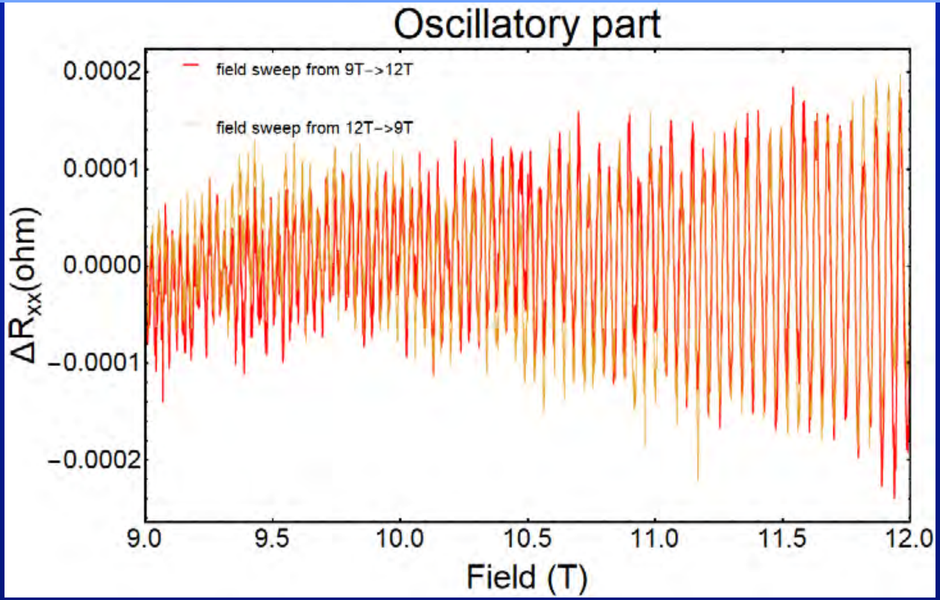


Are Ru Vacancies Responsible?



Superconducting Sr_2RuO_4 Films



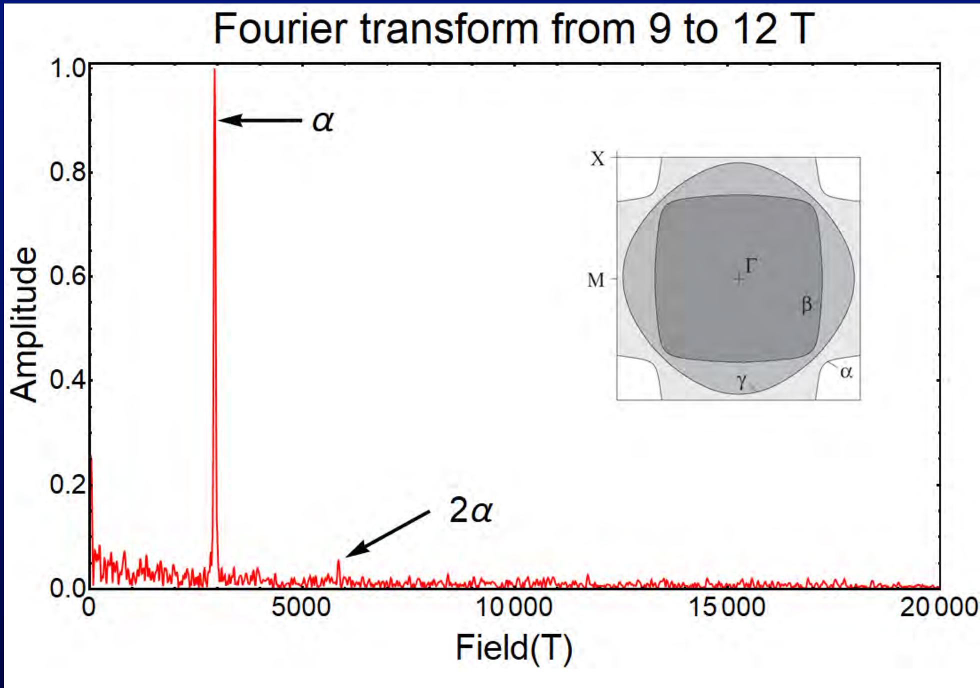


λ_{mfp} of film = 144 nm

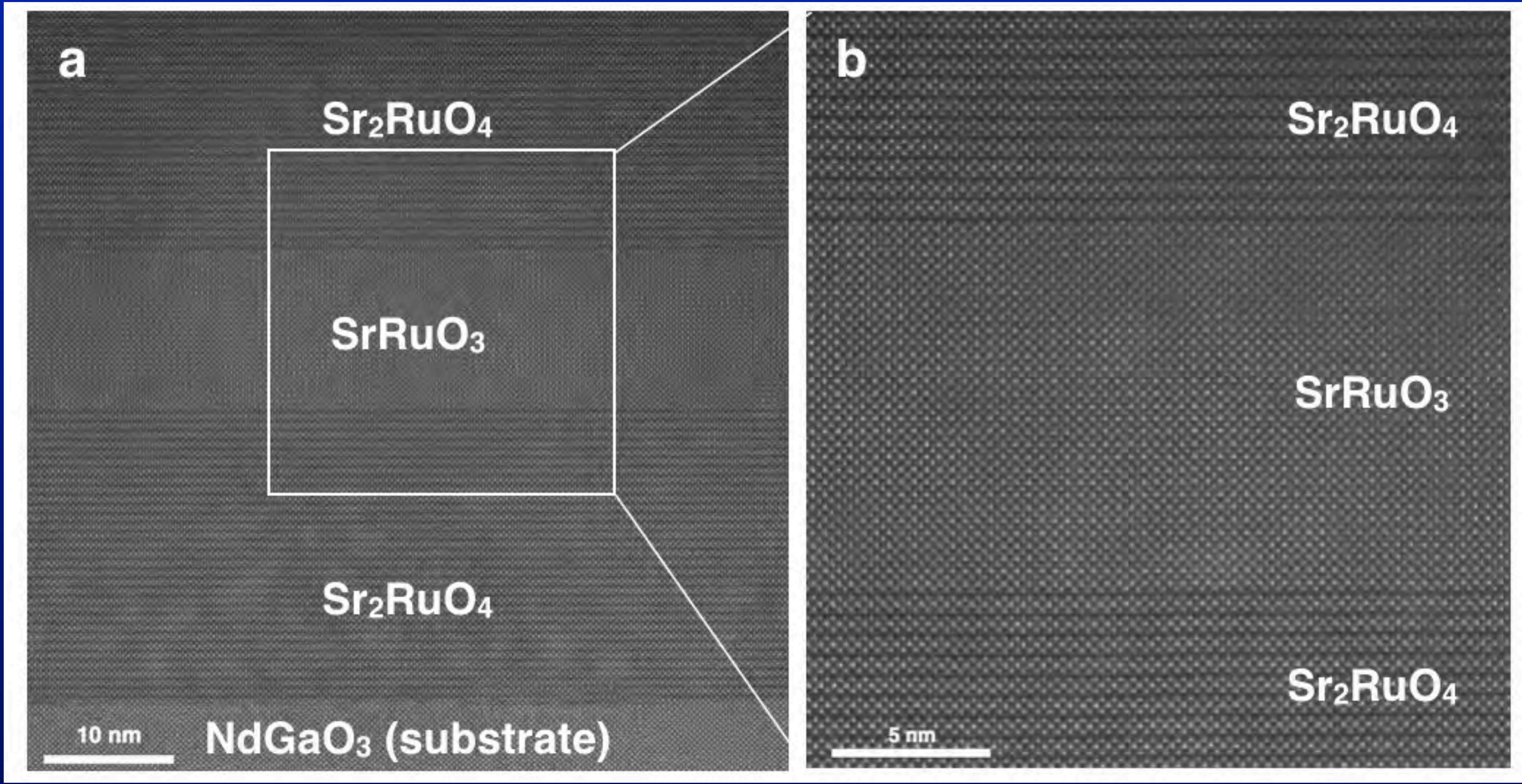
Brad J. Ramshaw (unpublished)

λ_{mfp} of single crystals
120–500 nm
for crystals with T_c 1.3–1.45 K

C. Bergemann, A.P. MacKenzie, S.R. Julian, D. Forsythe, and E. Ohmichi, *Adv. Phys.* **52** (2003) 639–725.



Triplet-Ferromagnet-Triplet



Sharp interfaces—no sign of interdiffusion

Potential to study triplet SC/FM/triplet SC physics

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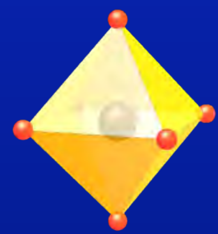
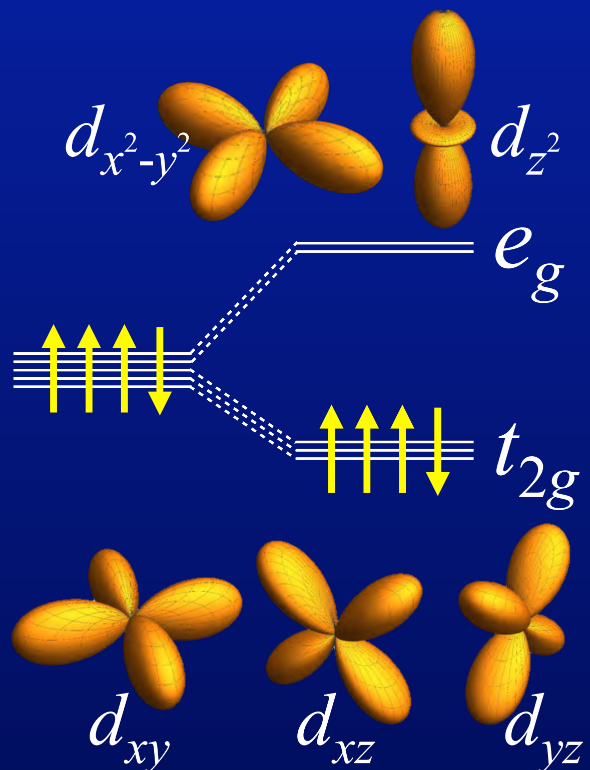
STEM: Berit Goodge and Prof. Lena Kourkoutis (Cornell U.)

Growth of $CaRuO_3$ and Ca_2RuO_4?

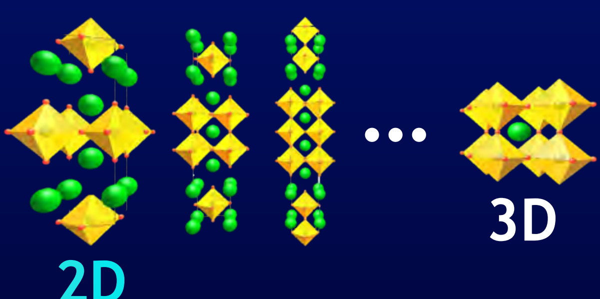
Ru^{4+} : $4d^4$



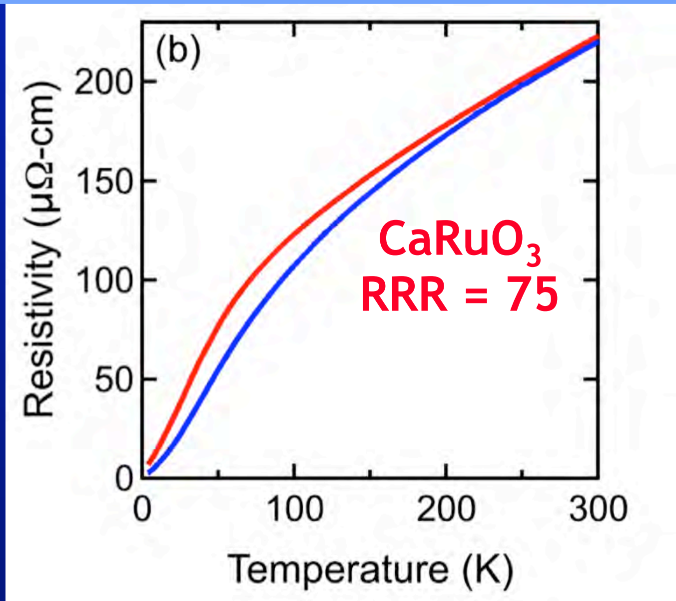
Ruthenates exhibit large changes in properties with rather minor changes in structure



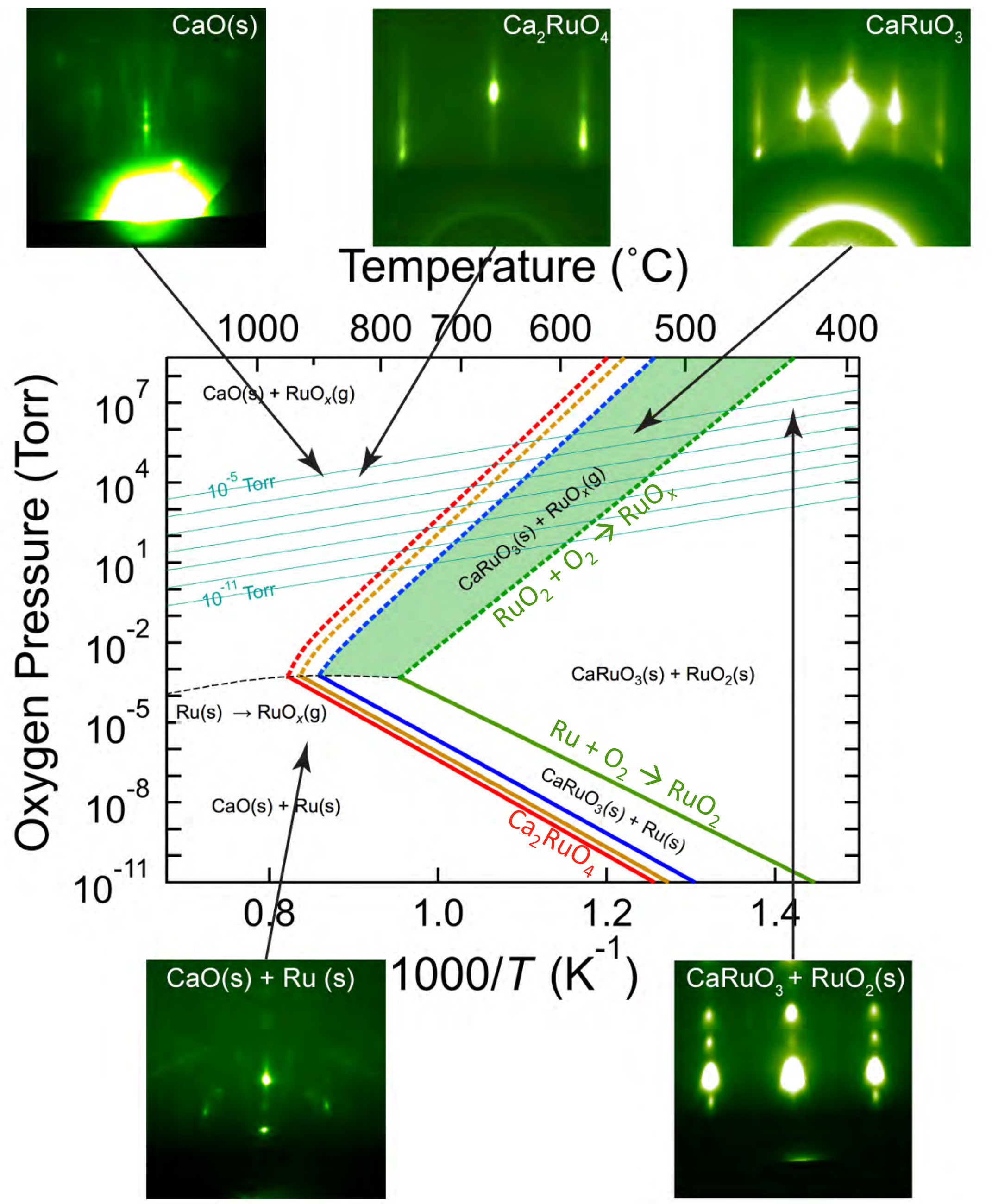
Compound	Dimensionality	Cation	Ground State
$CaRuO_3$	3D	Ca^{2+}	Paramagnetic non-Fermi liquid metal?
Ca_2RuO_4	2D	Ca^{2+}	antiferromagnetic Mott insulator
$SrRuO_3$	3D	Sr^{2+}	ferromagnetic metal
Sr_2RuO_4	2D	Sr^{2+}	odd-parity superconductor
$BaRuO_3$	3D	Ba^{2+}	ferromagnetic metal
Ba_2RuO_4	2D	Ba^{2+}	paramagnetic metal?



Thermo of $Ca_{n+1}Ru_nO_{3n+1}$ by MBE



H.P. Nair, Y. Liu, J.P. Ruf, N.J. Schreiber, S-L. Shang, D.J. Baek, B.H. Goodge, L.F. Kourkoutis, Z.K. Liu, K.M. Shen, and D.G. Schlom,
"Synthesis Science of $SrRuO_3$ and $CaRuO_3$ Epitaxial Films with High Residual Resistivity Ratios,"
APL Materials **6** (2018) 046101.



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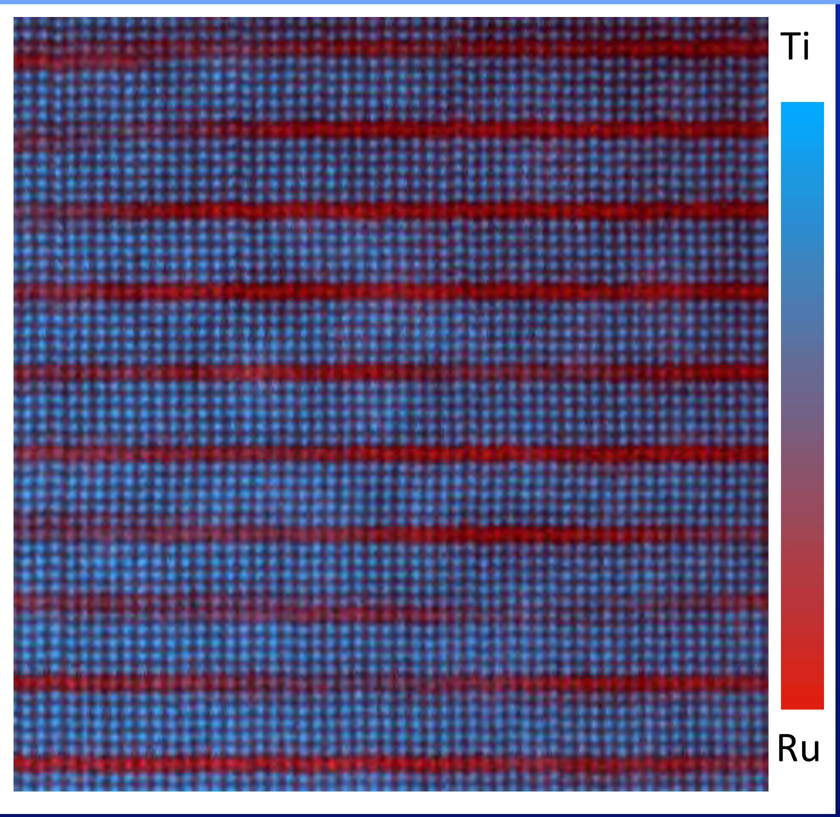
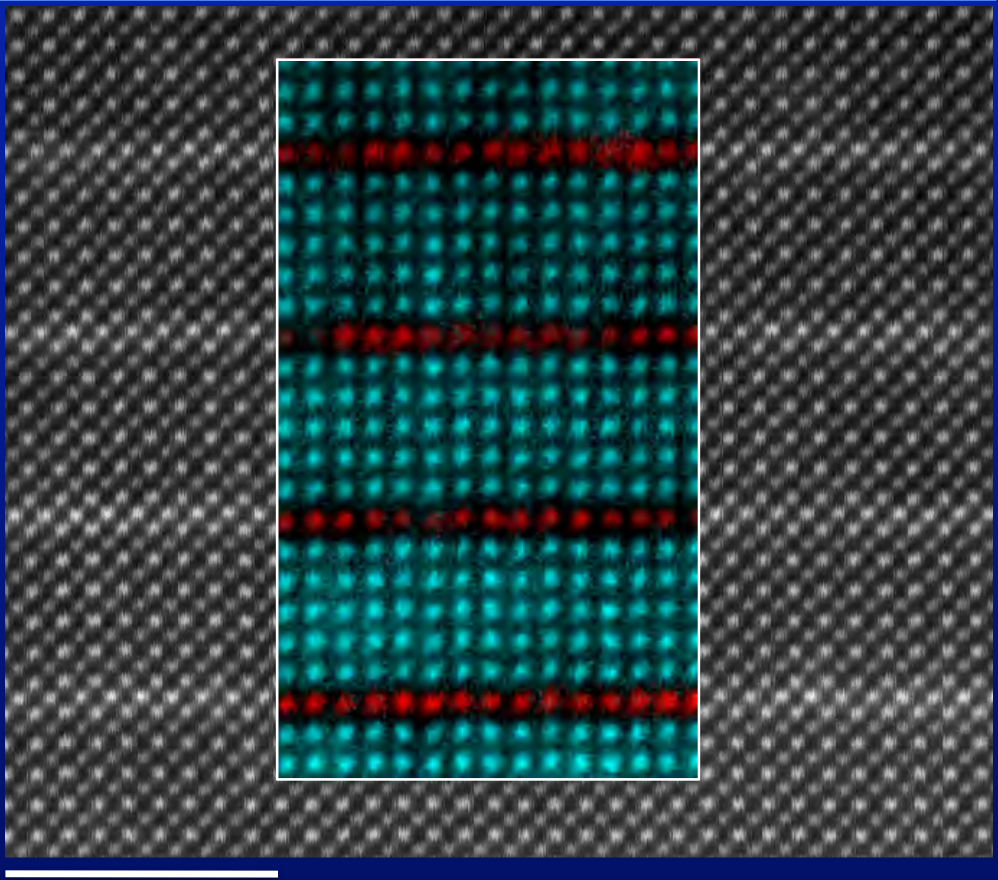
1 ML $SrRuO_3$ in $SrRuO_3/SrTiO_3$ SL





Red = Ru **Teal = Ti**

1 ML $SrRuO_3$ (sandwiched between $SrTiO_3$) is **conductive** and **ferromagnetic**

H. Boschker, T. Harada, T. Asaba, R. Ashoori, A.V. Boris, H. Hilgenkamp, C.R. Hughes, M.E. Holtz, L. Li, D.A. Muller, H. Nair, P. Reith, X.R. Wang, D.G. Schlom, A. Soukiassian, J. Mannhart, *Physical Review X* **9** (2019) 011027.

PARADIM

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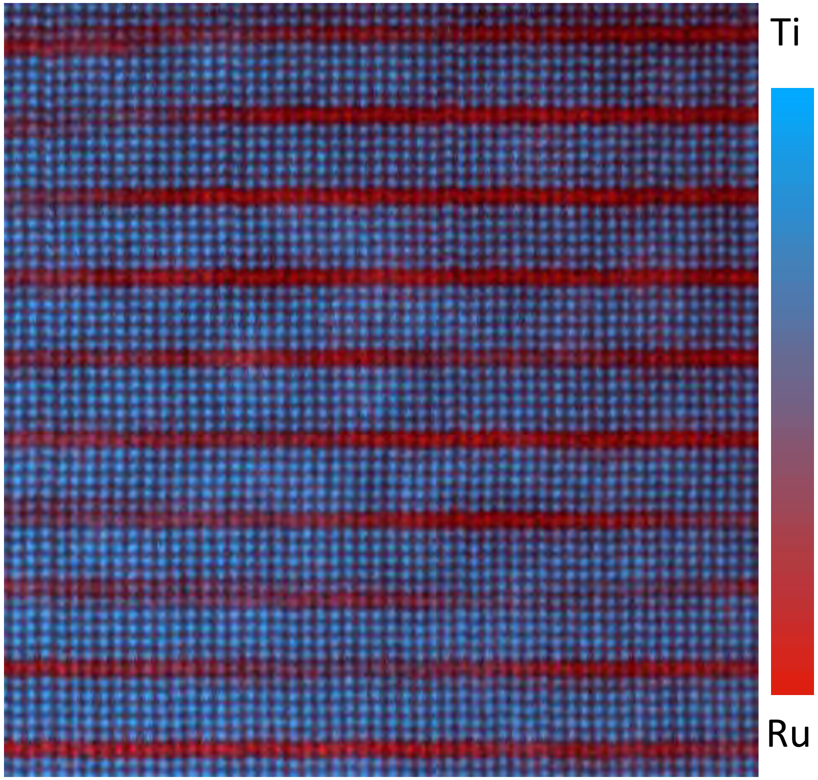

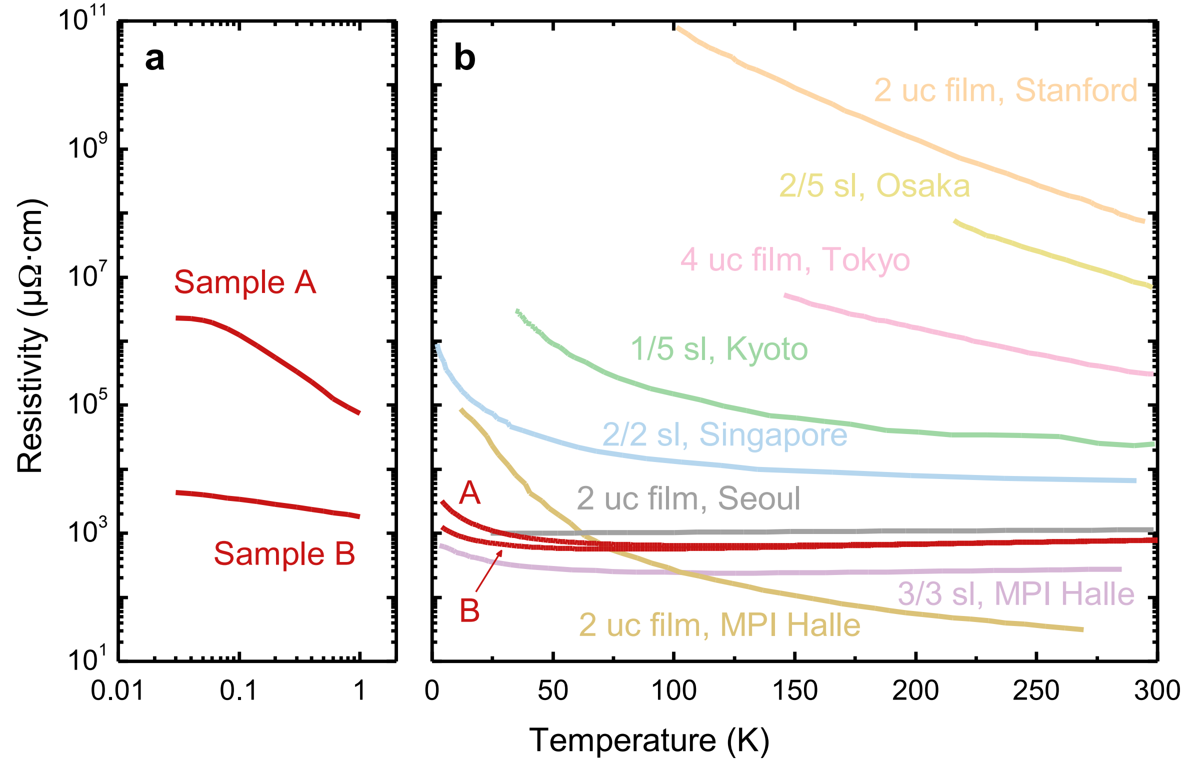

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Conclusions

Adsorption-Controlled growth conditions work well for films of $CaRuO_3$, $SrRuO_3$, Ca_2RuO_4, Sr_2RuO_4

- Highest RRR of all reported films
- RRR of $CaRuO_3$ and $SrRuO_3$ greater than best single crystals
- Highest T_c of all reported Sr_2RuO_4 films and reproducible
- Able to prepare Sr_2RuO_4 / $SrRuO_3$ / Sr_2RuO_4 heterostructures

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