

Atomic-layer engineering of high- T_c superconductors

Ivan Božović

Brookhaven National Laboratory, Upton NY 11973 USA

Collaborators:

G. Logvenov, V. Butko, A. Gozar, A. Bollinger, O. Pelleg, R. Pindak, H. Zhou (BNL),
N. Božović (SJSU), Z. Radović (Belgrade), P. Abbamonte and S. Smadici (UIUC),
L. Kourkoutis-Fitting and D. Muller (Cornell), Y. Yacobi (Hebrew U. Israel), N.
Gedik (MIT), A. Zewail (Caltech)

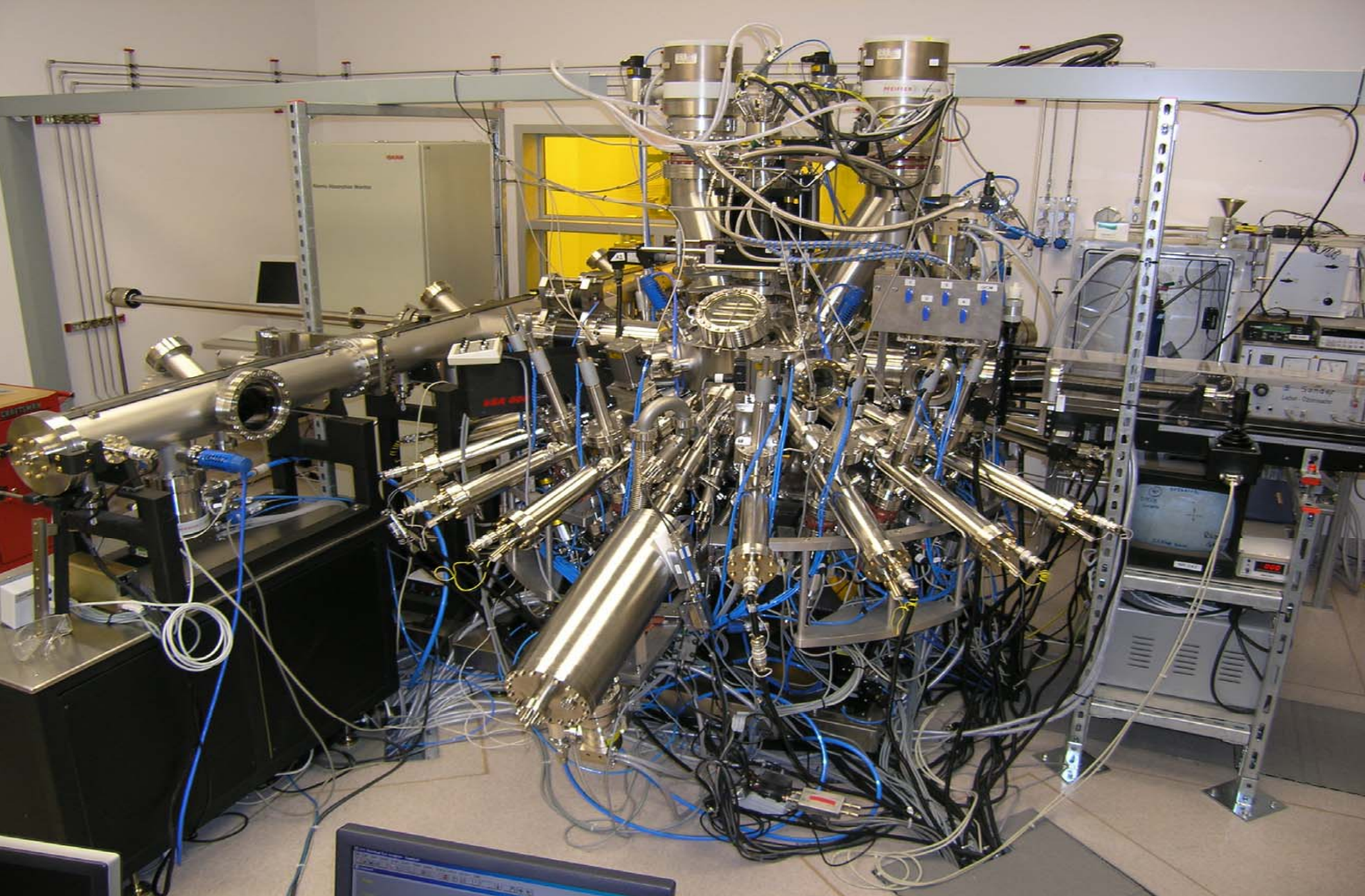
Q: Which of these is possible?

- **One-atom-thick HTS**
- **Non-zero E in superconductor**
- **Broken inversion symmetry**
- **Triplet superconductivity**
- **Quantum spin liquid**
- **Homogeneous cuprate**
- **Levitating ions**

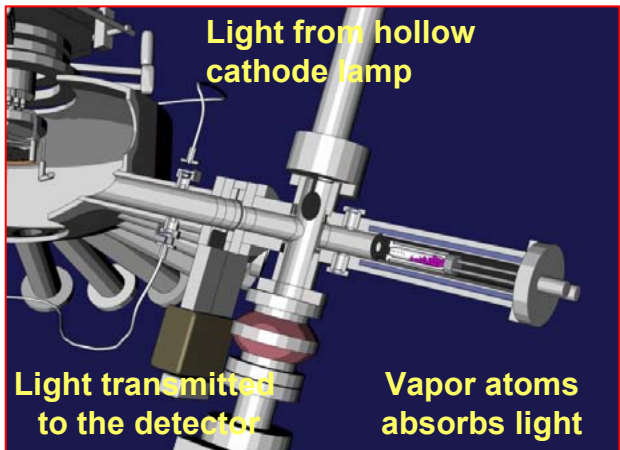
Technique: atomic-layer MBE

Cf. the talks by J. Eckstein, S. Stemmer

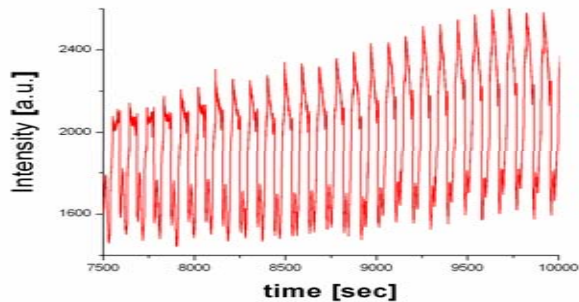
ALL-MBE SYSTEM AT BNL



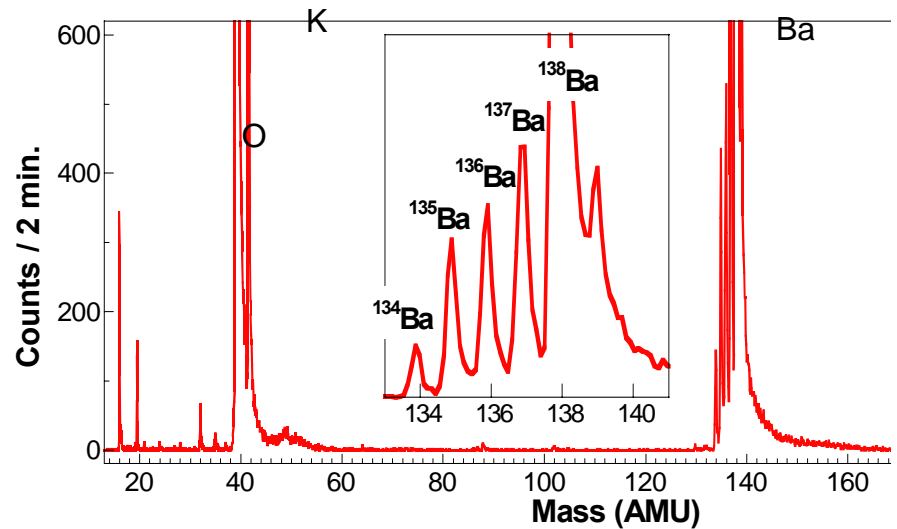
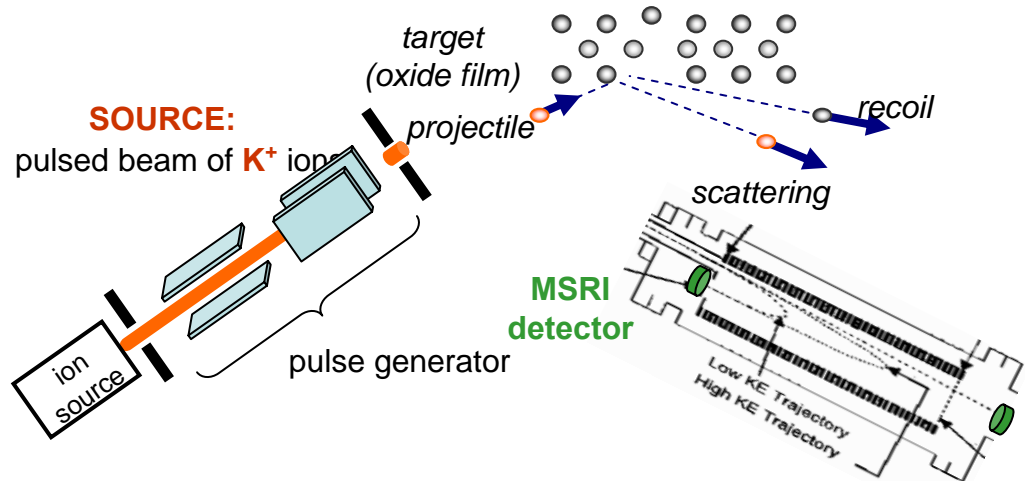
Atomic Absorption Spectroscopy



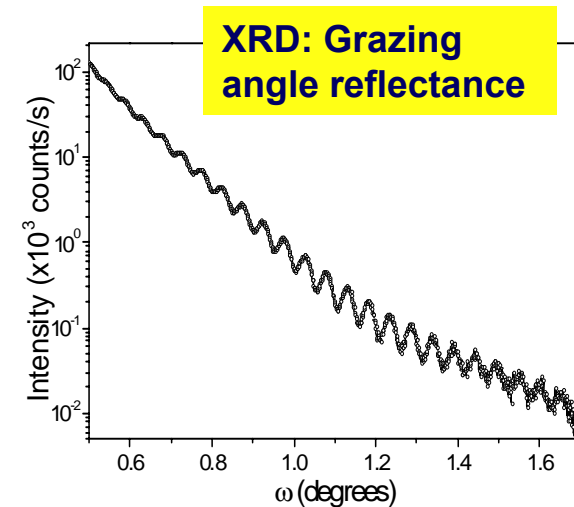
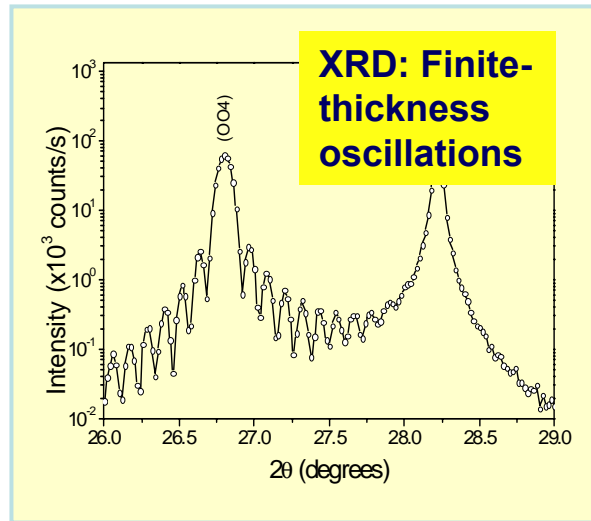
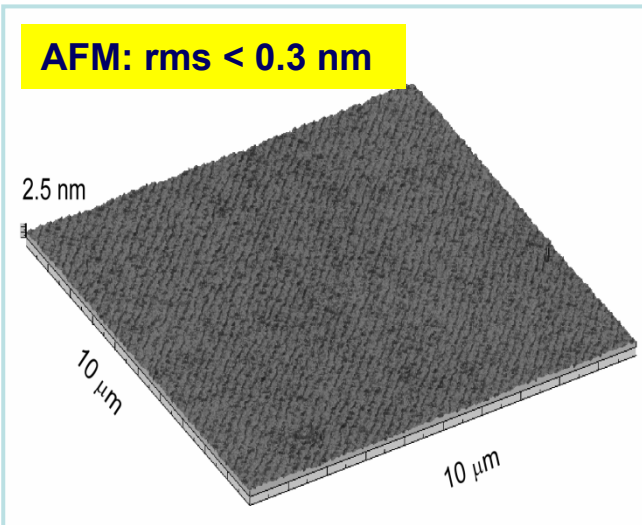
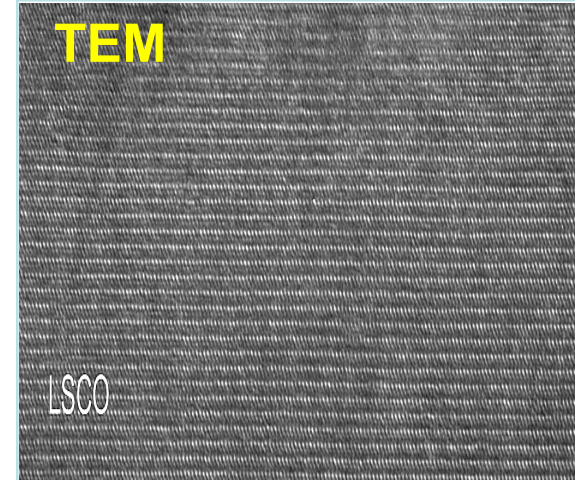
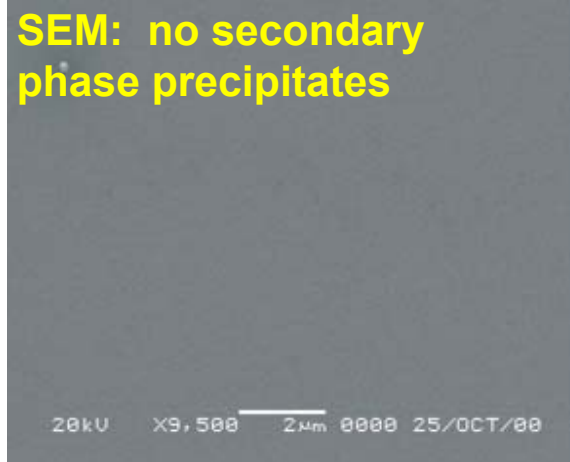
RHEED



TOF-ISARS



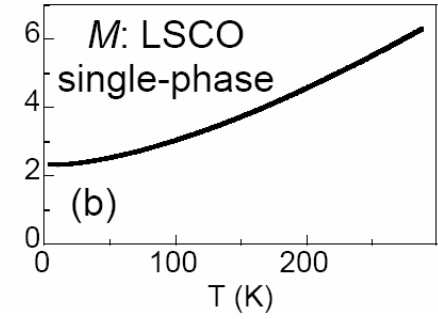
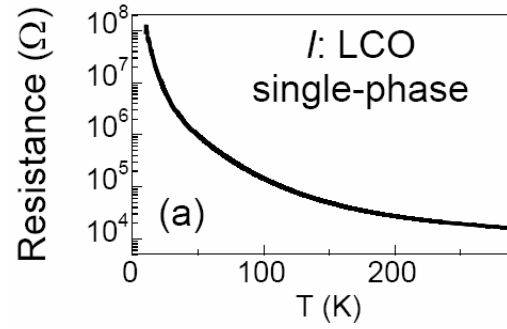
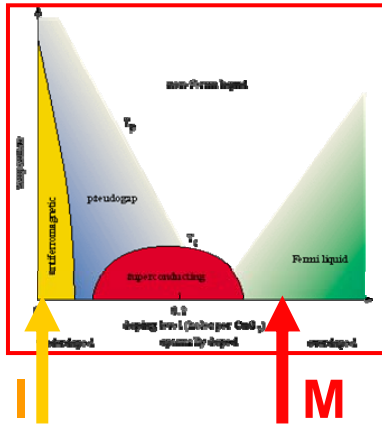
ATOMICALLY SMOOTH CUPRATE FILMS GROWN BY MBE



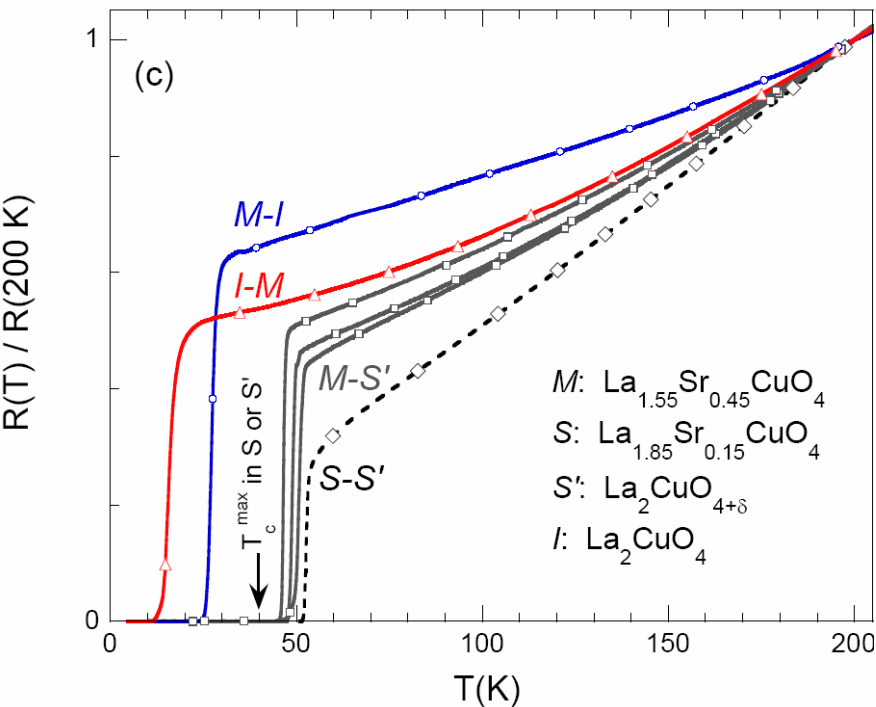
HTS in a single CuO_2 layer

Related talks: J. Mannhart, P. Abbamonte, S. Okamoto, H. Hwang,...

INTERFACE SUPERCONDUCTIVITY IN CUPRATES



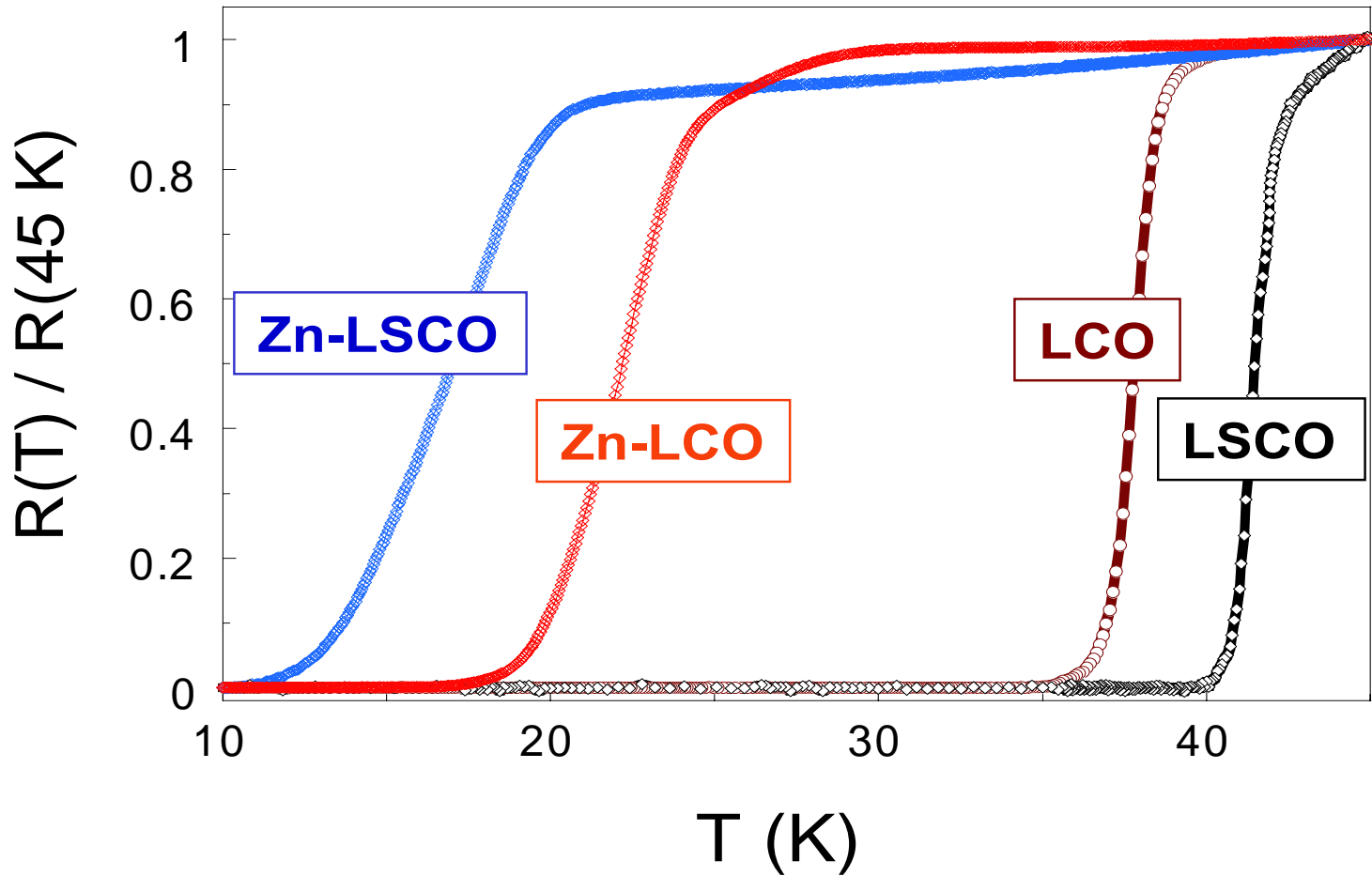
$R(T)$ for single-phase layers of *I* and *M*.



$R(T)$ for various bilayers.

I-M and *M-I* bilayers show superconductivity even though neither of the two constituents does.

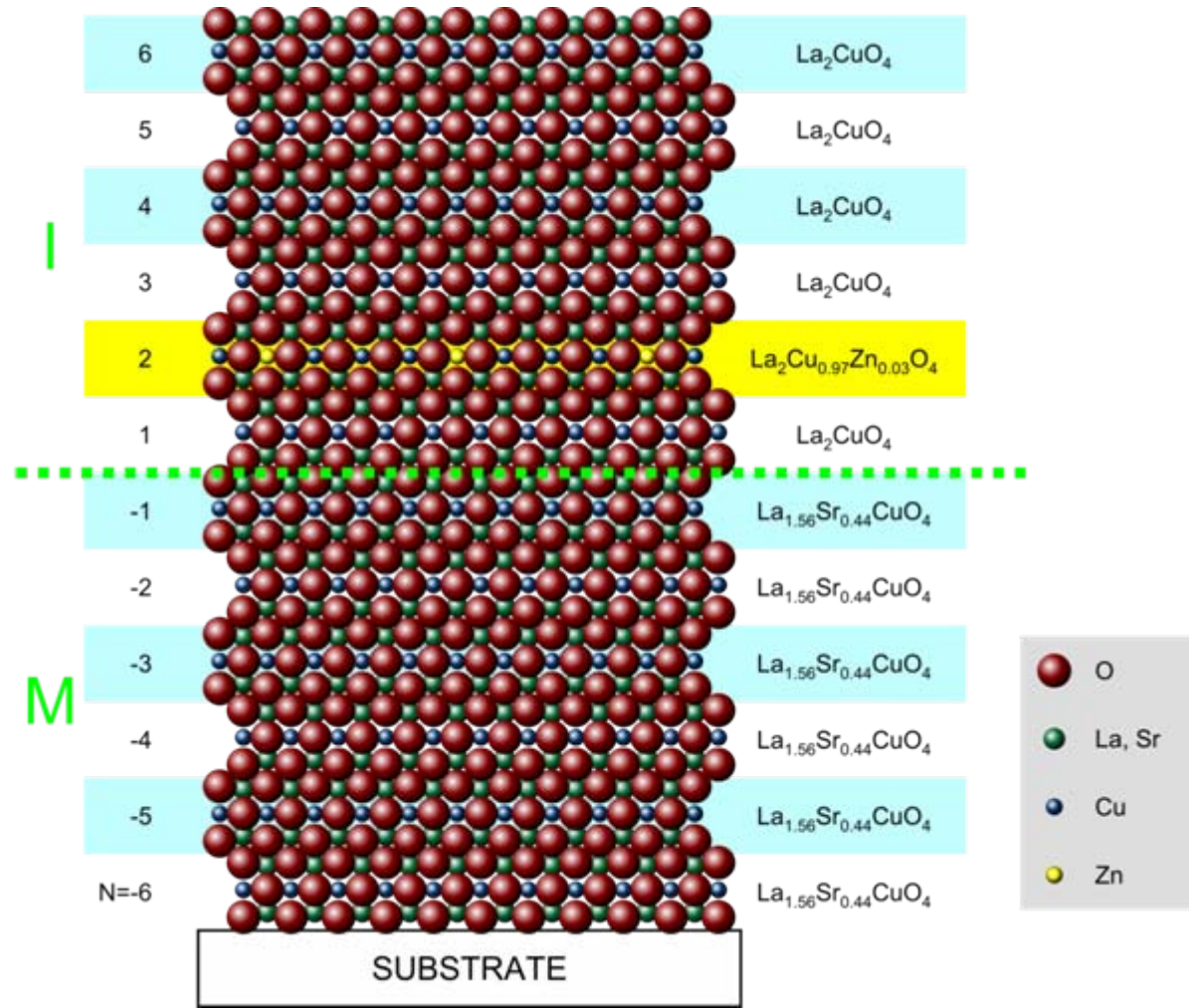
In single-phase *S* or *S'* films grown under the same conditions $T_c \leq 40$ K.



**(Isovalent) substitution of 3% Cu by Zn
causes pair breaking and reduces T_c**

δ -doping by Zn

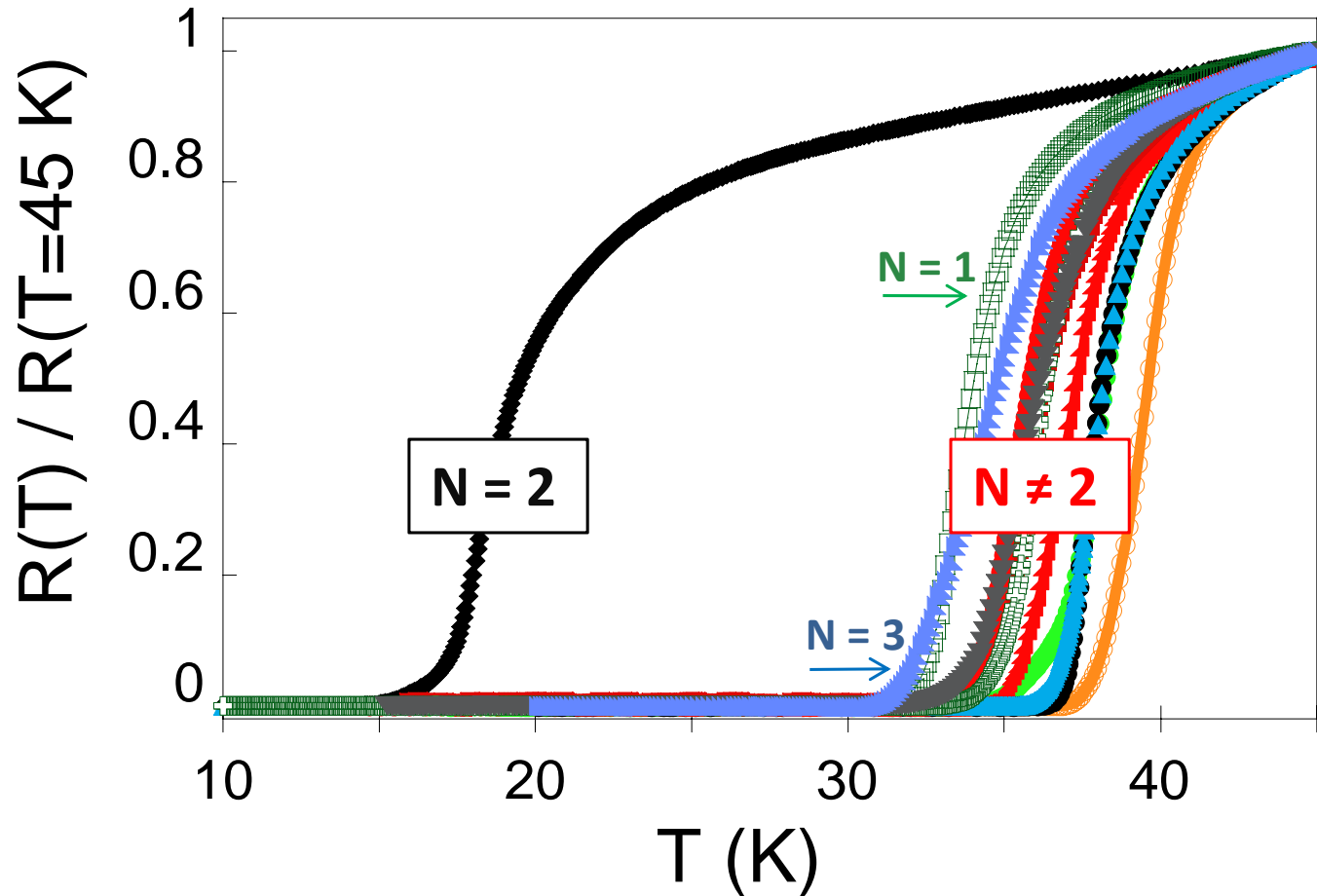
By virtue of digital (atomic-layer-by-layer) synthesis, it is possible to dope selectively at specific atomic sites, e.g., within a single CuO_2 plane.



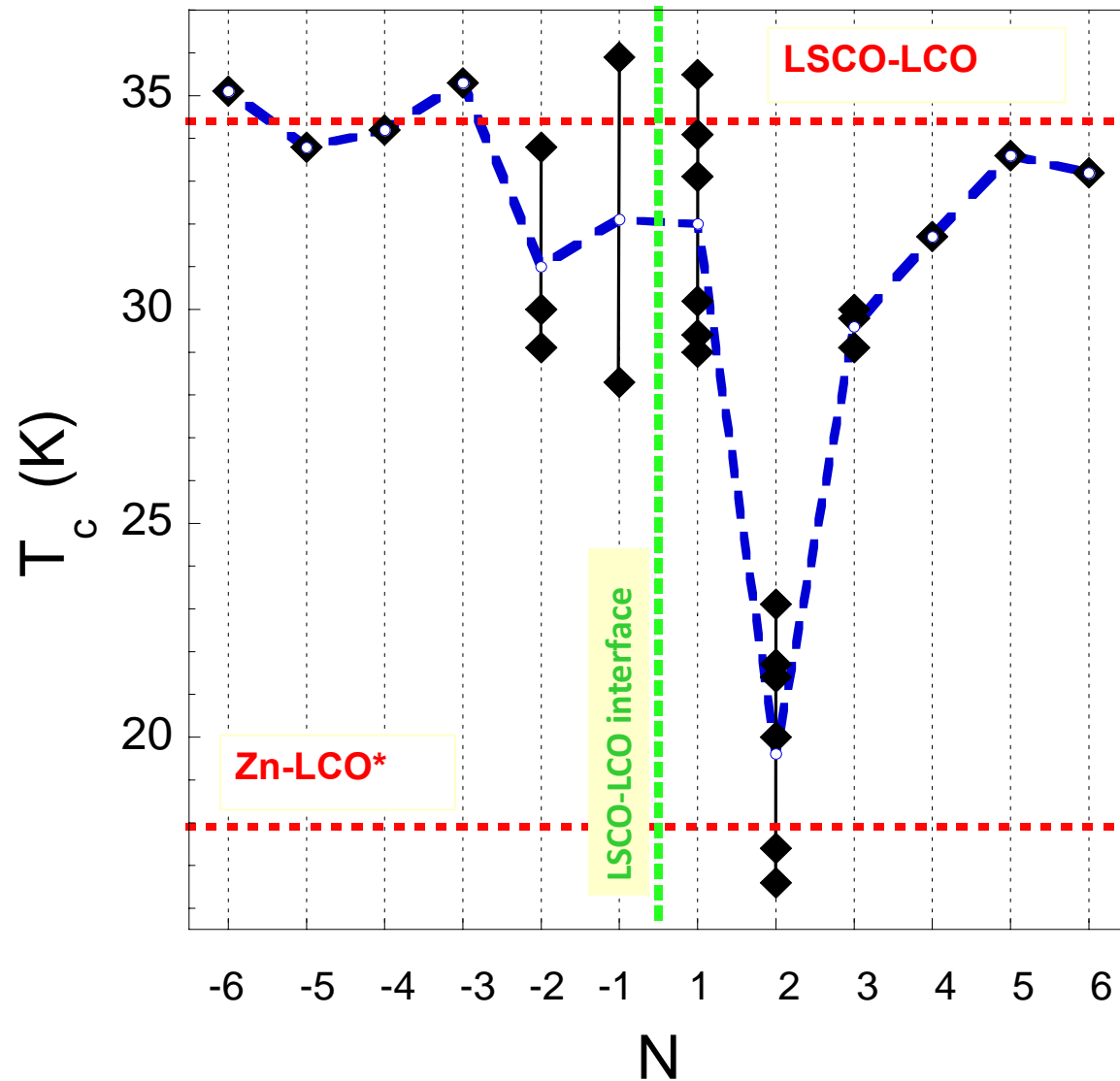
Science 326, 699 (2009)

Varying the selected CuO_2 plane: Zn δ -doping “tomography”

δ -doping tomography of M-I bilayers

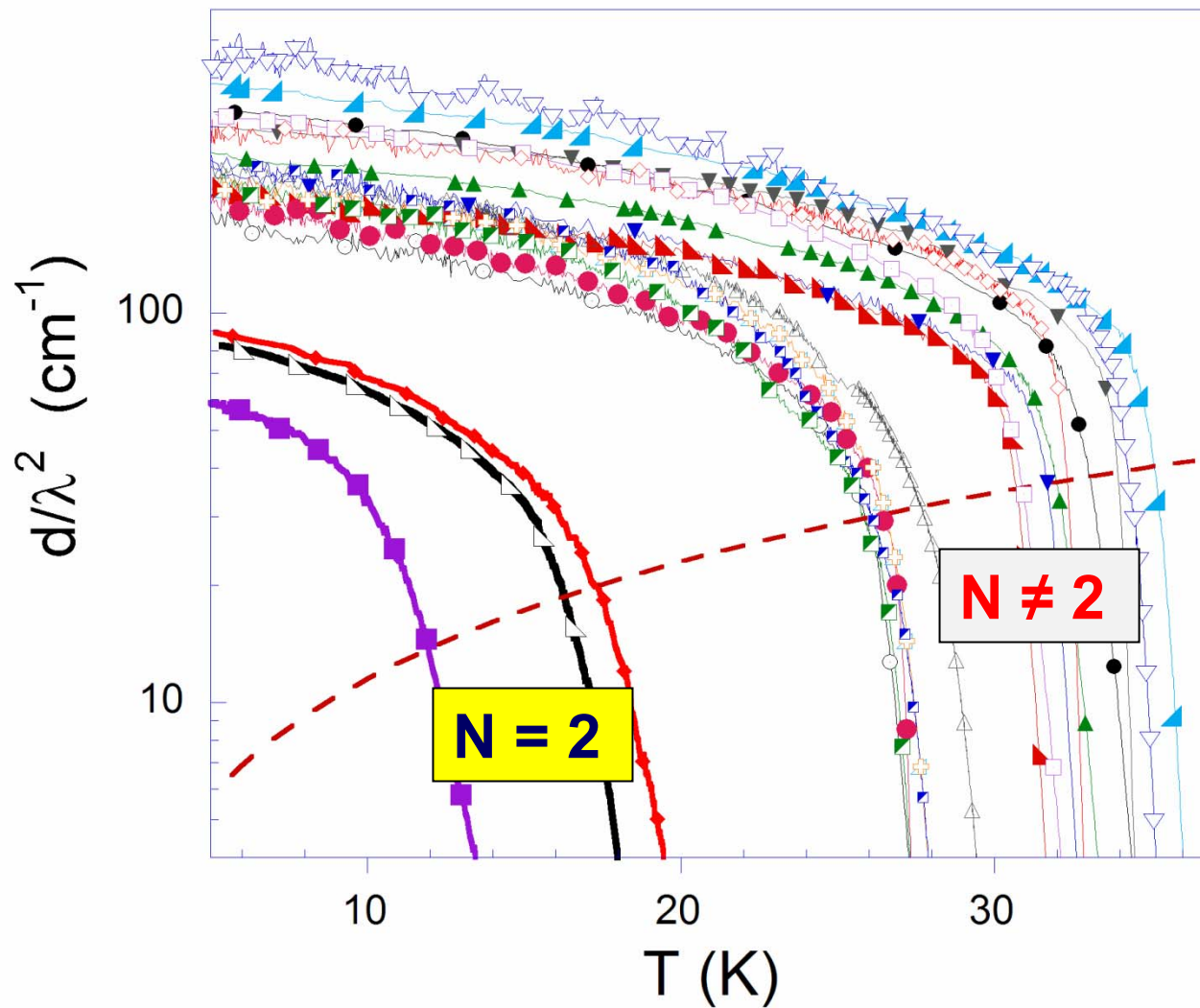


Only Zn doping in the second CuO_2 layer affects T_c !

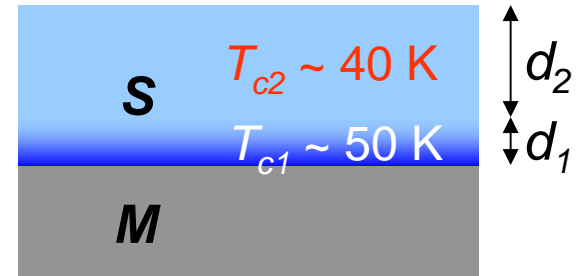
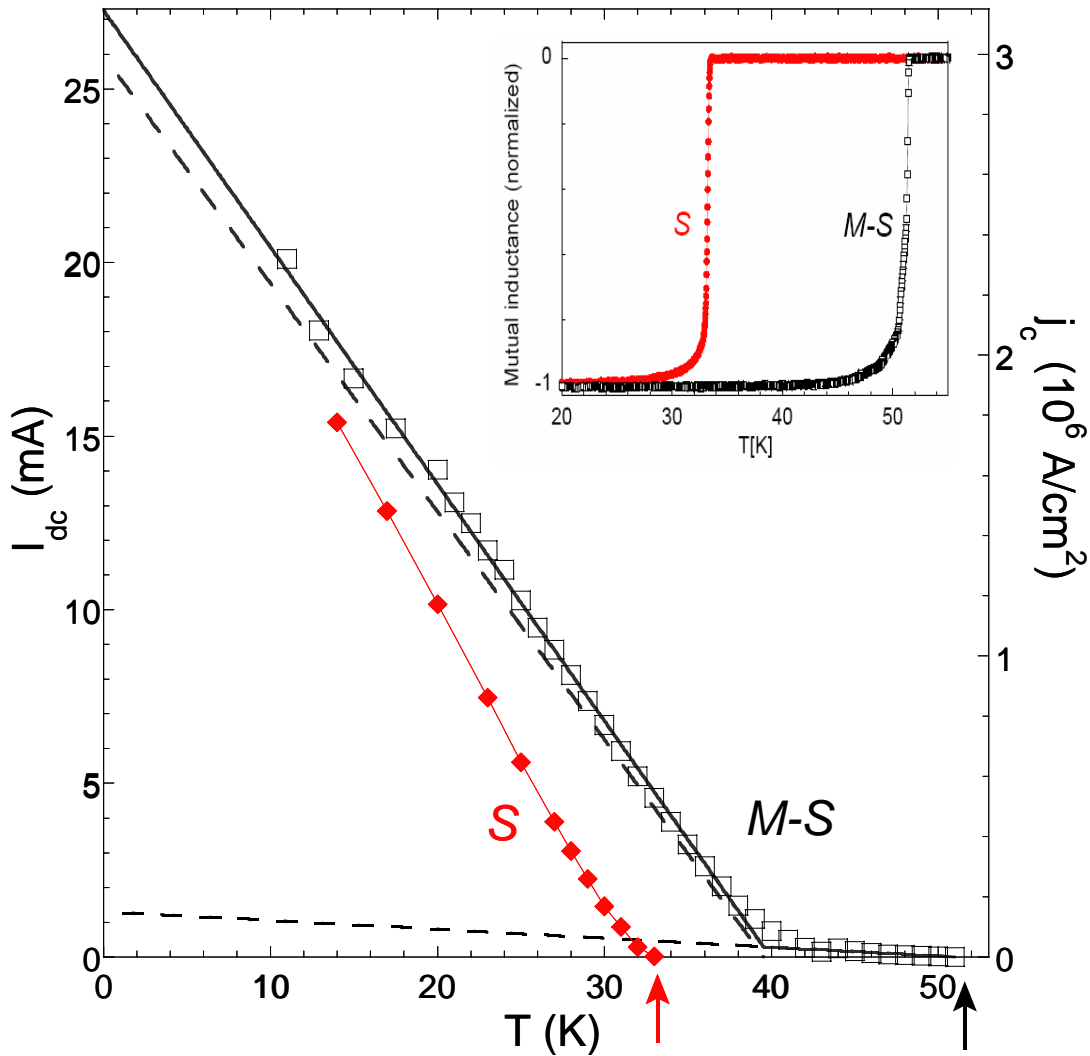


HTS with $T_c = 36$ K is confined to a single CuO_2 plane!

Magnetic measurements also show HTS in N=2 layer



INTERFACE-ENHANCED SUPERCONDUCTIVITY



$d_1 \sim 1\text{-}2 \text{ UC}$ ($\sim 2 \text{ nm}$)



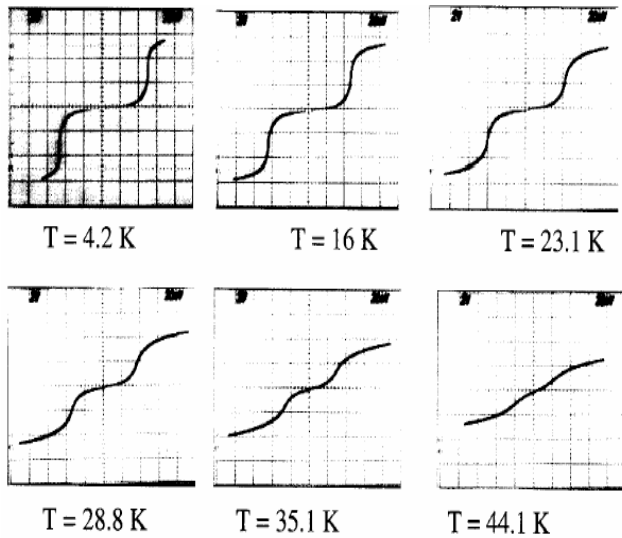
the 25% enhancement in T_c is an interface effect

[Nature 455, 782 (2008)]

Can HTS cuprates be homogeneous?

Related talks: J. C. Davis, D. Basov, S. Okamoto, L. Teillefer,...

ARTIFICIAL HTS SIS TUNNEL JUNCTION



Vertical scale: 20 mA/div; horizontal scale: 20 mV/div

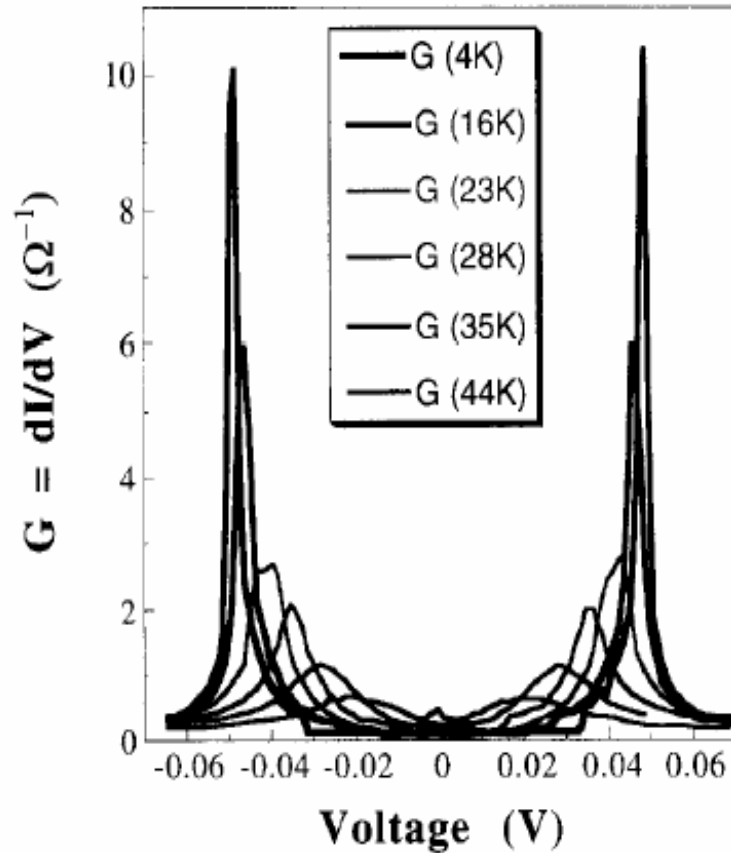
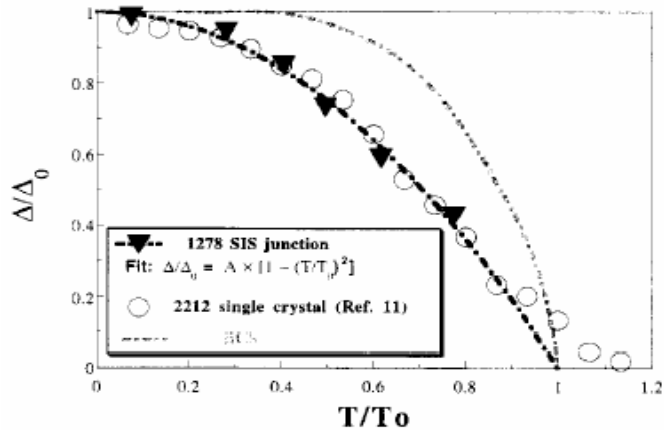
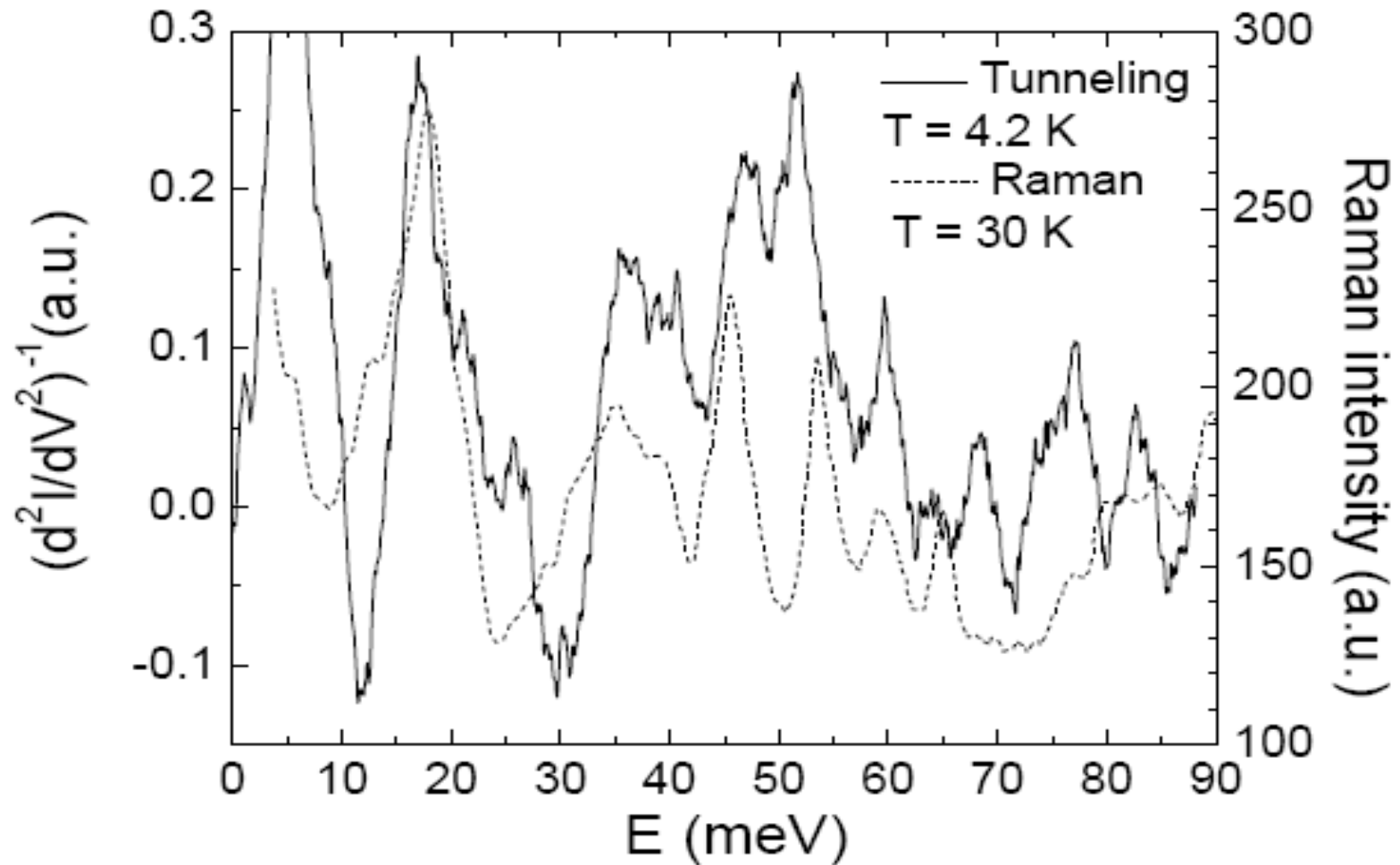


Fig. 5. Differential conductance ($G = dI/dV$) as a function of voltage, at different temperatures, for an intra-cell junction based on Dy-doped Bi-1278.

JAC 251, 201 (1997).

Sharp gap in $>1,000 \mu\text{m}^2$ device!

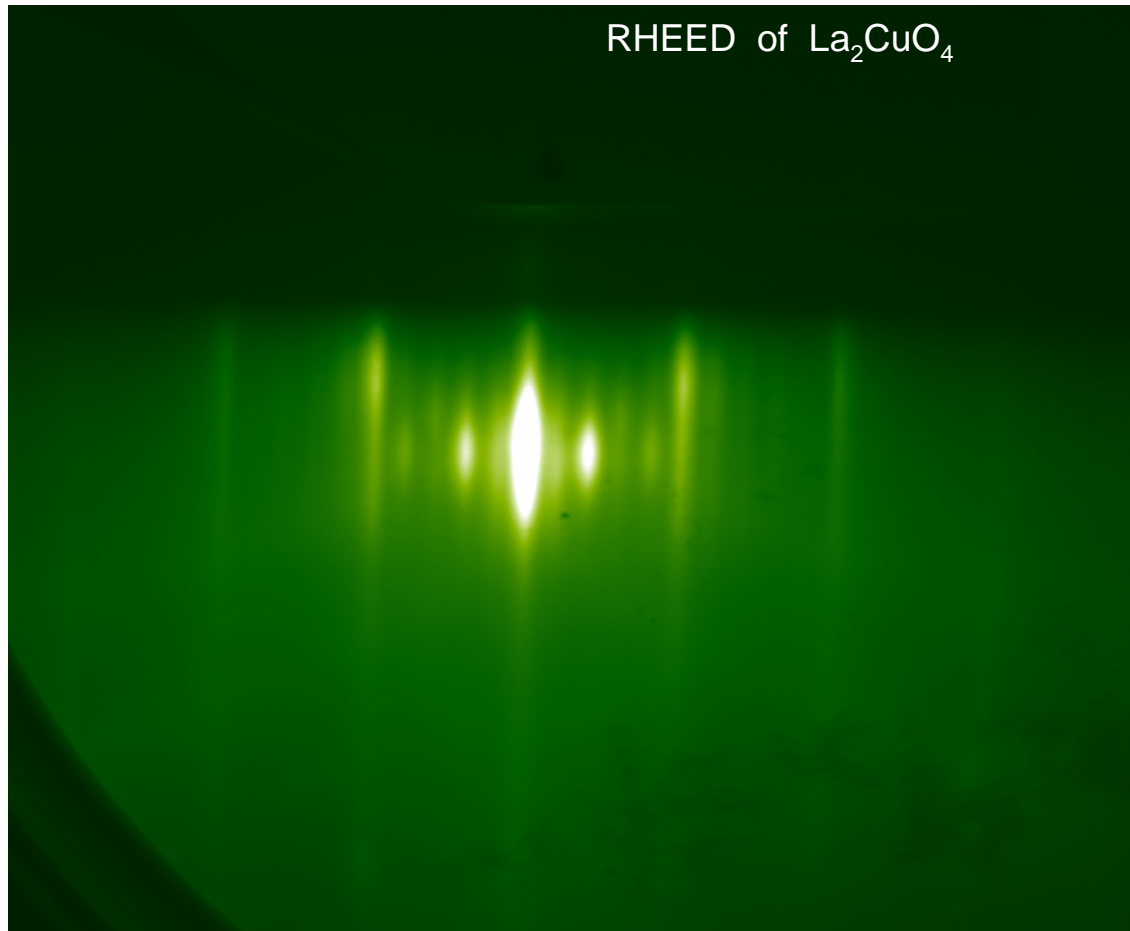
Tunneling data for SIS junction (LSCO grown on SrTiO₃ bicrystal)



Tunneling: Shim et al., PRL 2008

Raman: Sugai et al., SSC 1990

Surface \neq bulk

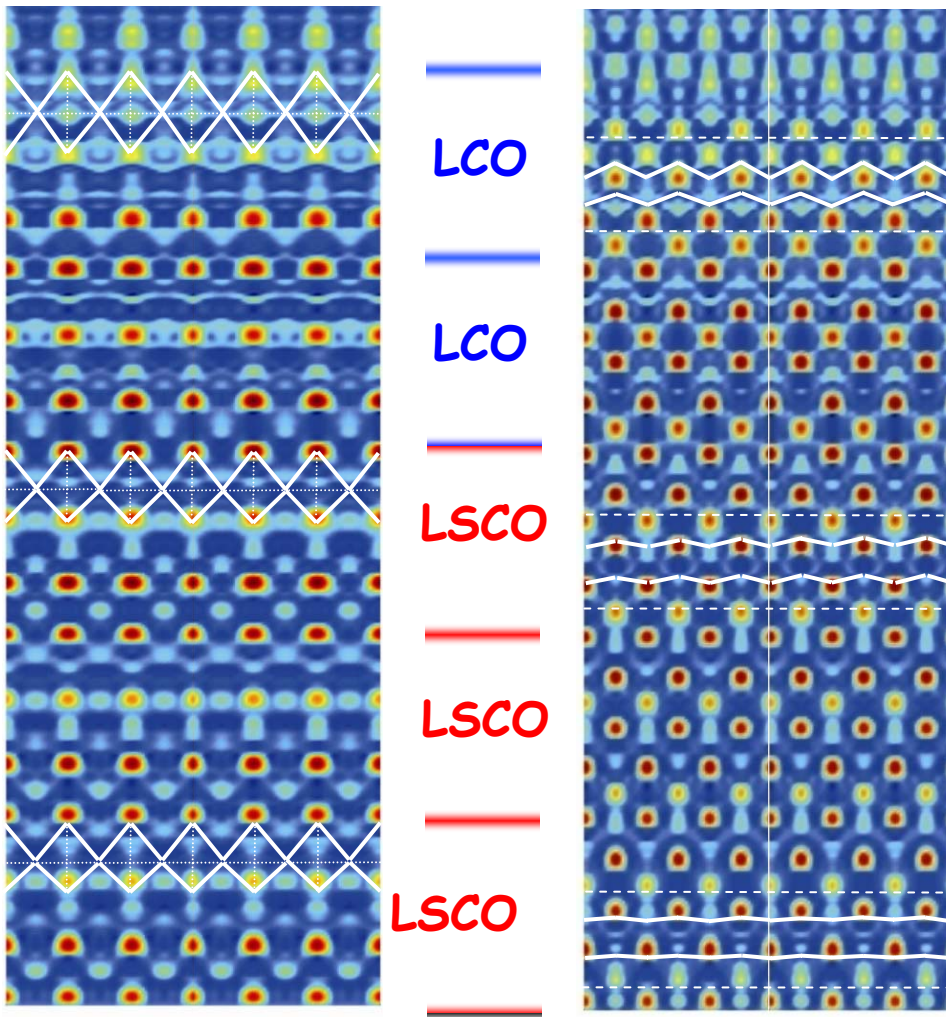


Surface reconstruction is expected to occur in ionic crystals!

NEAR THE SURFACE, APICAL OXYGEN SHIFTS BY 0.45 Å!

(100)

(110)



LSAO Substrate

Cross-sections through the **measured** 3D electron density map.

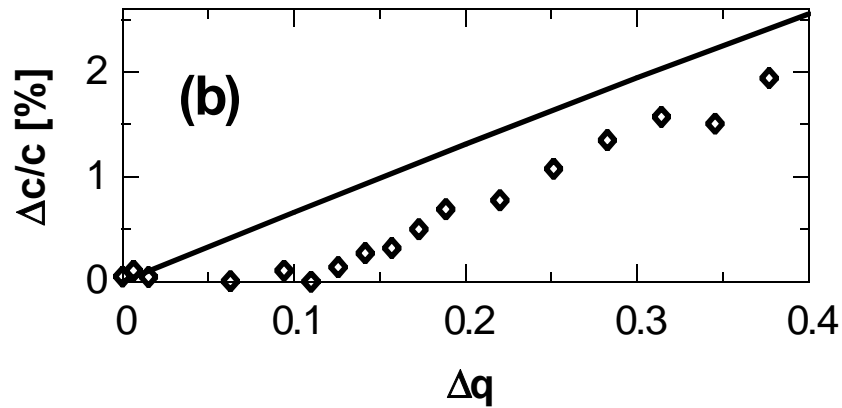
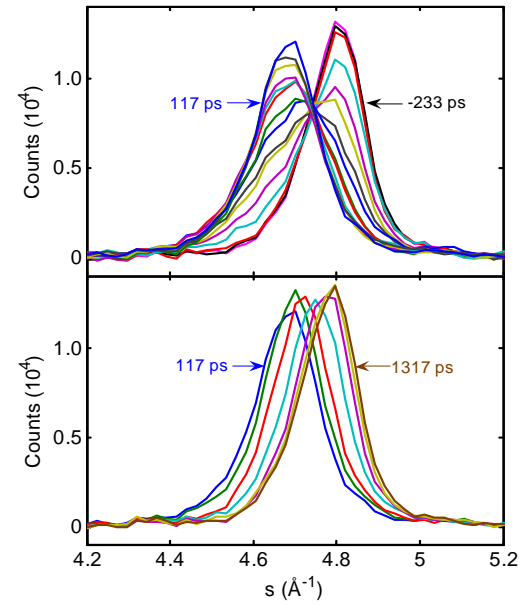
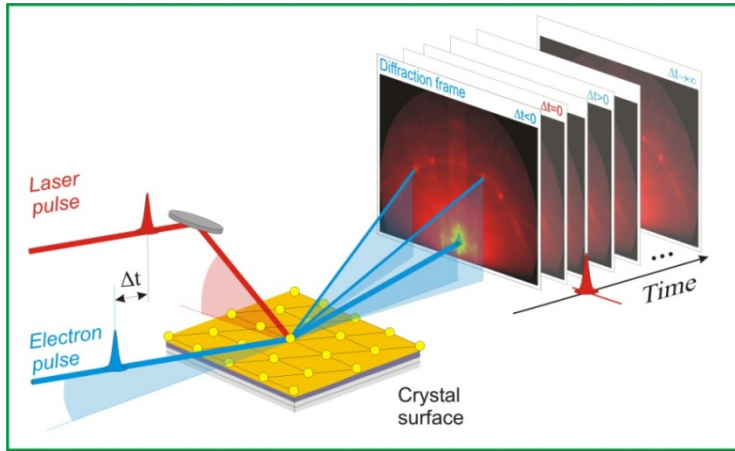
Left: atomic positions in the (100) plane. The CuO octahedra, outlined by the white lines, are significantly elongated near the surface.

Right: atomic positions in the (110) plane. The corrugation of La(Sr)-apical O planes, outlined by white lines, increases toward the surface.

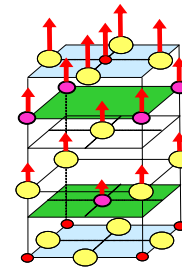
[Zhou et al., *subm. to PNAS*]

Electron-lattice interaction in cuprates

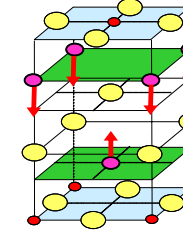
COLOSSAL PHOTO-INDUCED EXPANSION



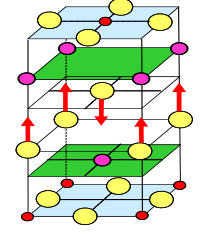
Science 316, 425 (2007); PRB 77, 092508 (2008)



Q_1
c-axis LAPs
 $k \ll 2\pi/d_f$



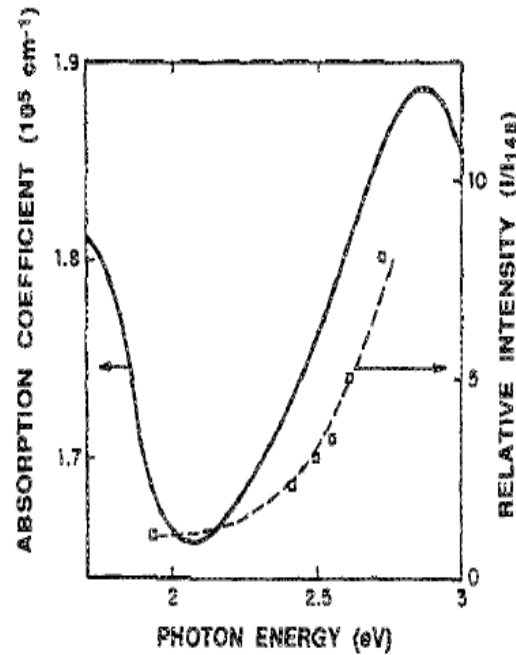
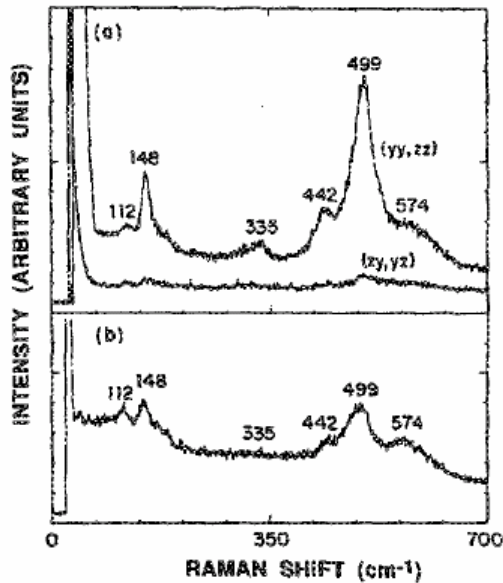
Q_2
 $k = 0$, A_{1g} RA
mode, $h\nu = 230$
 cm^{-1}



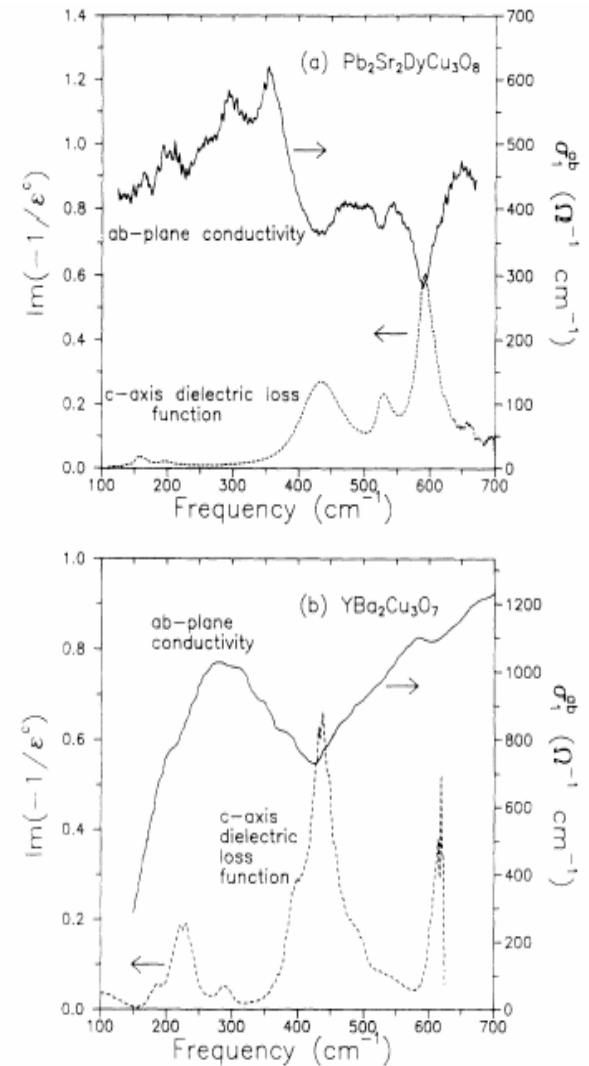
Q_3
 $k = 0$, A_{1g} RA
mode, $h\nu = 440$
 cm^{-1}

→ CHARGE-LATTICE COUPLING IS VERY STRONG!

Resonant Raman: E || ab, ions move along c-axis



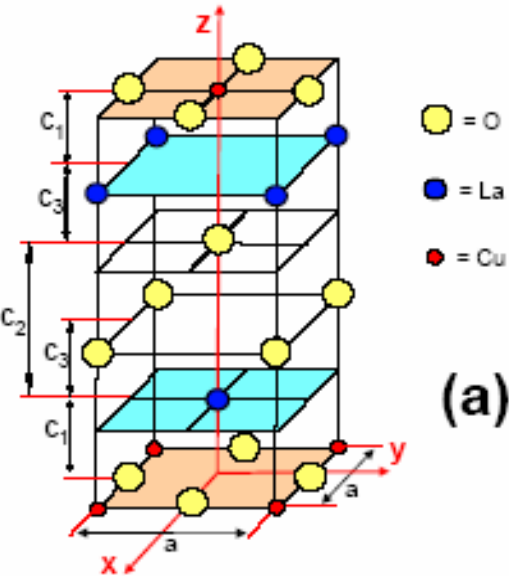
[J. Appl. Phys. 66, 977 (1989)]



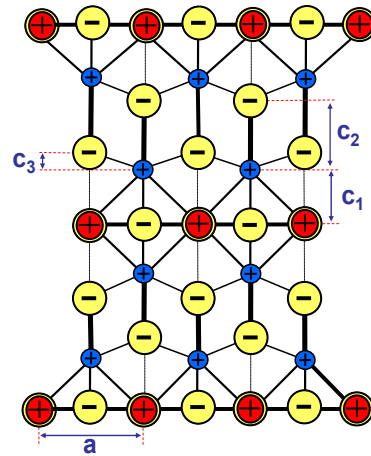
The same seen in Infrared spectra

Reedyk & Timusk PRL 69, 2705 (1992)

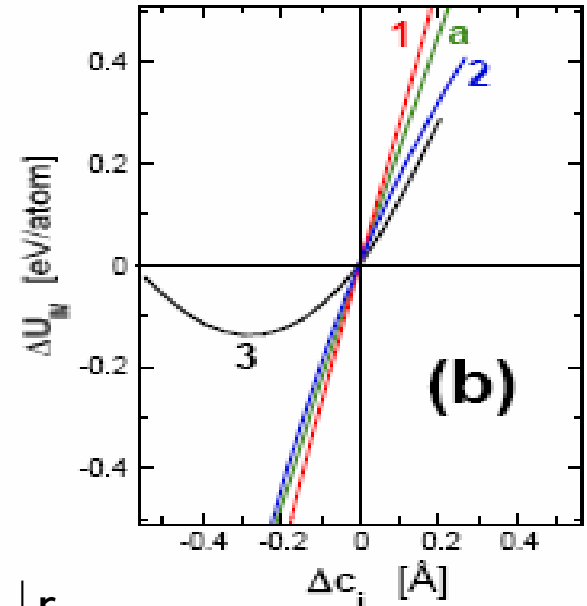
Madelung surprises



● = O
 ● = La
 ● = Cu



2.4 eV
 1.9 eV
 1.1 eV
 0.8 eV
 0.5 eV



The model: $U = (e^2/2)\sum q_i q_j / |r_i - r_j| + (1/2)\sum A_{ij} \exp(-B_{ij} |r_i - r_j|)$

A, B are chosen to reproduce the structure and fixed.

La-O is not flat – the corrugation is huge, 0.6 Å.

This is a purely electrostatic effect – Madelung levitation – **not JTE.**

ALL-MBE engineering of novel superconductors

Related talks: J. Mannhart, J. Eckstein, M. Greenbaltt, C. Varma, ...

ALL-MBE toolbox

- Epitaxial strain
- Epitaxial stabilization; Madelung strain; interface compounds
- Doping without disorder
- Interface-enhanced superconductivity
- Controlling displacements of apical oxygen
- Tuning charge-lattice coupling

ALL-MBE game plan

Synthesize

- various M-I bilayer combinations
- (metastable) superlattices using stable blocks

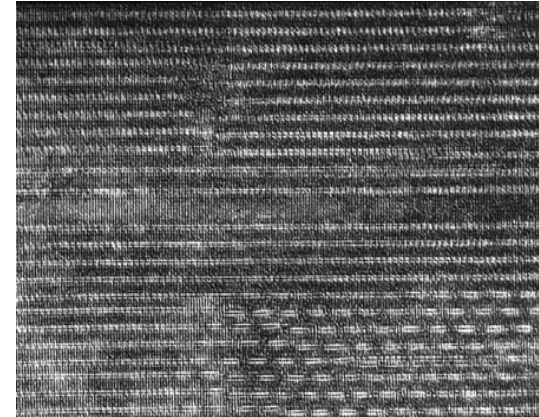
Characterize, measure, analyze, perform numerical simulations

Epitaxial stabilization and Madelung strain

Artificial metastable superconductors synthesized by ALL-MBE

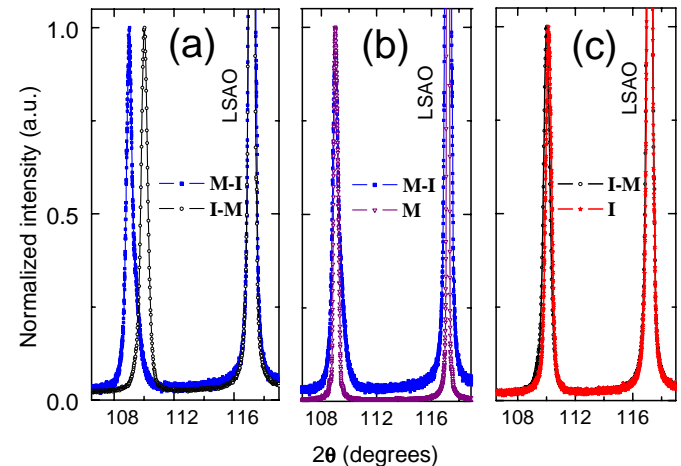
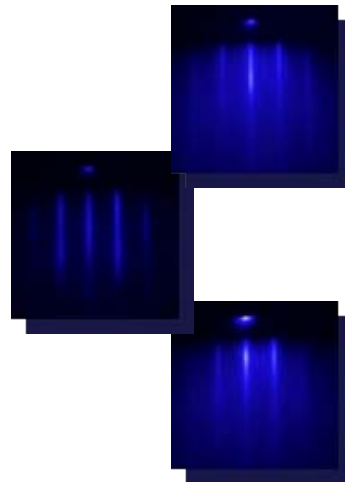
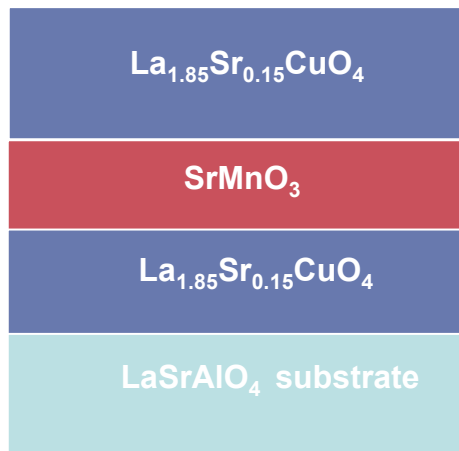
Bi-2278 ($T_c = 60$ K)

Bi-1278 ($T_c = 75$ K)



J. Supercond. 7, 187 (1994)

SrMnO₃ in perovskite structure

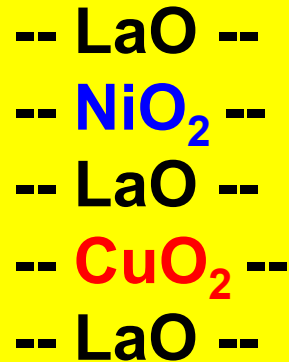


I-M ≠ M-I (b) M-I = M (c) I-M = I

Adv. Mater. 21, 1 (2009)

[Bulk SrMnO₃: $a = 5.454(1)$ Å, $c = 9.092(2)$ Å, SG: P6₃/mmc]

DIGITAL SYNTHESIS OF ARTIFICIAL HTS MATERIALS



NB: Artificially broken inversion symmetry!

Also, replace Ni with M = Ti, Mn, Co, Fe,...

$3x\text{La}^{3+}$, M^{3+} , Cu^{2+} : 14 electrons donated to 14 oxygen 2p states. This could be an (AF?) ionic insulator. However, some electrons could flow from MO_2 layer to CuO_2 layer because of the electro-chemical potential difference. This could make the MO_2 layer metallic, and CuO_2 layer superconducting.

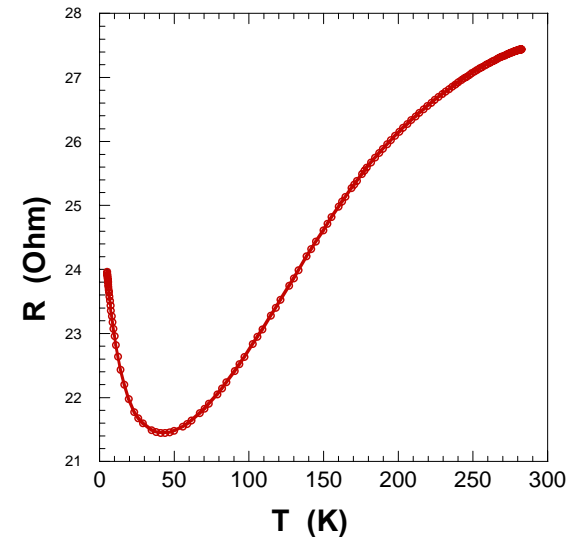
One can also try oxygen or Sr→La doping, as well as photo-doping. Photo-generated electrons and holes could migrate to separate layers.
=> Long lived excitons? Photo-induced HTS?

DIGITAL SYNTHESIS OF ARTIFICIAL HTS MATERIALS



-- BaO --
-- BiO₂ --
-- BaO --
-- LaO₂ --
-- BaO ----
-- BiO₂ -

NB: Artificially broken inversion symmetry!



This should be a realization of hole-doped, artificially-layered, quasi-2D BaBiO₃.

We have also experimented with ILC, Sr₂CuO_{4-d}, LaAlO₃, LaSrAlO₄, LaNiO₃, La_{2-x}Sr_xNiO₄, titanates, manganites, etc.

ALL-MBE → evidence for:

- **One-atom-thick HTS**
- **Non-zero E in superconductor**
- **Broken inversion symmetry**
- **Quantum spin liquid**
- **Homogeneous HTS**
- **Strong electron-lattice interaction in HTS**
- **... and more to come.**