2. Ultrafast optical pump – structural (diffraction) probe experiments

Q: Is electron-phonon coupling strong in cuprates, and what is its role?

A: ***NO/NONE:***

- **✶ Absence of OIE on T_c in optimally doped cuprates**
- **✶ Small λ (≈ 0.1-0.3) from slope and absence of saturation of R(T)**

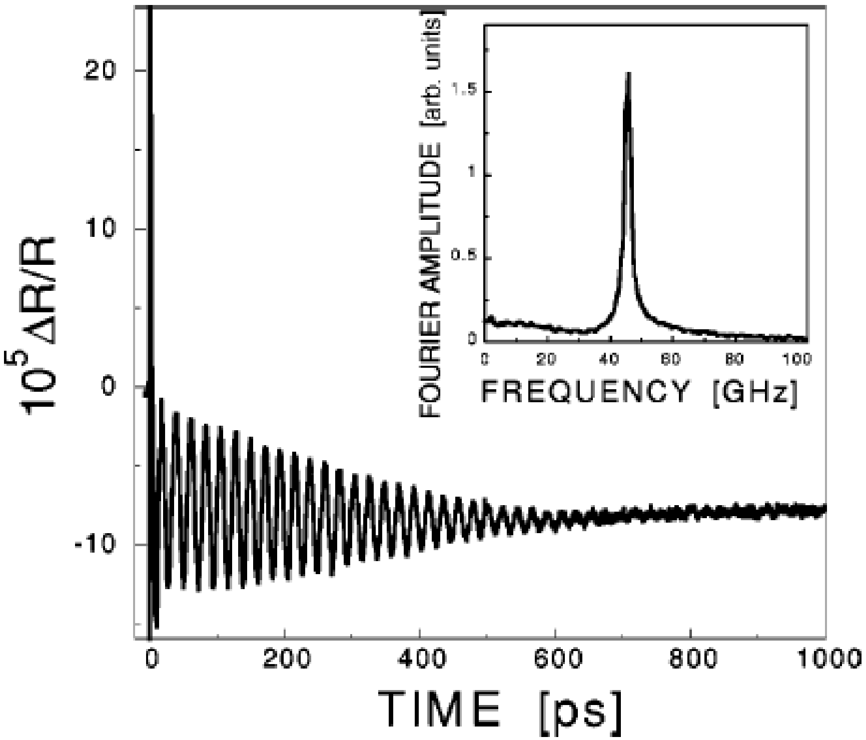
A: ***YES/IMPORTANT***

- **✶ Large OIE on T_c in underdoped cuprates**
- **✶ STS (phonon feature in d^2I/dV^2 seen above gap)**
- **✶ Phonon anomalies in neutron scattering**
- **✶ Bond-length splitting in EXAFS**

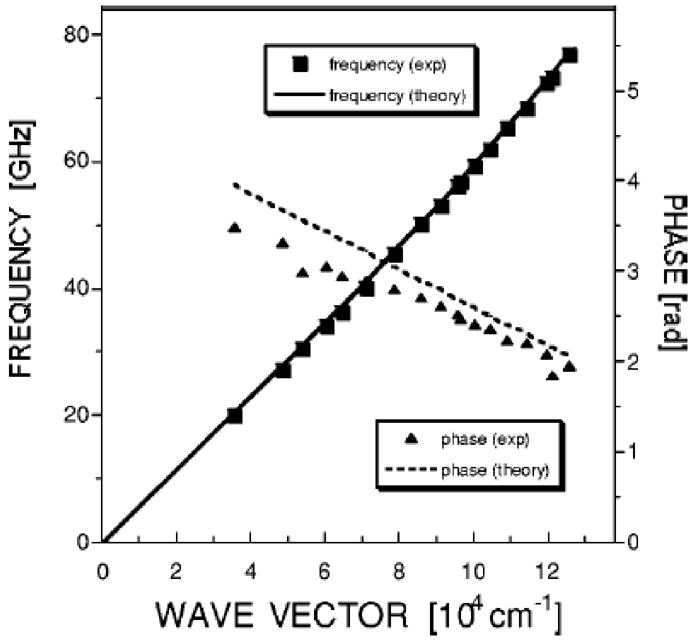
(Links: talks by Cohen, Ashcroft, Kresin, Grant, ...)

Ultrafast optical spectroscopy on $La_2CuO_{4+\delta}$

Long-lived coherent acoustic waves generated by femtosecond light pulses



[Bozovic *et. al*, PRB 2004]

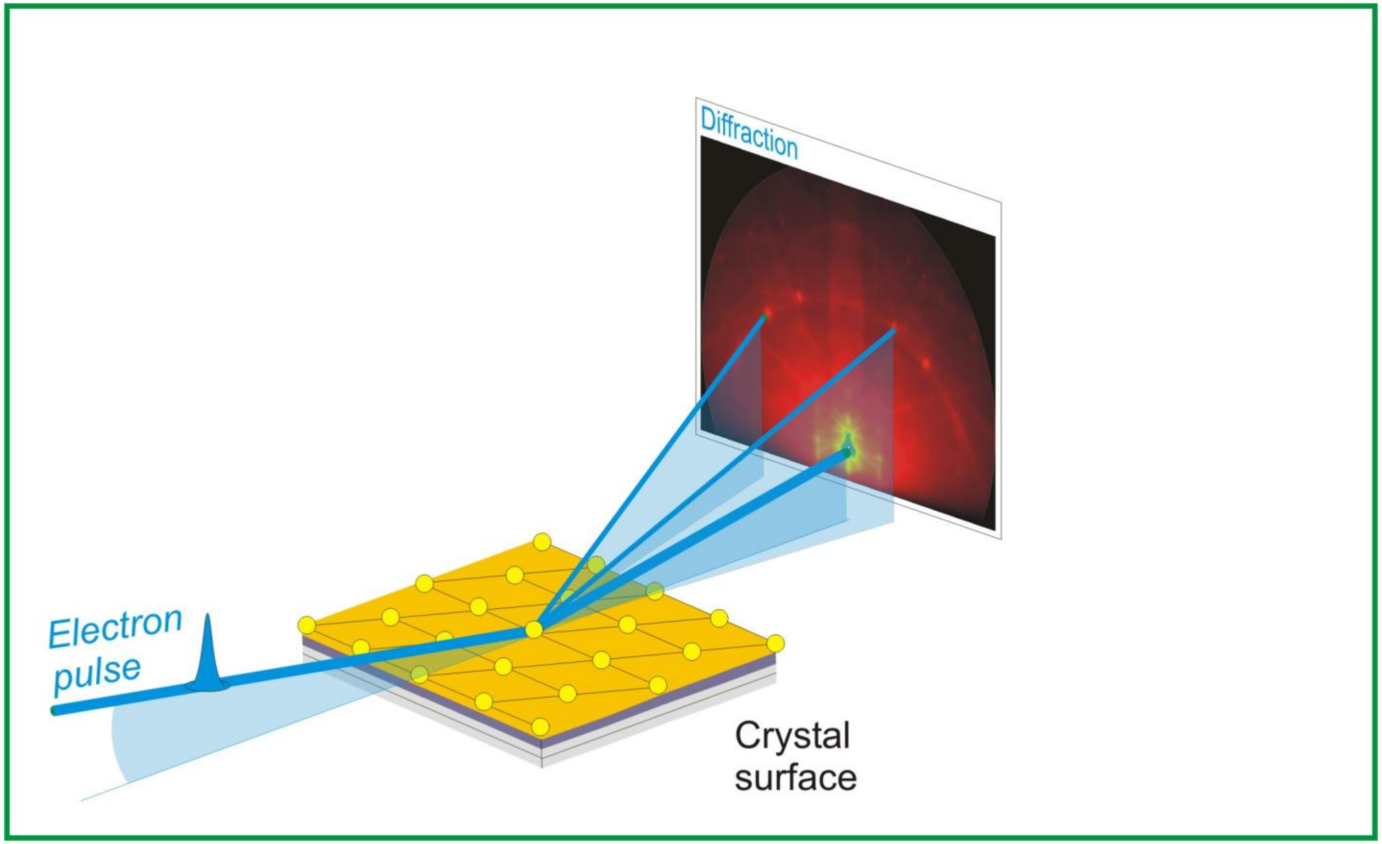


Initial very fast decay < 1 ps

Oscillation period ~ 20 ps

Damping ~300 ps

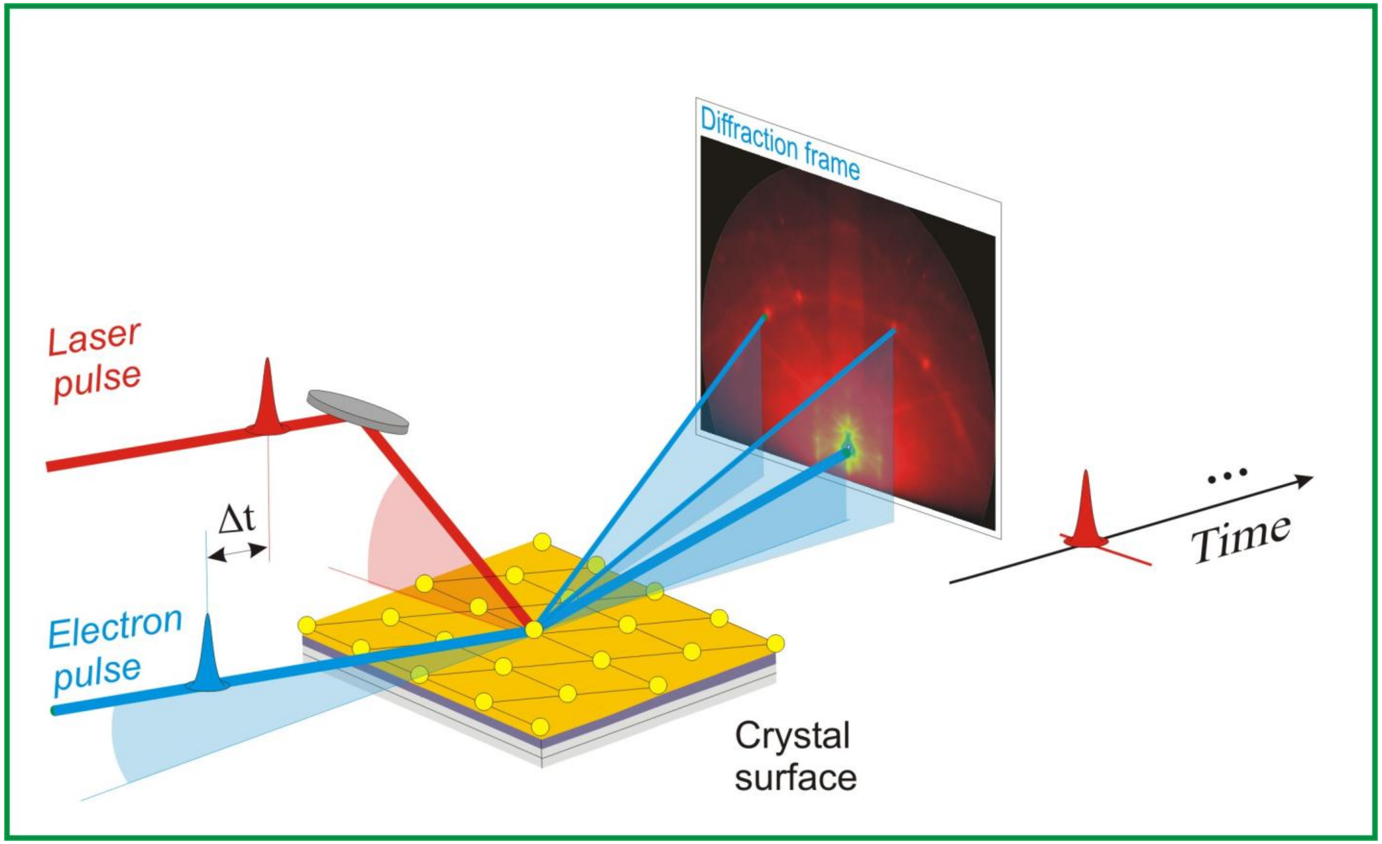
Ultrafast electron difraction



- Electron pulse as probe pulse
  - Diffraction pattern shows transient structure

Courtesy of N. Gedik

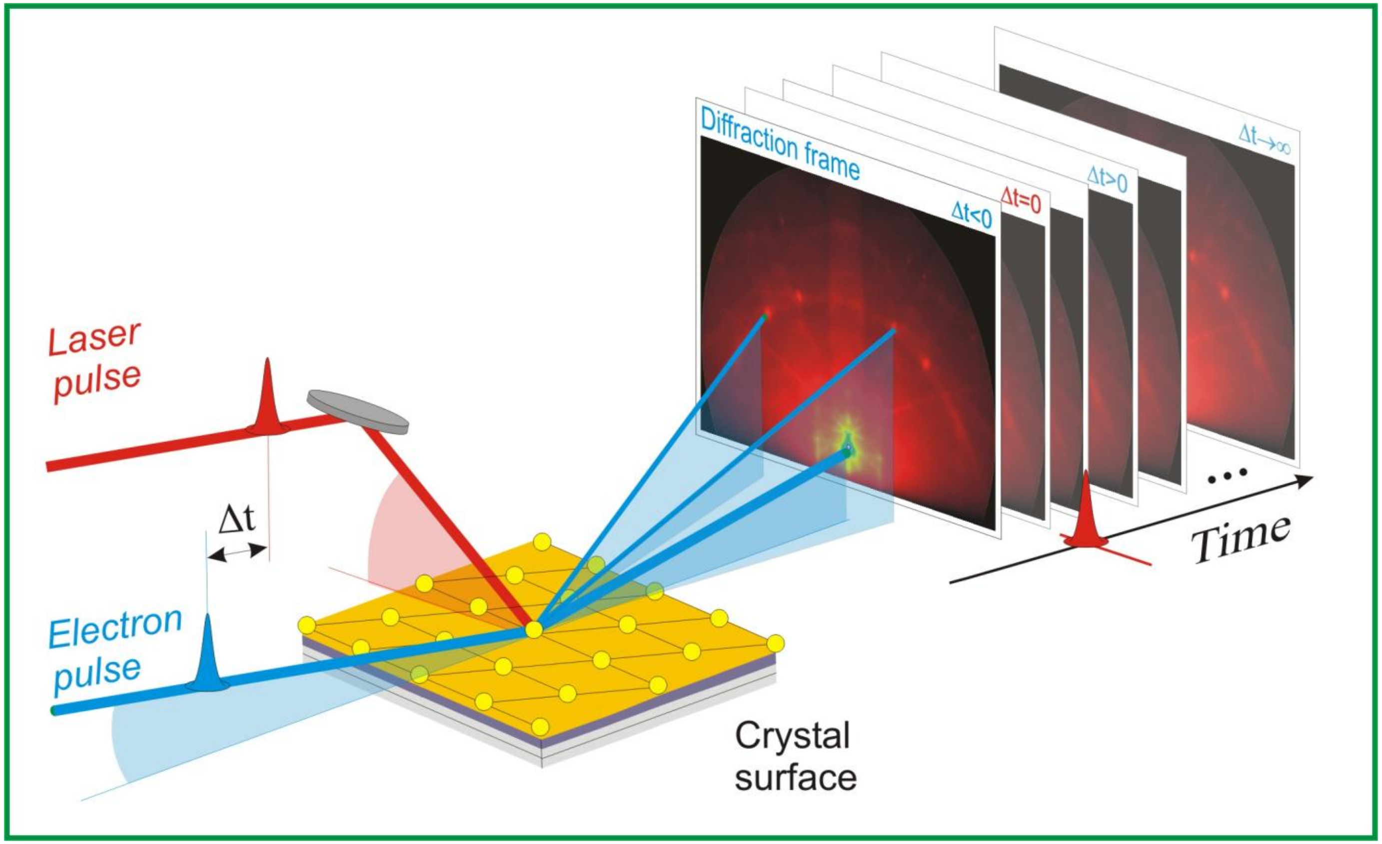
Femtosecond optical pump – UED probe



- Laser pulse as pump pulse
  - Initiate the dynamics
  - Serve as a reference point in time

Courtesy of N. Gedik

Ultrafast electron difraction movie

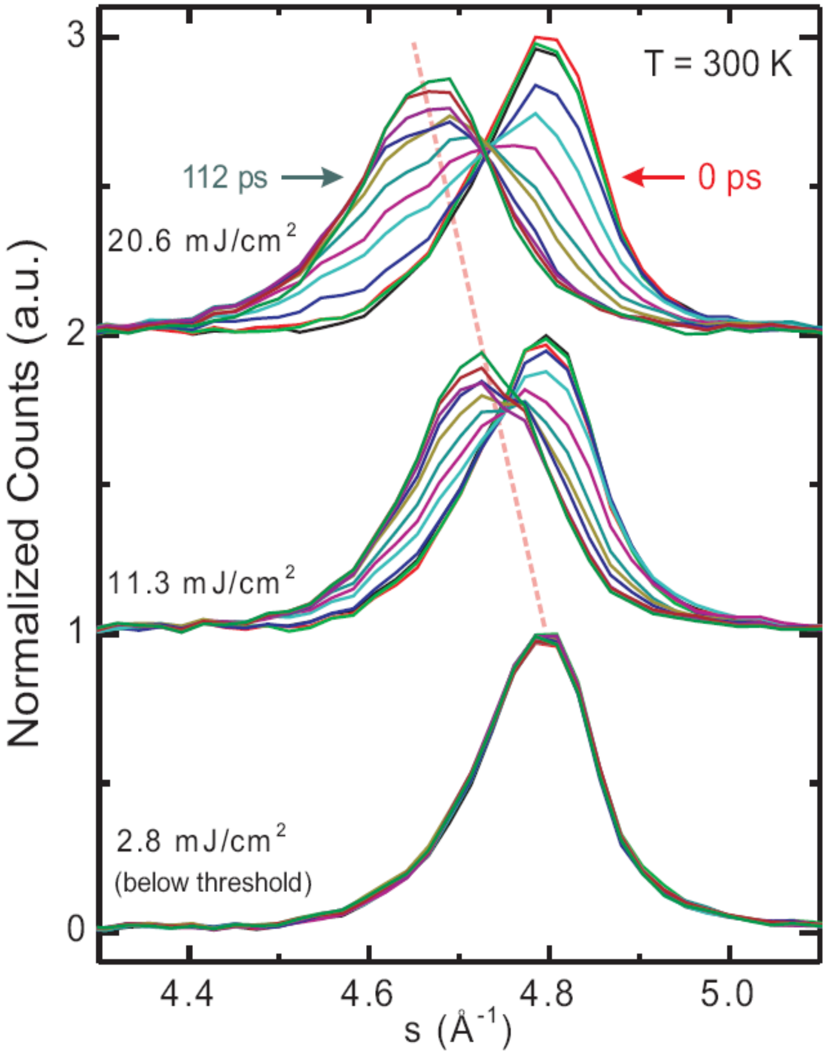


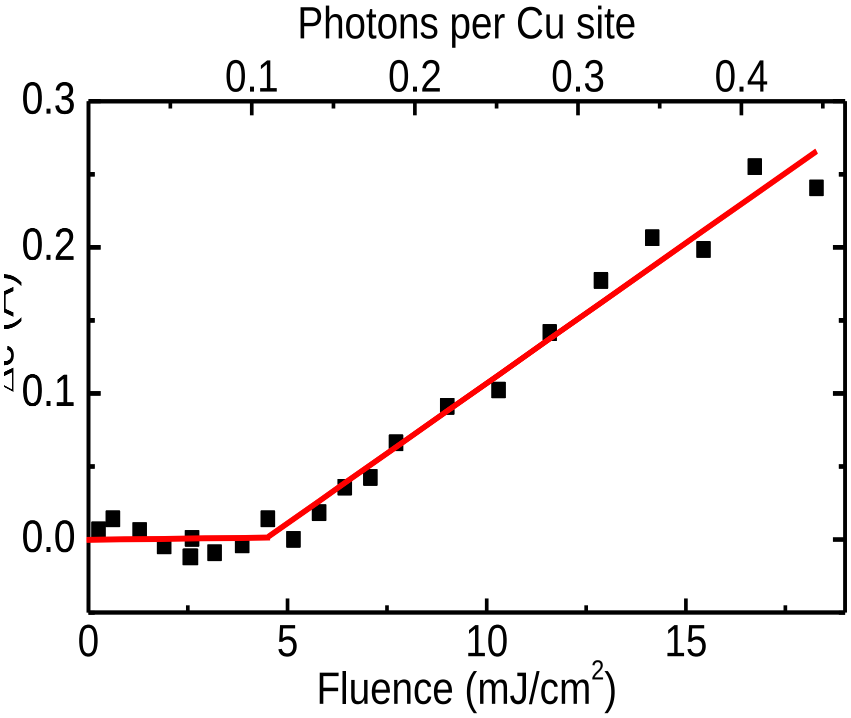
Delays between the pump (laser) — probe (electron) pulses

Time series of diffraction patterns: Movies of dynamics

Courtesy of N. Gedik

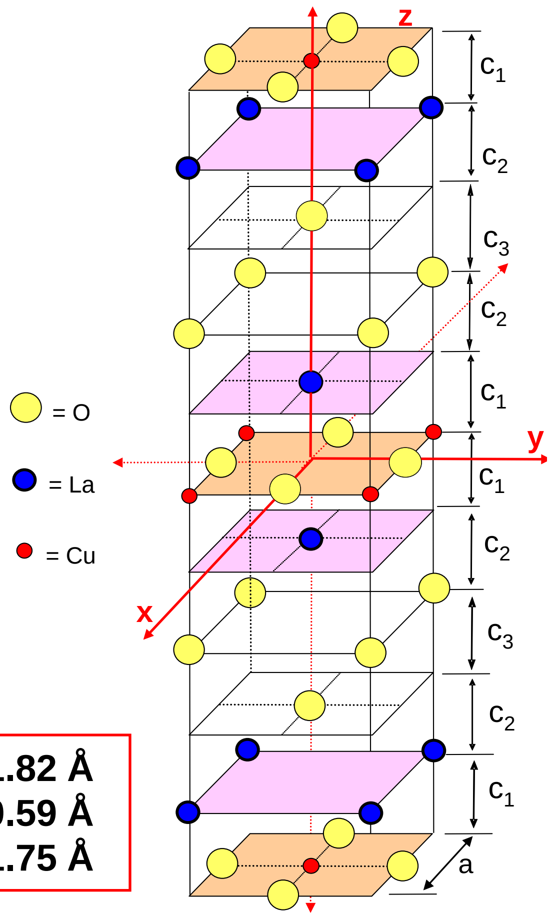
Intensity dependence





[Gedik et al., *Science* **316,** 425 2007]

The physics of colossal PI expansion



$C_1 = 1.82$ Å
$C_2 = 0.59$ Å
$C_3 = 1.75$ Å

La_2CuO_4

The model for cohesion energy:

$$U(a,c_1,c_2,c_3) =$$

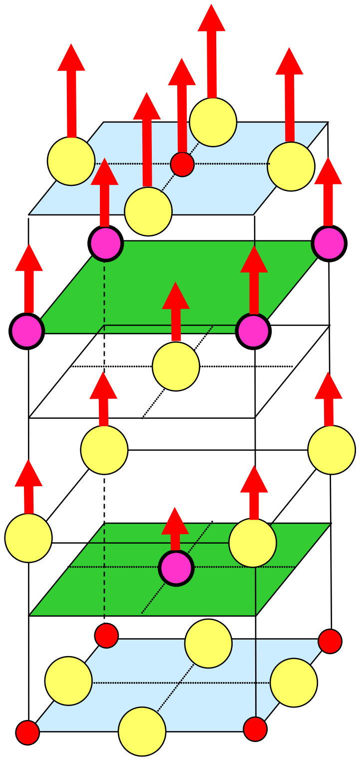
$$(1/2)\Sigma\, Q_iQ_j / \left| [\mathbf{r}_i + \mathbf{R} - \mathbf{r}_j - \mathbf{R'} \right| \quad +$$

$$(1/2)\Sigma\, A_{ij}{*}\exp(-B_{ij} \left| [\mathbf{r}_i + \mathbf{R} - \mathbf{r}_j - \mathbf{R'} \right|)$$

The Born-Meier parameters A_{ij}, B_{ij} are chosen to reproduce the crystal structure and elastic constants.

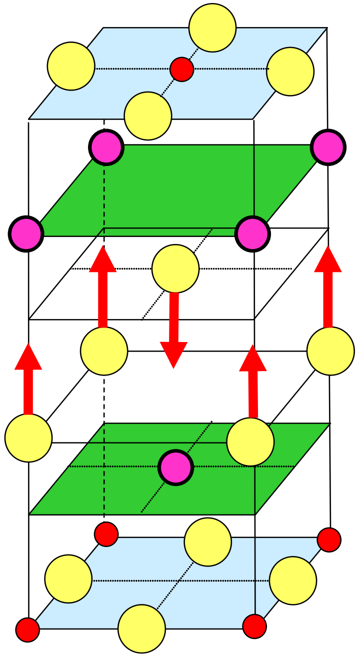
[Z. Radovic, N. Bozovic and I. Bozovic, unpublished]

The modes that strongly couple to in-plane charge excitations



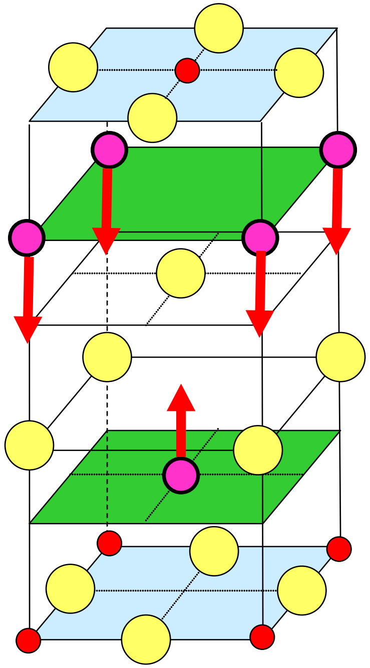
Q_1

c-axis LAPs
$k << 2\pi/d_f$



Q_2

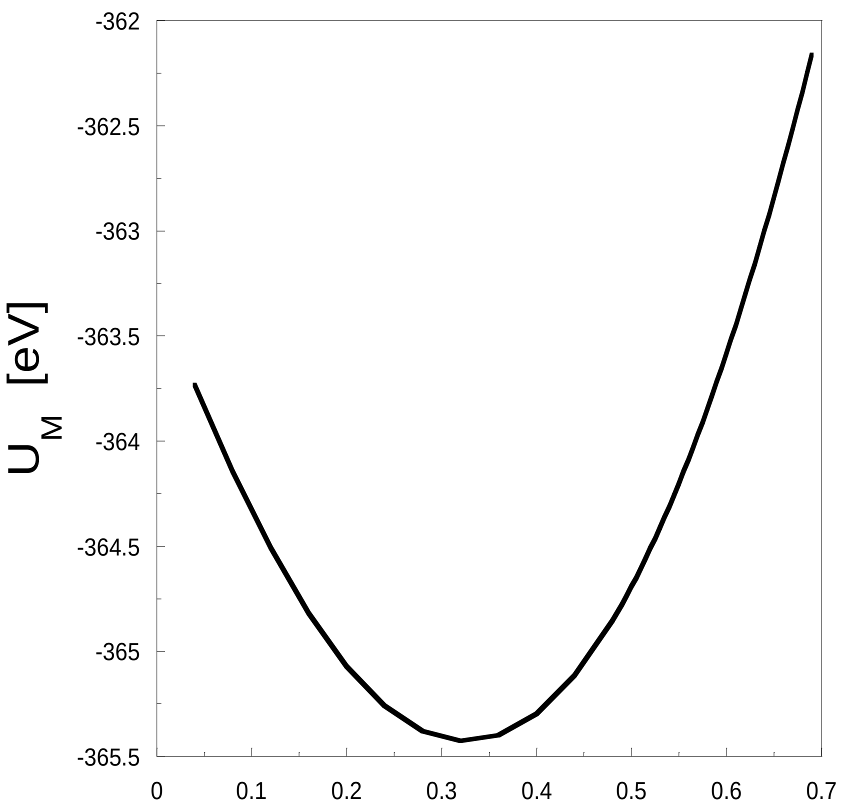
$k = 0$, A_{1g} RA mode,
$h\nu = 230$ cm^{-1}

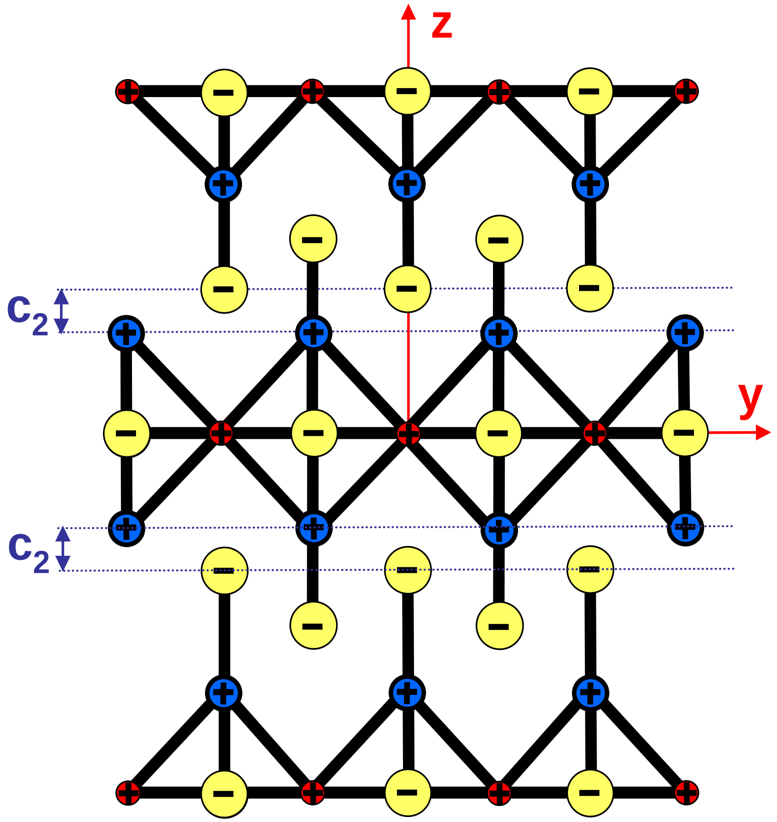


Q_3

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

A hidden soft coordinate: La-O layer corrugation





The calculated Madelung energy as a function of the La-O corrugation length c_2.

**LCO structure viewed along the x-axis.
The thick black lines indicate 'hard contacts'.
The rigid layers do not touch but 'levitate' on electrostatic forces.**

CONCLUSIONS

- **Colossal photo-induced expansion *proves* strong coupling of in-plane charge excitations to *c*-axis *acoustic* phonons.**
- **Cohesion-energy calculations show that charge excitations strongly couple to *out-of-plane optic* (RA-active) phonons, as well.**
- **LCO has a soft coordinate: La-O corrugation length.**
- **All of the above is true of other HTS cuprates.**

3. Rasing T_c by epitaxy

Rising T_c by epitaxial strain

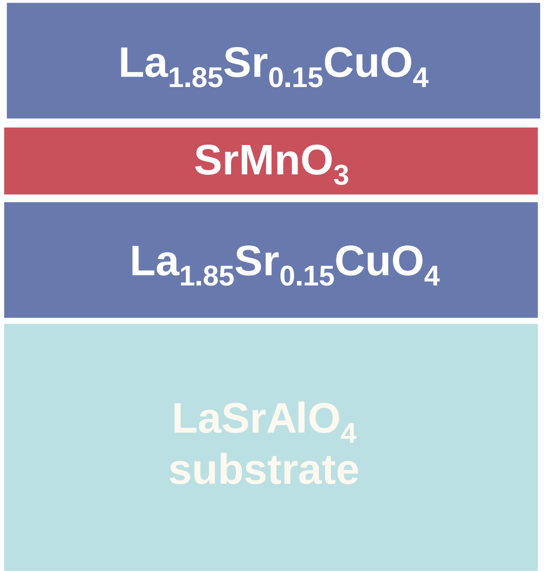
- **Bulk LSCO: $T_c \approx 36$ K.**
- **Cieplak, Rutgers [APL ’93]: LSCO on LSAO (compressive strain): $T_c = 44$ K.**
- **M. Naito, NTT [Phys C. ’97]: $T_c = 49$ K.**
- **Locquet, IBM-Zurich [Nature, 1998]: DOUBLING T_c ! (to 48 K).**
- **Several theory groups: Cu-O bond contraction causes ΔT_c, agreement < 1%.**
- **Bozovic [PRL ’02]: mostly oxygen, ±5 K from strain (mainly c-axis expansion).**
- **Pavuna [PRL ’04]: in-situ ARPES, strain affects FS.**

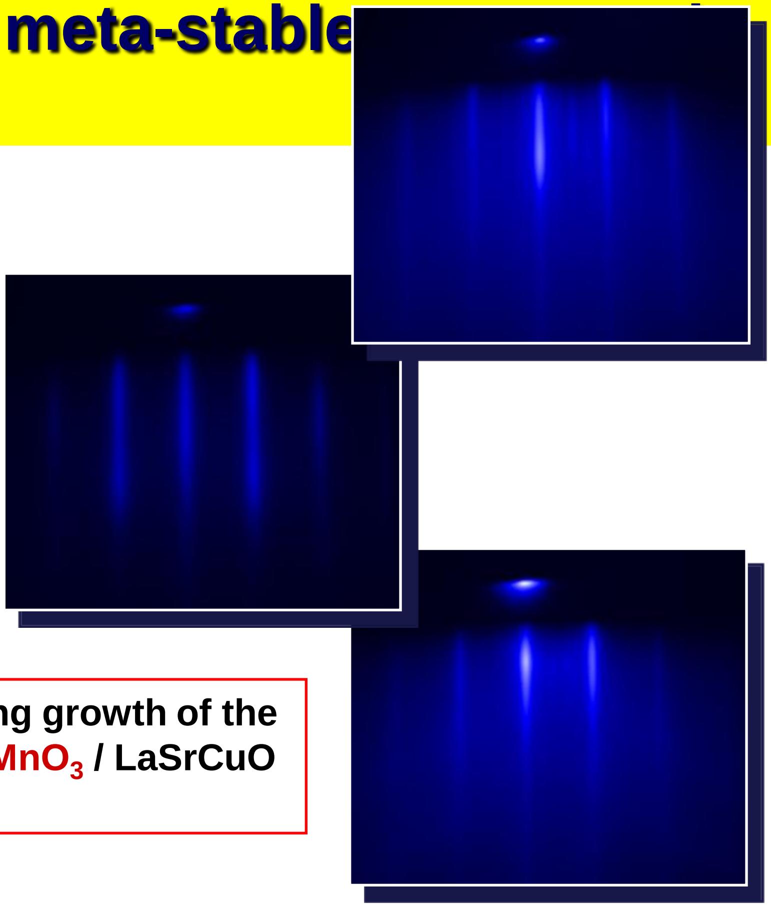
Links: talks by Pavuna, Ashcroft, Shimitzu

ALL-MBE synthesis of novel meta-stable

$SrMnO_3$ in *PEROVSKITE* structure.

[Normally it is hexagonal.]





RHEED during growth of the LSrCuO / $SrMnO_3$ / LaSrCuO trilayer

ARTIFICIAL SUPERCONDUCTORS:

- **Bi-2234: $T_c = 75$ K**
- **Bi-2278: $T_c = 60$ K**
- **(Bi:2201):(Bi:1278) superlattice: $T_c = 75$ K.**

BROOKHAVEN
NATIONAL LABORATORY

Ability to raise T_c by epitaxial stabilization and/or strain has been *demonstrated*.

Caveat:

T_c is a multi-variable function.

Apart from n and *p*, it depends on *x*, δ, Θ (buckling angle), (dis)order,...

4. *INTERFACE* SUPERCONDUCTIVITY

Interface vs strong correlations

- Near Mott Insulator state: competition of multiple order parameters
- Interface effects: strain, charge, fields, atomic and electronic reconstruction
- Interface effects can tip the balance in favor of desired ground state

Examples:

- ❖ High-mobility metal at interface of a Mott insulator ($LaTiO_3$) and a band insulator ($SrTiO_3$)

  [Ohtomo *et al* Nature ’02, ‘04]

- ❖ Ferromagnetism at interface of $LaMnO_3$ and $SrMnO_3$

  Koida *et al* PRB ’02]

Why is *IS* important?

- Enhanced phase fluctuations; novel vortex physics
- Strange response to magnetic field (reentrant SC vs Θ)
- Proximity effects; interplay of order parameters
- Higher T_c?
- New (interlayer) SC mechanisms?
  - Ginzburg …*M-I-M-I*…sandwich [Ginzburg ’64]
  - interlayer pairing; negative-U centers [Geballe ’05]
  - borrowed phase coherence [Kivelson ’02]

- Devices: SuFET, FEST [Ahn, Triscone & Mannhart ’03]

[Links: talks by Kivelson, Varma, Geballe, Grant, Mannhart]

Why is *IS* difficult?

PROBLEM

- **Conventional metals: n ~ 10^{23} cm^{-3} ⇒ ℓ_{TF} ~ 3-5 Å**
- **Conventional BCS superconductors: ξ ~ 100-1,000 Å**
  (870 Å in lead, 16,000 Å in Al,…)

⇒ the modified (interface) layer is too thin for SC to occur!

Plus, carrier density reduction generally *lowers* T_c.

SOLUTION: **Cuprates!**

- **n ~ 2-5*10^{21} cm^{-3} ⇒ ℓ_{TF} > 10 Å**
- **high T_c ⇒ short coherence length**
- **extreme anisotropy ⇒ ξ_c ~ 1-2 Å**
- **in OD cuprates, career density reduction *rises* T_c.**

⇒ a chance to realize interface superconductivity

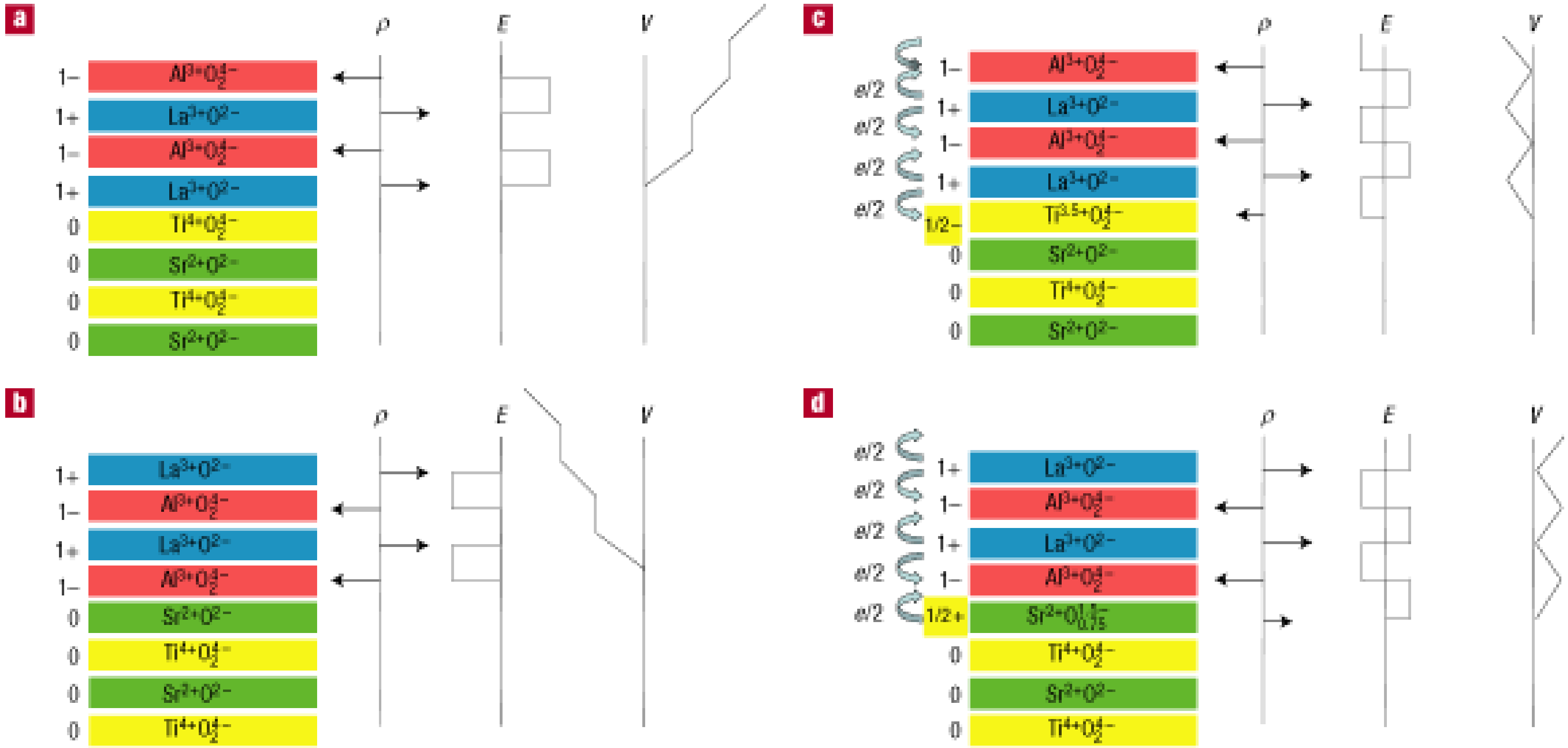
Why is *IS* difficult even with cuprates?

Because the interface must be *atomically* perfect!

PROBLEMS:

- **rms surface roughness (must be much less then 1 UC ≈ 1 nm)**
- **chemical inter-diffusion**
- **lattice mismatch and epitaxial strain**
- **structural reconstruction due to “polarization catastrophe”.**

“Why some interfaces cannot be sharp”



a. In AlO_2/LaO/TiO_2, charged layers produce *E*, leading to *V* that diverges with thickness.

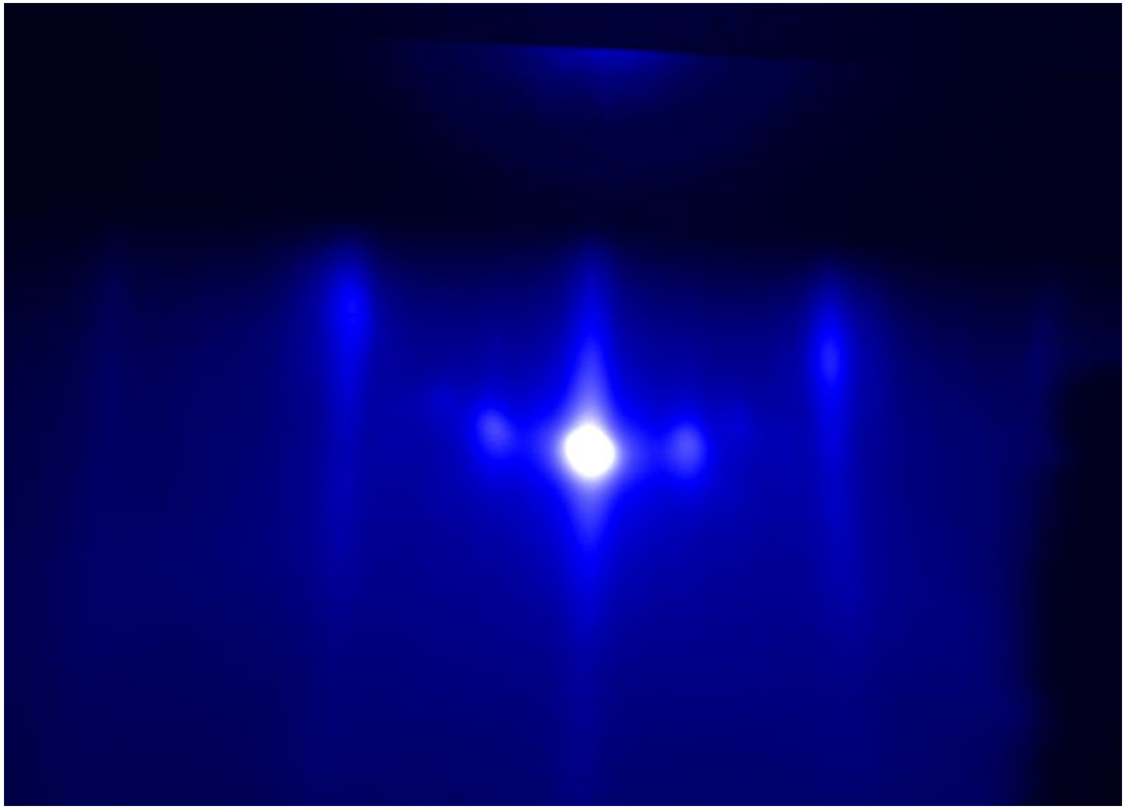
b. For AlO_2/SrO/TiO_2 interface, the potential diverges negatively.

c. The divergence catastrophe can be avoided if e/2 is added to the last Ti layer; this produces an interface dipole that causes the electric field to oscillate about 0 and the potential remains finite

d. It can also be avoided by removing half an electron from the SrO plane via oxygen vacancies.

Nakagawa, Hwang and Muller, *Nature Materials* (2006)

SURFACE ≠ BULK !



4x1 surface reconstruction in LSCO

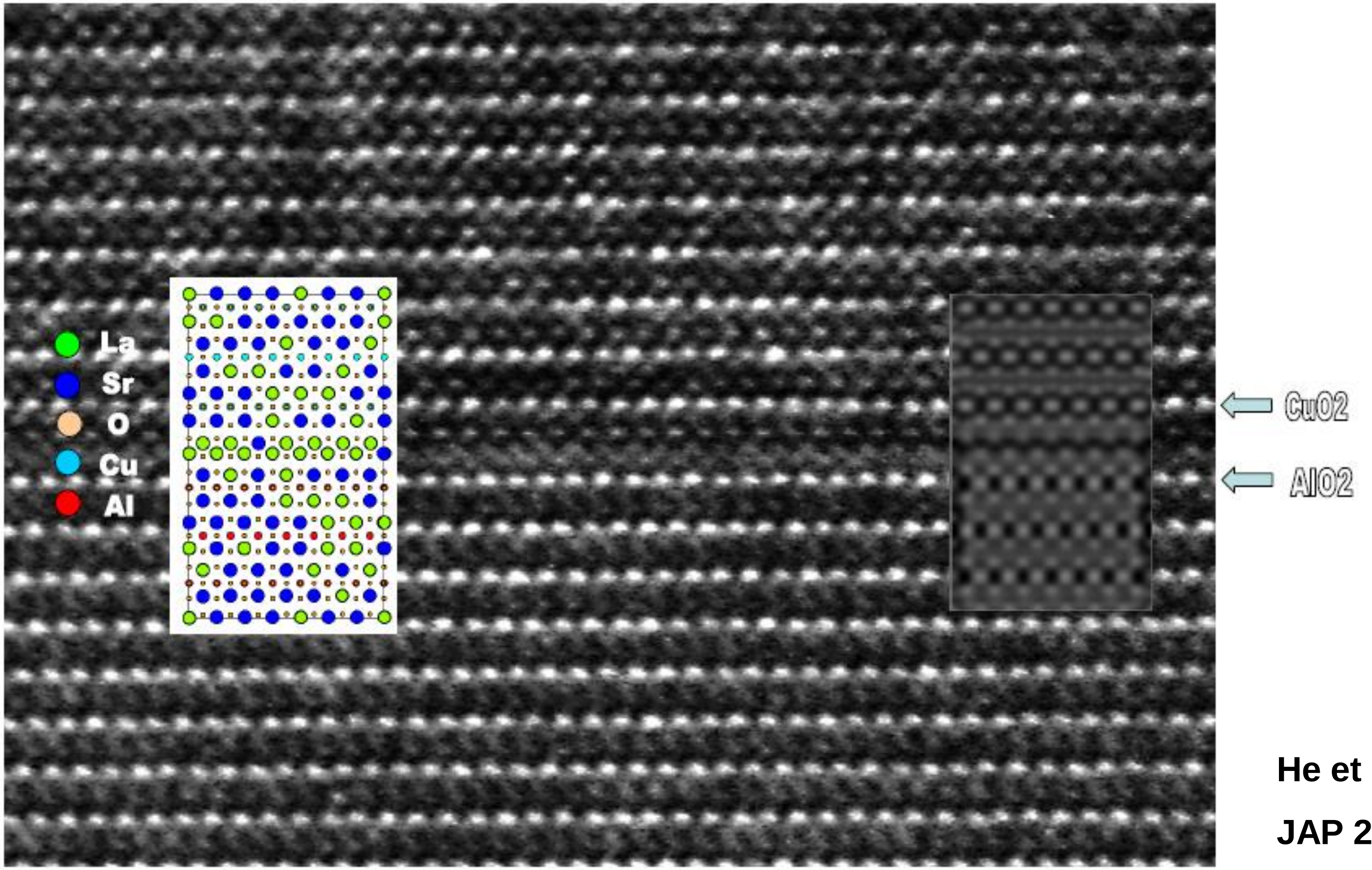
Problems: How to determine the structure of the top unit-cell layer?

How to know is it superconducting?

INTERFACE ≠ SURFACE ≠ BULK

LSCO
film

LSAO
substrate



He et al.,
JAP 2007

Interface compounds: the secret of perfect hetero-epitaxy!

INTERFACE SUPERCONDUCTIVITY IN CUPRATES

_I-M_ and _M-I_ bilayers both show robust superconductivity even though neither of the two constituents does.

Mid-point T_c ≈ 15 K in _I-M_ and T_c ≈ 30 K in _M-I_. In _M-S′_ and _S-S′_ bilayers T_c ≈ 50 K.

In single-phase _S_ or _S′_ films grown under the same conditions T_c never exceeded 40 K, the value marked by the arrow.

(the experimental results have been submitted for publication)

Mechanism of T_c enhancement

… is unclear.

What is clear is that this is an *interface* effect – the locus of enhanced SC is near the interface.

Candidate explanations:

- **doping without disorder**
- **suppression of a competing O/P**
- **inter-layer pairing and/or phase coherence**
- **…?**

5. FUTURE: RAISING T_c FURTHER

ATOMIC-LAYER ENGINEERING: CUPRATES & BEYOND

✶ **LSCO-ILC ($CaCuO_2$, $SrCuO_2$)**

✶ **(Bi-2201): (Bi-2234), (Bi-2201):(Bi-2278)**

✶ **$La_{2-x}Sr_xNiO_4$**

✶ **Layered $Ba_{1-x}K_xBiO_3$**

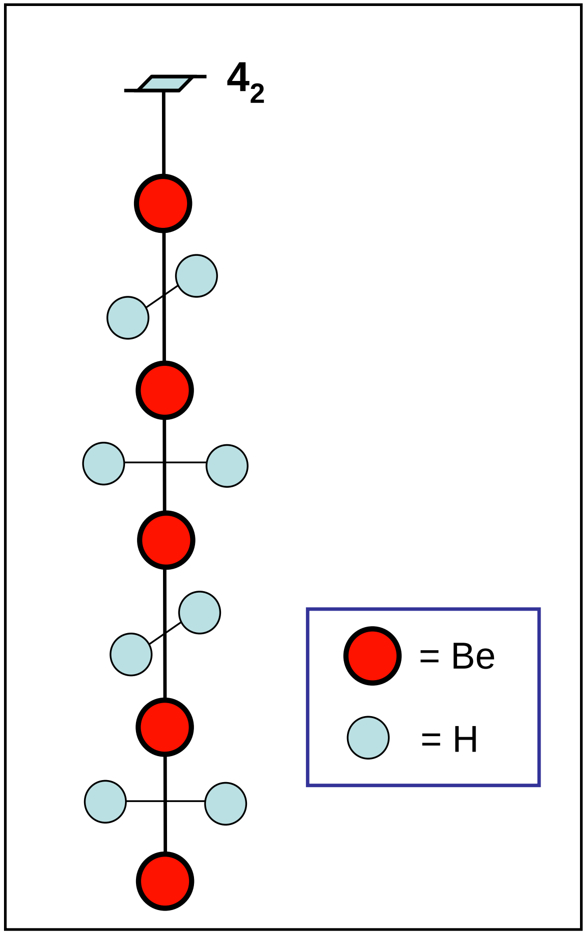
✶ **Li: $(BeH_2)_x$**

✶ **perovskite hydrides, layered**

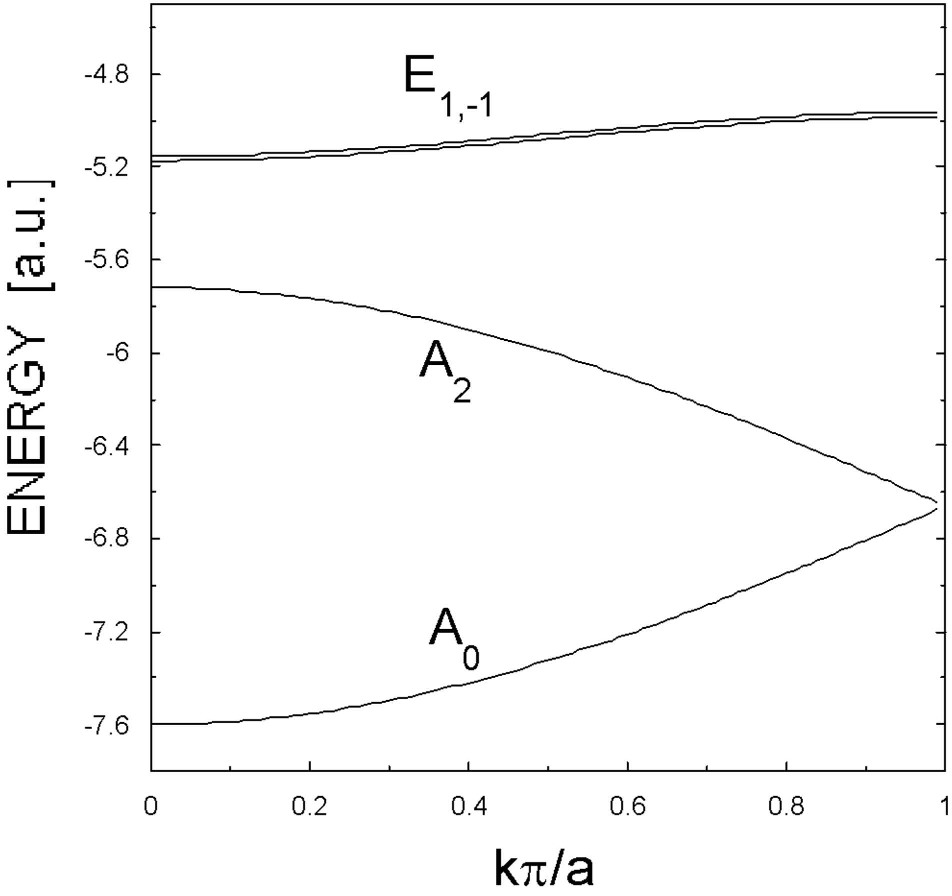
✶ **Ginzburgers**

(Cf.: Rice, Ashcroft, Varma, Kivelson...)

My best bet: Li-doped beryllium hydride

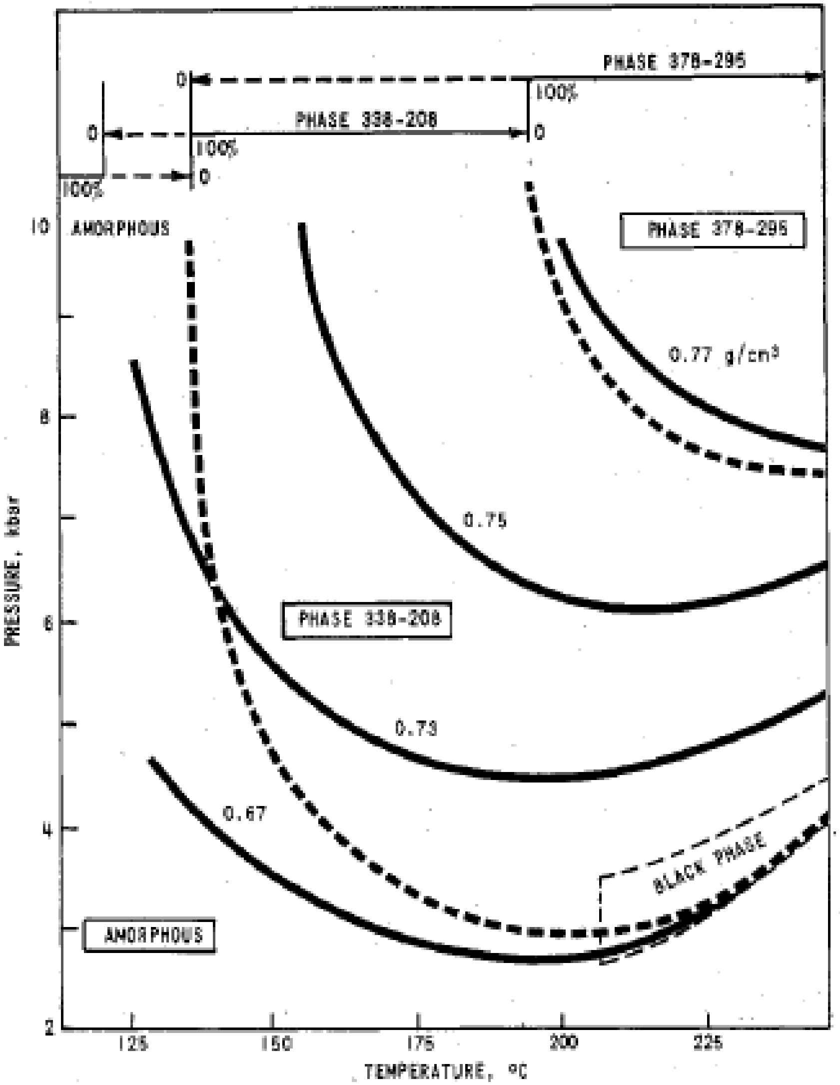


A model of $[BeH_2]_x$ polymer.
The line group is $L4_2/mcm$.



Simplified tight-binding band structure of $[BeH_2]$x polymer.
$E_{1,-1}$ band is twofold-degenerate throughout the BZ.
It is fully occupied, but gets partially occupied by Li doping.

A candidate for (band) Jahn-Teller effect and strong e-p coupling; high DOS and Θ_D.



. Pressure–temperature diagram for BeH_2 polymorphs.

Crystalline Beryllium Hydride

G. J. BRENDEL, E. M. MARLETT,* and L. M. NIEBYLSKI

Received June 28, 1978

Inorganic Chemistry, Vol. 17, No. 12, 1978 **3589**

Ethyl Corporation, Baton Rouge, Louisiana 70821

A curious form of BeH_2 was discovered during this study of crystallization variables. Normally, the compacted Li-doped BeH_2 was white to light gray in color. However, in several instances tests conducted in the relatively narrow regime of 2.75–3.8 kbar at 205 °C to 4.1–4.5 kbar at 245 °C gave a glassy, black product (d = 0.67–0.68 g/cm^3). Chemical, IR, and X-ray diffraction analyses showed it to be indistinguishable from the normal, compacted material. Surprisingly, there was no increase in free Be metal which could have accounted for

Acknowledgment. This research was supported by the Advanced Research Projects Agency and the Department of the Air Force. The authors are indebted t er

CONCLUSIONS

- ***The lattice matters!*** **Colossal photo-induced expansion *proves* strong coupling of in-plane charge excitations to *c*-axis *acoustic* phonons. *Out-of-plane optic* (Raman active) phonons couple strongly, as well.**

- **This enables epitaxial stabilization of artificial superconductors and/or rising T_c by epitaxial strain.**

- **Interface superconductivity with enhanced T_c has been demonstrated. The mechanism has yet to be clarified.**

- **Stay tuned for more to come – soon!**