Charge Density Waves and Superconductivity in High-$T_c$ materials

Ted Forgan

Elizabeth Blackburn, Amy Briffa, Martin Long (B’ham), Alex Holmes (Bham=>ESS)
Steve Hayden (Bristol) Johan Chang (Zurich)
Ed Yelland (ex St Andrews, Bristol)
Laurence Bouchenoire, Simon Brown (XMaS)
Ruixing Liang (UBC – Samples)
Georg Bednorz and Alex Muller’s discovery received the Nobel Prize 1987 for discovery of the first of the copper-oxide superconductors.

> 30 years & ~10^5 papers later and we still don’t understand these materials!

- applications are nothing like as widespread as hoped in those heady early days...

http://www.phys.ntnu.no/brukdef/prosjekter/super/Profiles/bednmull.jpg
High-$T_c$ properties versus hole doping

'\textit{Mott Insulator}'

Optimal doping

Underdoped

Pseudogap

Spin density wave

Non-Fermi Liquid

Overdoped

Fermi Liquid

Superconductor

modified from LCMI website
Some simple "chemistry"

La$_2$CuO$_4$

Lanthanum: 3+ ; La$_2$ => 6+
Oxygen: 2- ; O$_4$ => 8-

∴ Copper: 2+

Cu has 3d$^{10}$, 4s$^1$

∴ Cu$^{++}$ has 3d$^9$, i.e. 1 hole (unpaired electron) in the d-shell..

But La$_2$CuO$_4$ is a "Mott insulator": electron repulsion keeps them localised on Cu$^{++}$ and their spins line up antiferromagnetically.

Consider YBa$_2$Cu$_3$O$_7$: (slightly overdoped superconductor) Doing the same calculations, we get an average of 1.33 holes per Cu$^{2.33+}$

What happens as we go from an insulator to a metal?
High-\( T_c \) properties versus hole doping - current ideas

\[ T_c \& H_{c2} \text{ suppressed by Charge Density Wave} \]

\[ T^* \text{, Non-Fermi Liquid} \]

\[ \text{Fermi Liquid} \]

\[ \text{Pseudogap} \]

\[ \text{AF insulator} \]

\[ \text{CDW Superconductor} \]

\[ \text{doping =>} \]
Superconductivity vs. doping in YBCO

$B_{c2}$ drops down to $\sim 22$ T at the maximum CDW

Superconductivity vs. doping in YBCO

\[ T \text{ for } \rho = 0 \text{ as a function of doping for various fields.} \]

Superconductivity vs. doping in YBCO

\[ \frac{\delta E}{T_c^2} \] (J K^{-2} m^{-3})

\begin{align*}
\text{Hole doping, } p \\
0 & \quad 0.1 \quad 0.2 \quad 0.3
\end{align*}


Superconducting condensation energy versus doping.
Can the Charge Density Wave be avoided?

Not very good error bars, but it appears that pressure suppresses the CDW.

The max. value of $T_c$ rises and moves closer to the AFM region.

So it is important to understand the CDW.

What “should” a High- $T_c$ Fermi Surface look like?

2-dimensional: – look at $ab$ plane cross-section

Brillouin Zone holds 2 electrons or holes/cell

1 hole/Cu at zero doping: $\rho = 0$

This area would be $\propto (1+\rho)$ if all the electrons are free to move.
ARPES (photo-electron spectroscopy) shows changes in Fermi Surface with doping


“Fermi arc”

FS ends removed by “pseudogap”

Full Fermi surface
Some Quantum Oscillation Data

Overdoped – all holes visible – obeys Luttinger theorem

B. Vignolle et al. Comptes Rendus Physique (2011)

Underdoped – tiny number of electrons not holes

N.B. QOs give the area of the electron pocket, not shape
At low T, the Hall effect changes sign in underdoped YBCO$_y$

This suggests that for doping levels around $p \sim 1/8$
the Fermi surface changes topology below $\sim T_0$ ...

... from big hole FS ($R_H$ small, +ve ) to tiny electron FS ($R_H$ large, -ve )
What do we think is causing this?

Charge Density Wave (CDW) order - a tiny modulated charge density - and associated lattice distortion, - which forms in a wide range of slightly under-doped cuprate high-$T_c$ materials.

It is centred on the CuO$_2$ layers and competes with superconductivity.

Exaggerated view of CuO$_2$ plane displacements (oxygen, copper).

This CDW order has an incommensurate period ~3 unit cells along both $a$ and $b$. ($a$ shown)

It disappears as doping is increased to about optimum for superconductivity.
Observing the CDW by diffraction - 100 keV X-rays, 17 T

Our first experiment: was on YBCO\textsubscript{6.67} 3.1 x 1.7 x 0.6 mm\textsuperscript{3} 99\% detwinned \(T_c = 67\) K

Others measured at zero field using Cu-L-edge resonant X-rays*

BW5 - on DORIS (RIP), HASYLAB, DESY, Hamburg - using the Birmingham beamline cryomagnet - taken there by truck

Our results: a Field- & Temperature-dependent diffracted peak

\[ q_1 = (0.305, 0, 0.5) \]

Intensity: few \( \times 10^{-6} \) of the (200) (strongest charge peak)

Incommensurate

At zero field, adjacent cells along the \( c \)-direction in antiphase

Accompanied by a similar modulation along \( b \)
What happens as we change temperature?

CDW Peak is always finite width - order is finite range

CDW Peak disappears at high $T$

No field-dependence above superconducting $T_c$

However, at low $T$, superconductivity is suppressed by the B-field, and the CDW intensity increases
What happens as we change temperature?

\[
\begin{align*}
&\text{Intensity (counts/second)} \\
&0\quad 20\quad 40\quad 60\quad 80\quad 100\quad 120\quad 140\quad 160 \\
&0\quad 40\quad 80\quad 120\quad 160
\end{align*}
\]

\[T_{C} (= 67 \text{ K})\]

CDW & superconductivity compete
What happens as we change temperature?

![Graph showing temperature vs. intensity](image)

- $T_c (= 67 \text{ K})$
- 0 T
- 7.5 T
What happens as we change temperature?

![Graph showing intensity vs. temperature for different magnetic fields.](image)
What happens as we change temperature?

B-field suppresses superconductivity, enhances CDW
Field dependence of CDW Intensity

not quite saturated

Above $T_c$: no effect of B-field on CDW

High- $T_c$ properties versus hole doping including CDW
What is the *structure* of Charge Density Waves?

Measure sufficiently many (>200) different X-ray diffraction satellites due to the CDWs to derive the atomic displacements that fit the data. Needs zero $B$-field for flexibility.

If possible, deduce something about the physics of the CDW from these atomic displacements.

But non-resonant X-rays see ALL the 13 atoms in the YBCO unit cell, so the results are difficult to analyse!

Group theory allows us to solve this problem; the symmetry of the derived displacements is quite surprising.

We then use the properties of the CDW to propose how the Fermi Surface reconstruction occurs - and learn something about High-$T_c$.
Apparatus: the XMaS (UK) beamline at ESRF

4-circle geometry allows wide range of CDW reflections

Sample mounted on cryocooler & covered with Beryllium dome

14 keV X-rays into detector reflect from c-face of sample
Considerations used in analysis of results

Non-resonant X-rays are insensitive to small charge density changes.
Instead they respond to the associated/resultant atomic displacements from their usual positions.
(because ALL the electrons in a displaced atom scatter X-rays)

A single CDW can be described by an incommensurate $q$-vector along either the $x$ or $y$ ($a$ or $b$) crystal directions.

Adjacent unit cells in the $c$-direction are in antiphase (Doubled cell indicated by CDW satellites at half-integral $\ell$)

CDWs are longitudinal, with atomic displacements (e.g. for $q \parallel y$) along both $y$ & $z$ directions.
Temp-dependence of CDW order in YBCO$_{6.54}$

Make all observations of CDW intensities at $T_c$ (superconductivity) = 60 K
Typical observations of CDW satellites at 60 K

- $(0, 1-q, 16.5)$ strong
- $(0, 1-q, 15.5)$ weak
- $(0, 3+q, 4.5)$ too weak to see
- $(0, 1-q, 4.5)$ occasional spurion
A typical CDW satellite intensity pattern

You can always get from a model to the diffraction pattern - but not vice versa

not a simple pattern
so the displacements
do not involve just
one or two atoms

A total of 269 satellite positions observed for $q_b$
and 193 for $q_a$

Area of circle $\propto$ Intensity

blank = not measured
We expect atomic displacements with this symmetry

\[ \leftrightarrow \text{ motion is even in } z \text{ about bilayer, and } \uparrow \downarrow \text{ is odd in } z \]

Next unit cell in antiphase 
(\( \equiv \ell = 0.5 \))

Expected structure of the CDW order

\[ \text{CDW} \leftrightarrow \text{atomic displacements} \]

also \( \exists \) c-axis displacements

\[ \Rightarrow \text{total of 13 atomic motion variables to fit the data} \]
How to deduce atomic displacements $u$ in the CDW

CDW satellite intensities are proportional to $(Q \cdot u)^2$
So we can detect basal and $c$-axis displacements $u_y u_z$.

- $Q \sim (0, 0.3, 5.5)$ sensitive to $u_x$'s
- $q \sim (0, 0.3, 0.5)$

$b*c*$ plane of reciprocal space:
- typical lattice Bragg peak
- typical CDW satellite

... but 1.6 million attempts
(different initial signs/values of 13 variables)
failed to iterate to a fit of the data!
Only other possible model for the atomic movements.

We are forced to consider displacements of this *symmetry*:

\[ \uparrow \downarrow \text{ motion even in } z \text{ about bilayer, and } \leftrightarrow \text{ odd in } z \]

CuO\textsubscript{2} bilayers *sheared* - not compressed

Next unit cell in antiphase ($\equiv \ell = 0.5$)

$y$ & $z$ atomic displacements $\Rightarrow$ total of 13 variables

fits the data!
Good fit - bad fit...

CuO$_2$ bilayers sheared

CuO$_2$ bilayers compressed
The motif which is modulated to form the CDW

- from the results of the good fit to the $q_b$ mode

For each atom, $r_0 \rightarrow r_0 + u(r_0)$

$u(r_0) = u_c \cos (q \cdot r_0) + u_b \sin (q \cdot r_0)$

In zero field, next unit cell along $c$ is in antiphase
The motif which is modulated to form the CDW

- concentrating on the c-axis displacements which dominate

“The change in strain is mainly out of plane”

Cu’s in the planar bilayers move together
- with the Y’s

Actual amplitude ~ $10^{-3}$ of an atomic spacing!

Can this tiny effect be important? Yes!

CuO chains don’t move (symmetry)
Resulting modulated ionic displacements

period only ~ 3 unit cells
so $\pi$ phase change in only $1\frac{1}{2}$ cells

not tilted CuO$_5$ half-octahedra

Plus a similar modulation in the perpendicular direction

Almost certainly in the same region of space:

“double-$q$” or “biaxial” order $\Rightarrow$ Fermi surface reconstruction
STM suggests “\(d\)-density wave” on planar oxygens

A \(\text{CuO}_2\) plane

\[\text{Strong evidence for this from STM measurements in Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \& \text{Ca/NaCuO}_2\text{Cl}_2\]

... but this looks like our unsuccessful model!

S. Sachdev & J.C. Seamus Davis group, PNAS 2014
A plot of the modulated oxygen $z$-displacements

for a single CDW mode

modulation direction $\Rightarrow$

You have seen this pattern before...

Motion of an ion in the $z$-direction can alter the local doping

So our CDW shear is a “bond $\sigma$-density wave”

CDW Structure determination: Nature Comms. 2015
Electron states in a CuO$_2$ bilayer in YBCO$_{6.5}$

Superconductivity resides mainly in the CuO$_2$ planes

Cu O chains: O $\frac{1}{2}$ occupied
- electrically inactive

Cu O$_2$ plane

Y layer

Cu O$_2$ plane

"A"

"B"

There are two ways of combining the wavefunctions of the states in the two halves of a bilayer
Single-layer & Bilayer Fermi Surfaces - no reconstruction

1-layer

hole surface

filled states

2-layer

"A"

"B"
Reconstruction by CDW with basal wavevectors $\delta_a$ & $\delta_b$

states can pick up
wavevector of CDW
Reconstruction by CDW with basal wavevectors \( \delta_a \) & \( \delta_b \)

states can pick up wavevector of CDW

and may hybridise where degenerate
Reconstruction by CDW with basal wavevectors $\delta_a$ & $\delta_b$

states can pick up wavevector of CDW

and may hybridise where degenerate

$\frac{1}{2}(\delta_a, \delta_b)$

$A - B$ degeneracy

$A - A$ & $B - B$ degeneracy
Reconstruction by CDW with basal wavevectors $\delta_a$ & $\delta_b$

states can pick up wavevector of CDW

and may hybridise where degenerate

$A - B$ degeneracy

$A - A$ & $B - B$ degeneracy
Due to bilayer-split FS, QO results in YBCO show multiple Fermi Surface areas

How does this all hold together? “SU(2) theory”

A CDW can be regarded as the Bose condensation of electron-hole pairs

A superconductor can be regarded as the Bose condensation of electron-electron (Cooper) pairs

An underdoped cuprate has a superposition of both orders related by an SU(2) symmetry

How does antiferromagnetism come in?
The CDW occurs near the AFM “hot spots” where the SU(2) symmetry is exact and AFM fluctuations cause pairing
How does this all hold together? “SU(2) theory”

calculation* of SU(2) fluctuations vs. doping =>

It is proposed that these fluctuations create the pseudogap
- which removes the ends of the “Fermi arcs”
- and creates the conditions for the CDW and Fermi Surface reconstruction to occur

*C. Pepin group, Phys Rev. B 95 104510 (2017)
How High- $T_c$ theory appears to me in 2017

CDW appears in fairly flat parallel regions of Fermi surface

Antiferromagnetic fluctuations link CDW & Superconductivity

The CDW and the superconductivity share the same $d$-wave symmetry (though they don’t need to by theory), and they compete for the same electrons

Highest $T_c$ where SU(2) fluctuations/pseudogap are reduced

Workers on LBCO or LSCO who see antiferromagnetic + CDW stripes as important would not agree!
Some numerology

Kamerlingh Onnes 1911  - explained 46 years later

- or 32 years after Quantum Mechanics came along in 1925
Some numerology

John Bardeen, Leon Cooper & Bob Schrieffer 1957

Kamerlingh Onnes 1911 - explained 46 years later
- or 32 years after Quantum Mechanics came along in 1925
- 1986 + 32 = 2018 - are we approaching the explanation of HiTc?
That's all Folks!