Investigating the mechanism of High Temperature Superconductivity by Oxygen Isotope Substitution

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How can we study a complex system?

Apply a perturbation and check what happens.
Outline:

- Cuprates - a complicated system...
- What is the source of critical doping variations?
  - CLBLCO
  - NMR
  - Results
  - Conclusions
- Oxygen Isotope Effect on the Néel temperature.
  - The Isotope Effect
  - μSR
  - Results
  - Conclusions
- CLBLCO: is it all about disorder?
  - Impurities in CLBLCO
Cuprates

http://www.fis.unipr.it/~derenzi

S. Chakravarty et al. PRB 63, 094503

Lee, Nagaosa, and Wen, Rev. Mod. Phys 78, 17 (2006)
The CLBLCO Compound

\[(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y\]

- \(y\) controls the total charge (doping).
- \(x\) controls the charge location.
- The total cation charge does not change with \(x\).
- There’s a 30% difference in \(T_C^{max}\) between the families.

Critical Doping levels \(x=0.1\) (black)
Stretching each family data by a factor of $K(x)$ creates identical critical doping levels.

Is there a physical explanation?
Previous Results - CLBLCO

- **XAS- Cu**
  - Graph showing the intensity of XAS with respect to copper content.

- **XAS- O**
  - Graph showing oxygen isotope effects with different copper contents.
  - Inset showing expanded view of XAS peaks.

- **Cu NMR**
  - Graph showing NMR signals for varying copper contents.

- **BVS calculations - Cu**
  - Graph showing BVS calculations with respect to oxygen concentration.

- **The hole density of Copper is x invariant: “Two Fluids”**

References:
- S. Sanna et al. EPL 86, 67007 (2009)
Oxygen 17 NMR

- $^{17}$O nucleus has a quadrupole moment. It is sensitive to both electric and magnetic field distributions.

$$H = H_{\text{Zeeman}} + H_{\text{Quadrupole}}(EFG)$$

- In the doping process holes are induced in the planar oxygen orbitals.
- $^{17}$O has a relatively small spectral width.
The Enrichment System

The Enrichment process:

- Samples are put in the furnace.
- The furnace is sealed and vacuumed.
- Gas containing the desired isotope - either $^{18}\text{O}$ or $^{17}\text{O}$ - is released into the tube with the sample.
- The furnace is heated to allow the isotope to diffuse into the sample.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{16}\text{O}$</td>
<td>99.76%</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>0.038%</td>
</tr>
<tr>
<td>$^{18}\text{O}$</td>
<td>0.21%</td>
</tr>
</tbody>
</table>
Nuclear Quadrupole Resonance
The Quadrupole Frequency measures the Charge Distribution around the nucleus.
Nuclear Magnetic Resonance

\[ E = \frac{5}{2} I \]

\[ H_0 \]

\[ \text{Zeeman} \]

\[ \text{Quadrupole} \]

\[ h\nu \]

\[ \text{NMR Spectrum:} \]

\[ H_{\text{Zeeman}} = -\gamma \hbar H_0 (1 + \sigma) I + \frac{1}{6} \nu_Q \left[ 3I_z^2 - I^2 + \eta \left( I_x^2 - I_y^2 \right) \right] \]

\[ H_{\text{Quadrupole}} \]

\[ \nu \rightarrow \text{freq.} \]

\[ \propto \nu_Q \]
The parameters $x$ and $y$ change the quadrupole frequency.
The contributions to the planar oxygen $\nu_Q$:

1. Holes in the oxygen $2p_\sigma$ orbital
2. Holes in copper orbitals
3. Surrounding atoms (La, Ba, Ca)

- We compare samples with different doping levels.

$\nu_Q$ measures the number of planar oxygen $2p_\sigma$ holes
$^{17}$O NMR of CLBLCO
The ratio between the slopes is equal to \( K(x=0.1) \) over \( K(x=0.4) \).
For \( y < y_N \) the number of planar O 2p\(_\sigma\) holes does not change.
The critical doping values are global and depend only on the number of $2p_\sigma$ holes created by doping.
The CLBLCO phase diagram is scaled with no adjustable parameter.

Scaling:
- Dividing by $T_c^{\text{max}}(x)$
- Replacing $T_N$ with $J$

The CLBLCO phase diagram is scaled with no adjustable parameter.

The maximum $T_c$ is defined by the AFM coupling $J$. 
• We compared the number of $2p_\sigma$ holes of CLBLCO samples with different $x$ and $y$ values using $^{17}$O NMR.

• The critical doping values are global and depend only on the number of $2p_\sigma$ holes created by doping.

• The CLBLCO phase diagram (with $T_{C}^{\text{max}}$ difference of 30%) is scaled with no adjustable parameter.

• The maximum $T_C$ is defined by the AFM coupling $J$. 
“THE main facts which a theory of superconductivity must explain are (1) a second-order phase transition at the critical temperature, $T_c$, … (5) the dependence of $T_c$ on isotopic mass, $T_c \sqrt{M} = \text{const}$. We present here a theory which accounts for all of these…”


The Isotope Effect was one of the key experimental findings in the path to understanding conventional superconductivity.
The Isotope Effect is the change in the critical temperature due to isotopic substitution:

\[ \alpha \equiv -\frac{d \ln T_q}{dm} \quad \leftrightarrow \quad T_q \propto m^{-\alpha} \]

For a small effect:

\[ \alpha = -\frac{\Delta T_q}{T_q} \cdot \frac{m}{\Delta m} \]

- \( T_q \) - the critical temperature.
- \( m \) - the element’s mass.
- \( \Delta \) – the change caused by substitution.
For most conventional superconductors $\alpha = 0.5$,
as explained by BCS theory:

$$T_c \approx 1.13\Omega e^{-\frac{1}{N(0)V}}.$$ 

The Cooper pairs are phonons mediated.
Isotope Effect in Cuprates

Why is there IE in Cuprates?

IE in Cuprates: Theories

- Phonons
  BCS (1957), A. Bill (1996).

- Zero point motion

- Polaron

- Normal doping

- Superfluid density
  M. Serbyn (2010).

Exploring the AFM phase may improve our understanding of the SC phase.

\[
T_c = 1.13 \Omega e
\]

\[
\mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{E_F}{\Omega} \right)}
\]

\[
m^* = m_e e^{\omega}
\]
Why is \((\text{Ca}_{0.1}\text{La}_{0.9})(\text{Ba}_{1.65}\text{La}_{0.35})\text{Cu}_3\text{O}_y)\) ideal for this experiment?

More accurate measurements can be performed.

**Muon**- A Lepton with a mass of 105.7 MeV, The charge is identical to a positron (or an electron). Spin-½, Life time-2.2 micro-seconds. Gyromagnetic ratio- $135.5 \times 10^6$ Hz/T. Decays into a positron (+ neutrino and anti-neutrino).

The direction of the emitted positron:
A beam of polarized muons hits the sample. Each muon rotates and decays into a positron.
The muons polarization is:

$$P_z(t) = P_n e^{-\Delta t} + P_m (ae^{-\lambda_1 t} + (1-a)e^{-\lambda_2 t} \cos(\omega t))$$

Non-magnetic phase (high T)

Magnetic phase (low T)

Oscillations at the Larmor frequency $\omega$
Choosing Order Parameter

In order to increase the sensitivity we defined a new order parameter:

\[
\text{OP}(T) \equiv \frac{< P_{\text{inf}} > - < P(T) >}{< P_{\text{inf}} > - < P(0) >}
\]

\[
P_z(t) = P_n e^{-\Delta t} + \left( P_m e^{-\lambda_1 t} + (1 - a)e^{-\lambda_2 t} \cos(\omega t) \right)
\]
Results

\[ \text{OP} (T) \equiv \frac{\langle P_{\text{inf}} \rangle - \langle P(T) \rangle}{\langle P_{\text{inf}} \rangle - \langle P(0) \rangle} \]

\[ P_z(t) = P_n e^{-\Delta t} + P_m (ae^{-\lambda_1 t} + (1-a)e^{-\lambda_2 t} \cos(\omega t)) \]
Results

There is no IE on $T_N$: $\alpha_N = 0.005 \pm 0.011$

$$T_N \propto m^{-\alpha_N}$$

$\text{OP (T)} \equiv \frac{< P_{\text{inf}} > - < P(T) >}{< P_{\text{inf}} > - < P(0) >}$

$$P_z(t) = P_n e^{-\Delta t} + P_m (ae^{-\lambda_1 t} + (1-a)e^{-\lambda_2 t} \cos(\omega t))$$
The oxygen isotope effect changes with sample’s doping:
In the SC phase $\alpha > 0$;
In the AFM phase $\alpha < 0$
In the SC phase $\Delta n < 0$;
In the AFM phase $\Delta n < 0$

A change of about 1% in the number of planar holes between the isotopes may explain the effect.

• We compared the Néel temperature of samples with $^{16}$O and $^{18}$O using µSR.

• The isotope coefficient was found to be $\alpha_N = 0.005 \pm 0.011$

• Isotope substitution does not change the magnetic excitations.

• The isotope effect in cuprates can be explained by a change in the doping efficiency.

• In order to use isotope experiments to understand the mechanism of superconductivity, precise measurements should be performed on materials where $T_C$ does not depend on doping.
Could it be that it's all about impurities?

- $y$ controls the total charge (doping).
- $x$ controls the charge location.
- The total cation charge does not change with $x$.
- There’s a 30% difference in $T_C^{\text{max}}$ between the families.
There are three oxygen cites in CLBLCO:

- Planar oxygen- $O_{2,3}$
- Bridging oxygen- $O_1$
- “Chain” oxygen- $O_4$  
  - has a wider peak

The widths of NMR signals are similar for all families.

Quadrupole frequency as inhomogeneity measurement

Charge inhomogeneity
The quadrupole frequency distribution

The widths of NMR signals are similar for all families.
Quadrupole frequency as inhomogeneity measurement

- NMR does not show any difference in crystal quality of the different CLBLCO families.

- Impurities cannot explain the big difference in $T_{c}^{\text{max}}$ of the families.
Summary: Small Effects in the Cuprates Phase Diagram

The "hole" effect can be misinterpreted as some more exotic mechanism...
• It is very difficult to distinguish between the different contributions.

**Planar Oxygen**

- $Cu\ 3d_{x^2-y^2}$
- $O\ 2p_\sigma$
- $Cu\ 3d_{z^2}$
- $O\ 2p_z$
- $Cu_{II}$
- $Cu\ 4s$

**Planar Copper**

http://www.chemcomp.com
Comparing samples of different families:

The typical length changes, but the symmetries of the electronic wavefunctions do not change.

\[ \Delta v_Q C a^3_x = \Delta n_p \]

\( \nu_Q \) measures the number of planar oxygen 2p\( \sigma \) holes
The NMR Field Sweep Method

We measure at a constant frequency and change the external magnetic field. For each field we integrate the real part of the spectrum. The theoretical line is:

\[
S(H, f) = \sum_{m=-\frac{3}{2}}^{\frac{5}{2}} W(m) \int_{\nu=0}^{\infty} d\sigma'_{\text{iso}} e^{-\frac{1}{2} \left( \frac{\sigma'_{\text{iso}} - \sigma_{\text{iso}}}{\Delta \sigma'_{\text{iso}}} \right)^2} \int_{\nu=0}^{\infty} dv'_Q e^{-\frac{1}{2} \left( \frac{v'_Q - v_Q}{\Delta v'_Q} \right)^2} \cdot \int_{\theta=0}^{\pi} \cos(\theta) d\theta \int_{\phi=0}^{2\pi} d\phi \delta \left( f(H, m, \sigma'_{\text{iso}}, v'_Q, \eta, \theta, \phi, f) - f \right)
\]

\[
f(H, m, \sigma, v'_Q, \eta, \theta, \phi) = \gamma H \left[ 1 - \sigma_{\text{iso}} \right] + v_q \left[ \frac{1}{2} (3 \cos^2(\theta) - 1) - \frac{1}{2} \eta \sin^2(\theta) \cos(2\phi) \right]\left( m - \frac{1}{2} \right)
\]

where \( S(H, f) \) is the intensity at external field \( H \) and frequency \( f \).