Title: NMR signature of charge order in high Tc cuprates revisited

Date: May 25, 2017 11:00 AM

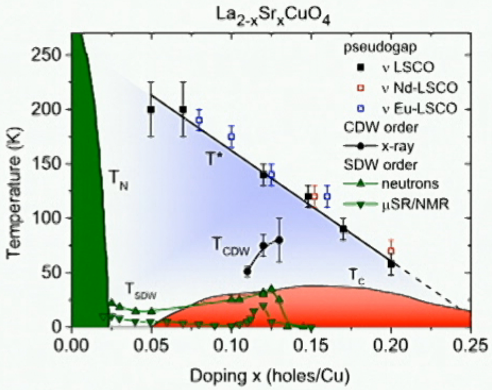
URL: http://pirsa.org/17050084

Abstract: In 1999, A. W. Hunt et al. discovered that all the NMR anomalies detected at the charge density wave (CDW) order transition Tcharge ~ 60 K of nearly non-superconducting La1.48Nd0.4Sr0.12CuO4 are shared by superconducting La1.88Sr0.12CuO4 (Tc ~ 30K) [1]. The unexpected finding inevitably led us to conclude that charge order must exist even in the superconducting La2-xSrxCuO4, sending a shockwave in the high-Tc community [2]. Subsequent search of charge order peaks based on scattering techniques, however, failed to detect additional evidence for charge order until very recently. In view of the recent confirmation of charge order in many superconducting cuprates by X-ray diffraction techniques, we revisit the old problem of charge order using newer NMR techniques that have become available in recent years.

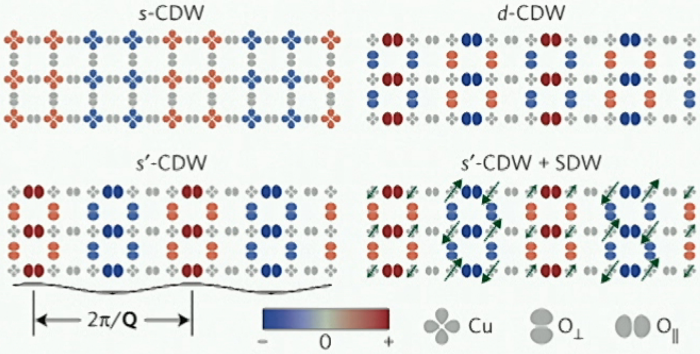
NMR signature of charge order in high T_c cuprates revisited --- ^{63}Cu and ^{139}La NMR study of $La_{1.885}Sr_{0.115}CuO_4$ (T_c~31K, T_{charge}~80K) using a modern 21st century NMR spectrometer

Takashi Imai
McMaster University and CIFAR

T. Imai, M. Fujita, W. He, Y.S. Lee *et al.*, in preparation.
A.W. Hunt, P.M. Singer, T.Imai *et al.*, PRL **82** (1999) 4300; PRB **64** (2001) 134524.



Phase diagram by
Croft et al. PRB **89** (2014) 224513



Charge density pattern examined by
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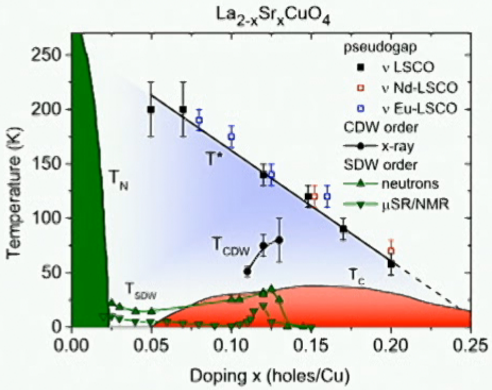

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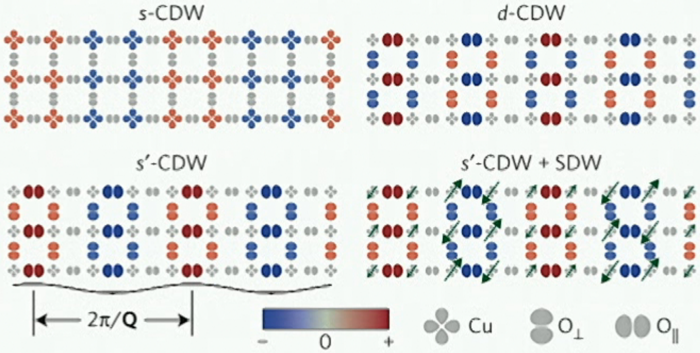

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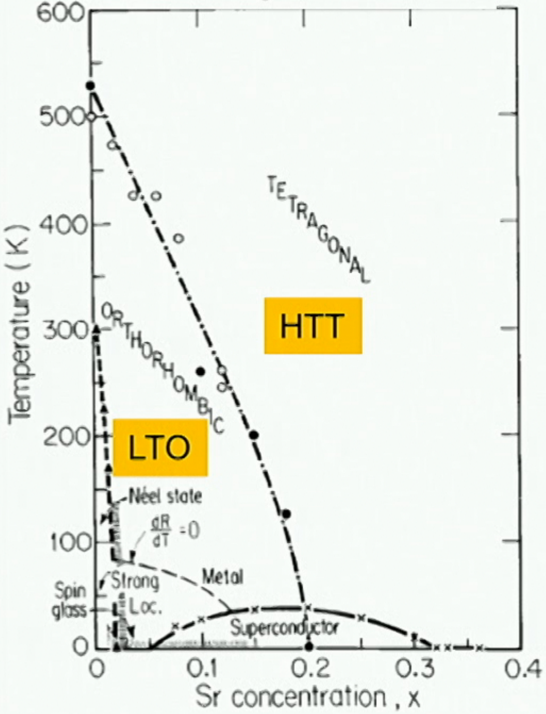
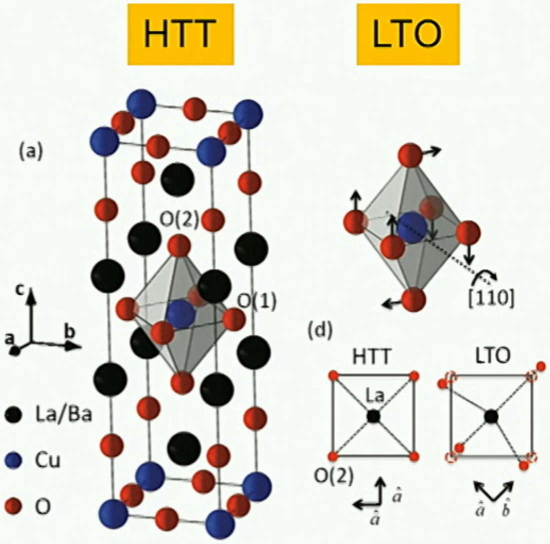
“Original” phase diagram of $La_{2-x}Sr_xCuO_4$ high T_c cuprates in the early 1990’s

Shirane, Birgeneau





“1/8 anomaly” : Nd^{3+} substitution into La^{3+} sites of La$_{2-x}$Sr$_x$CuO$_4$ stabilizes the LTT structure and suppresses T$_c$ around x ~ 1/8

M.K. Crawford *et al.*, PRB **44** (1991) 7749

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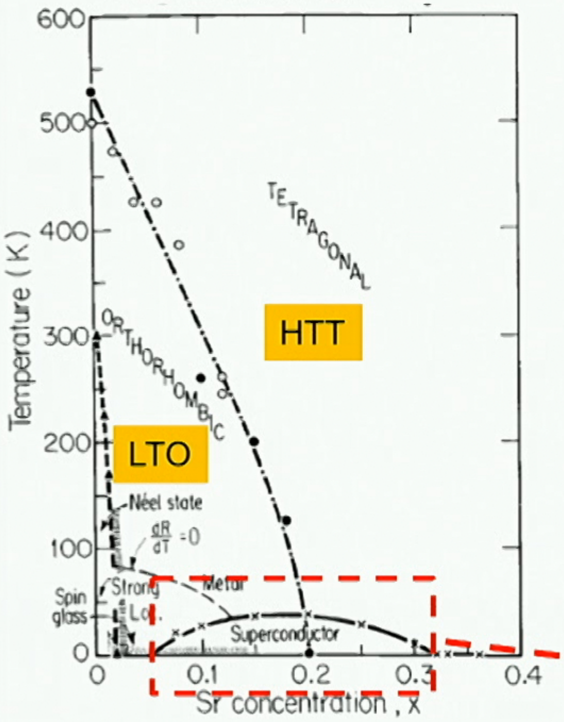
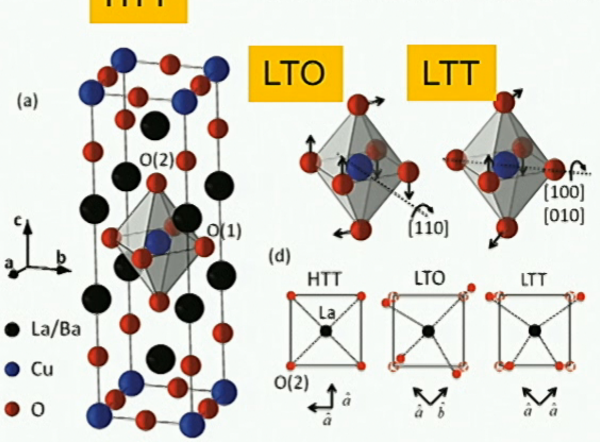
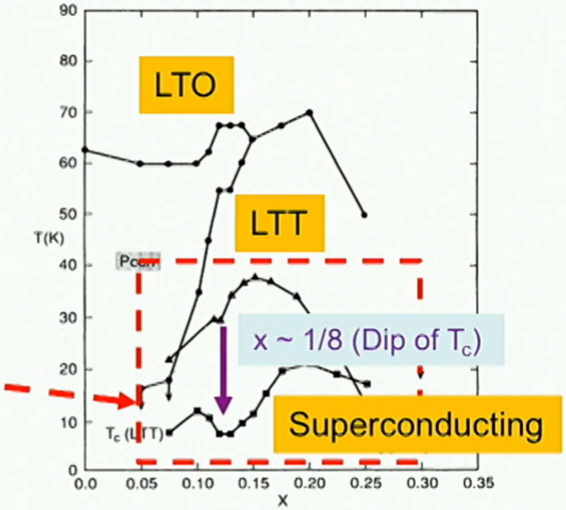
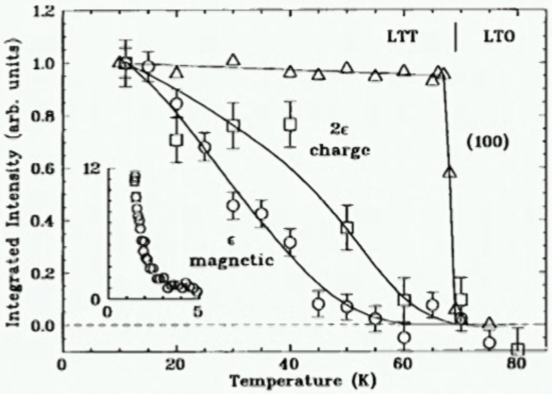






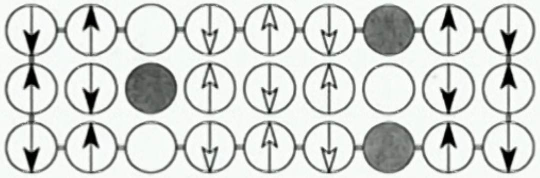
x ~ 1/8 (Dip of T$_c$)

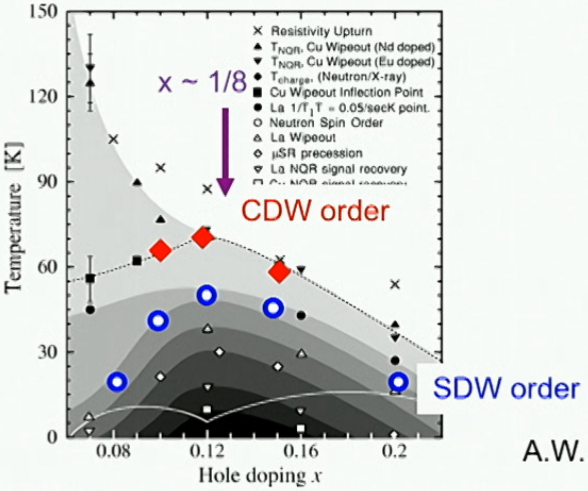
The 1/8 anomaly in the phase diagram of $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ high T_c cuprates arises from Charge and Spin Density Wave Orders



J. Tranquada *et al*., Nature **375** (1995) 561

(Note: the SDW order was first discovered for the 1/8 phase of $La_{1.875}Ba_{0.125}CuO_4$ by G. Luke et al., Physica C **185-189** (1991) 1175).





A.W. Hunt, T.I. *et al*., PRB **64** (2001) 134524

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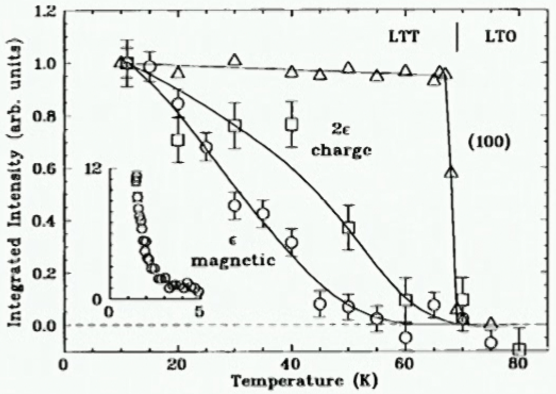

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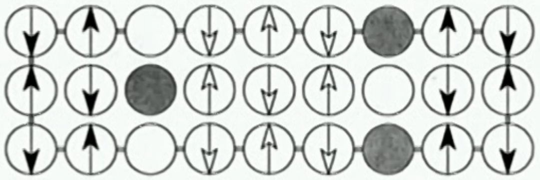

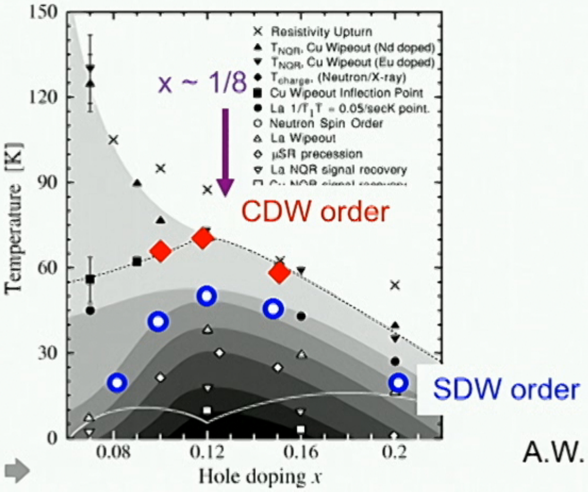

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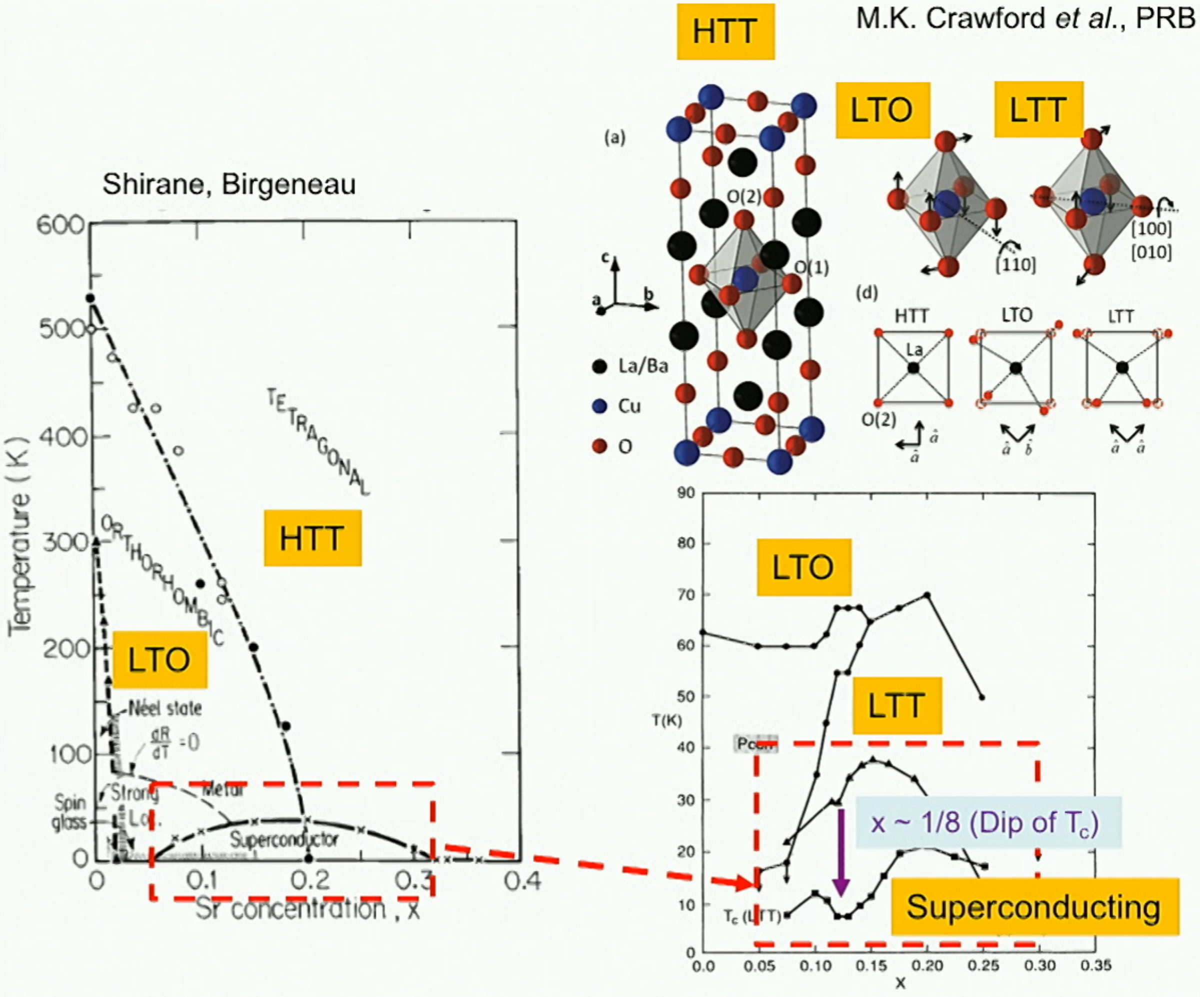

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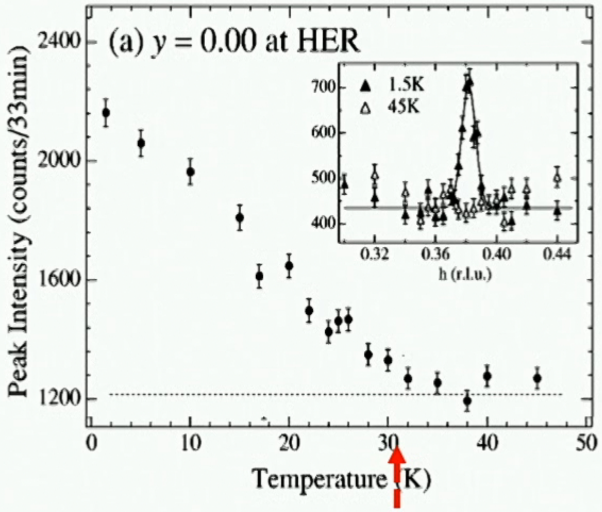
July 1998: it turned out that the SDW anomaly for x ~ 1/8 exists even in superconducting $La_{1.88}Sr_{0.12}CuO_4$ with the LTO structure (without the LTT structural phase transition)

Magnetic Bragg peak intensity in $La_{1.88}Sr_{0.12}CuO_4$

Kimura et al., PRB **59** (1999) 6517



$T_{c\,(onset)}$ ~ 31 K

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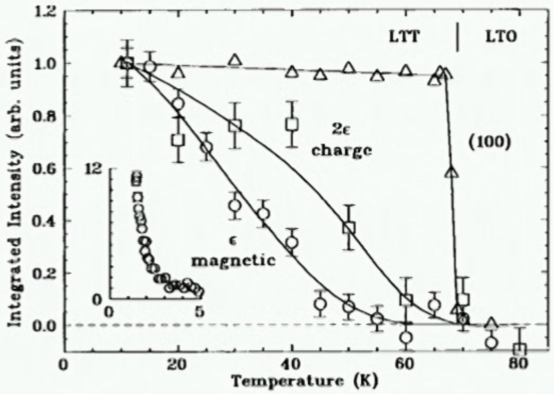

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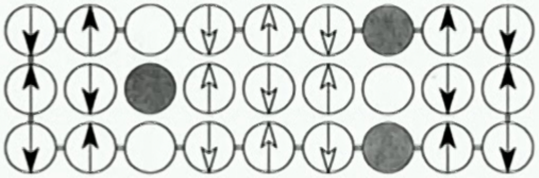

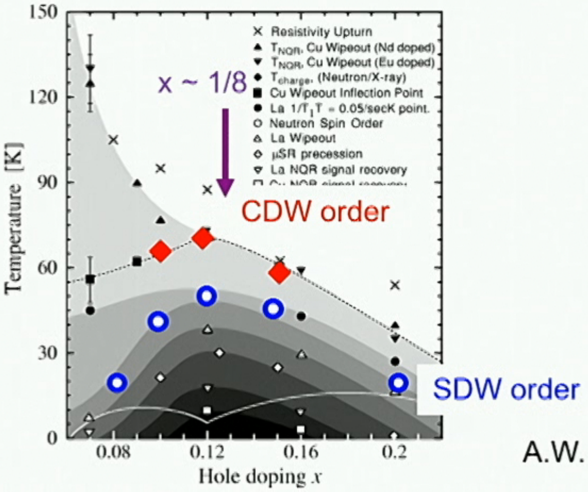

x ~ 1/8

CDW order

SDW order

A.W. Hunt, T.I. *et al.*, PRB **64** (2001) 134524

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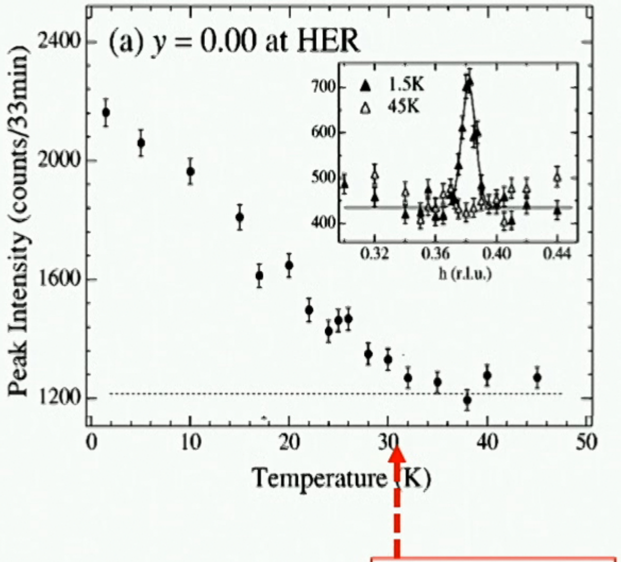

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Does superconducting $La_{1.88}Sr_{0.12}CuO_4$ also undergo a CDW order?

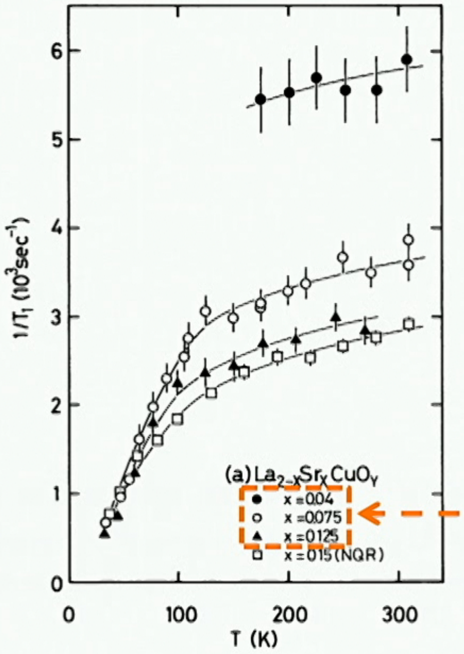
From the late 1980's, we knew that ^{63}Cu NMR signals in LSCO (x ~ 1/8) begin to lose its intensity below about 50 K. We didn't know why. Is it related to charge order?!

Journal of The Physical Society of Japan
Vol. 59, No. 11, November, 1990, pp. 3846-3849

LETTERS

^{63}Cu NMR Study of Spin Dynamics in $La_{2-x}(Sr, Ba)_xCuO_y$ $(0.04 \leqq x \leqq 0.16,\ 3.99 \leqq y \leqq 4.03)$

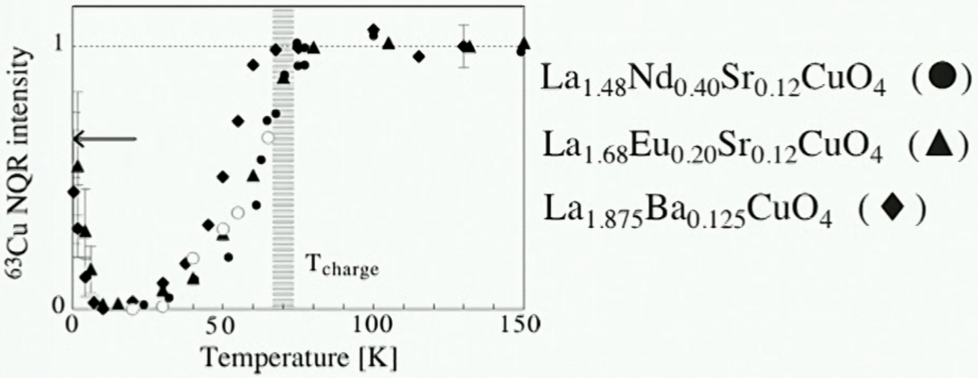
Takashi IMAI, Kazuyoshi YOSHIMURA,[†] Takashi UEMURA,[†]
Hiroshi YASUOKA and Koji KOSUGE[†]

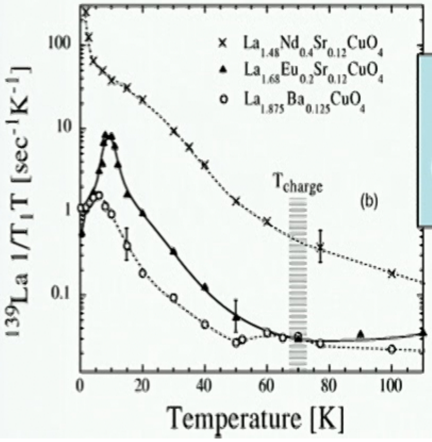


"New data" of 1990 didn't even show results at lower temperatures, because paramagnetic ^{63}Cu NMR signals disappear, a mystery at that time.

Confirmation: $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ indeed shows analogous ^{63}Cu NMR signal intensity anomaly exactly at the CDW order temperature, T_{charge} ~ 65 K, accompanied by enhanced spin fluctuations

A.W. Hunt, T.I. *et al.*, PRB **64** (2001) 134524





$$(T_1T)^{-1} \sim \frac{\sum_{\vec{q}\in B.Z.} \chi''(\vec{q}, f_{NMR})}{f_{NMR}}$$

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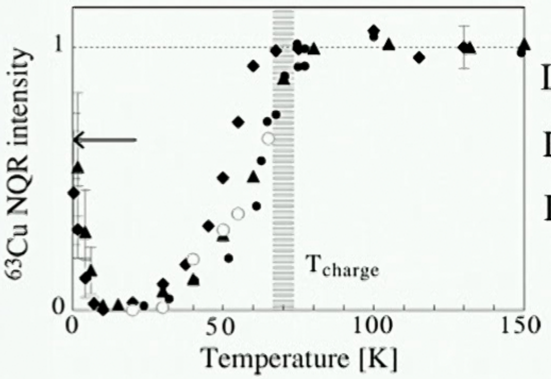
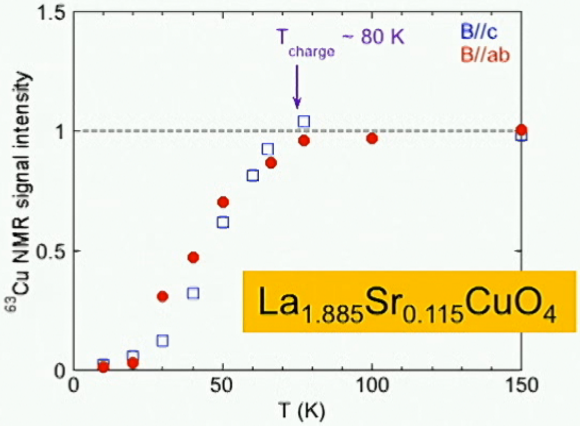
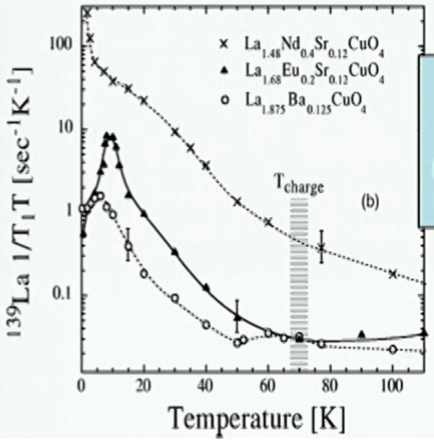


$La_{1.48}Nd_{0.40}Sr_{0.12}CuO_4$

$La_{1.68}Eu_{0.20}Sr_{0.12}CuO_4$

$La_{1.875}Ba_{0.125}CuO_4$ (◆

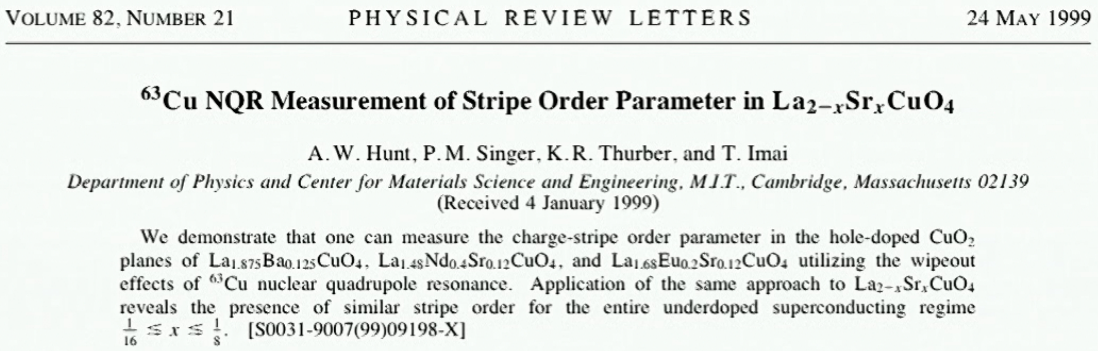




$(T_1T)^{-1}$

^{63}Cu single crystal NMR data of $La_{1.885}Sr_{0.115}CuO_4$ shows analogous anomalies below as high as T_{charge} ~ 80 K!!

T. Imai and K. Hirota
Unpublished data first presented at Aspen Winter Conference on *Quantum Critical Phenomena* in January 1999.
(T_{charge} ~ 80 K seemed too high, as there is no LTT transition)



VOLUME 82, NUMBER 21 PHYSICAL REVIEW LETTERS 24 MAY 1999

^{63}Cu NQR Measurement of Stripe Order Parameter in $La_{2-x}Sr_xCuO_4$

A. W. Hunt, P. M. Singer, K. R. Thurber, and T. Imai

Department of Physics and Center for Materials Science and Engineering, M.I.T., Cambridge, Massachusetts 02139

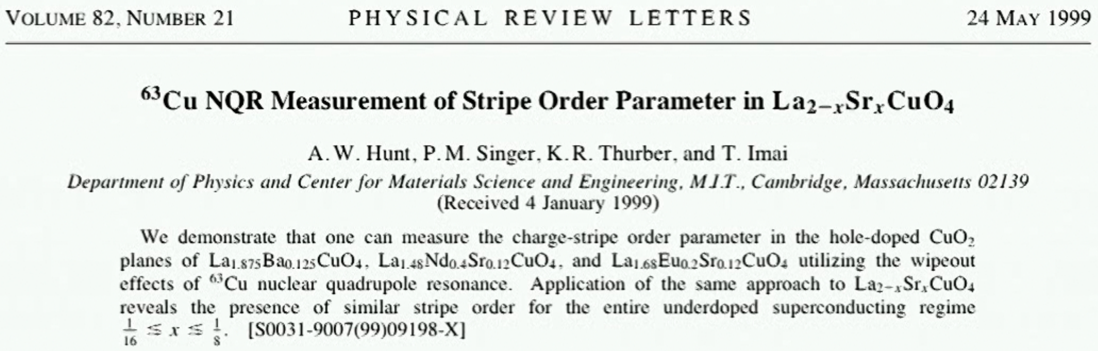
(Received 4 January 1999)

We demonstrate that one can measure the charge-stripe order parameter in the hole-doped CuO_2 planes of $La_{1.875}Ba_{0.125}CuO_4$, $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$, and $La_{1.68}Eu_{0.2}Sr_{0.12}CuO_4$ utilizing the wipeout effects of ^{63}Cu nuclear quadrupole resonance. Application of the same approach to $La_{2-x}Sr_xCuO_4$ reveals the presence of similar stripe order for the entire underdoped superconducting regime $\frac{1}{16} \lesssim x \lesssim \frac{1}{8}$. [S0031-9007(99)09198-X]

The primary conclusion: $La_{1.88}Sr_{0.12}CuO_4$ (as well as $La_{1.68}Eu_{0.2}Sr_{0.12}CuO_4$, $La_{1.88}Ba_{0.12}CuO_4$, and La_2CuO_{4+y}) undergoes charge order at a comparable temperature as $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$

Highlighted in Science magazine in 1999 & cited over 200 times to date

A big problem…… Nobody else could confirm charge order ***for years***



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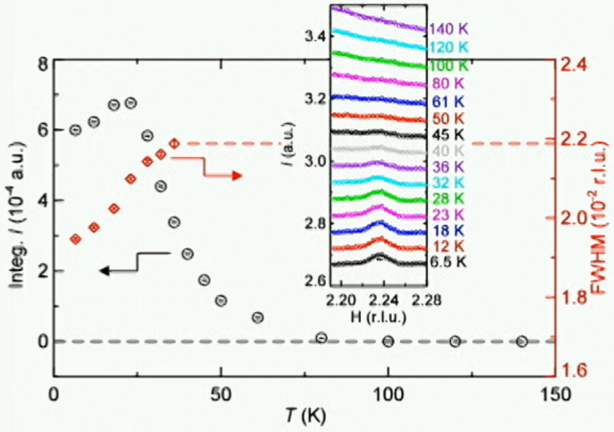
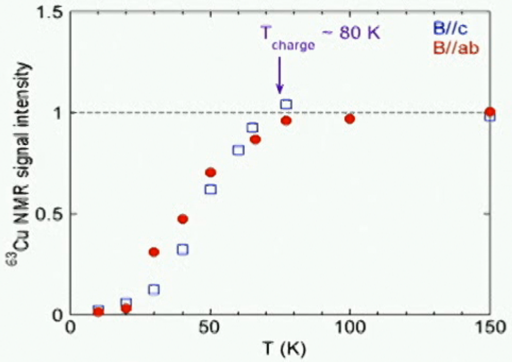


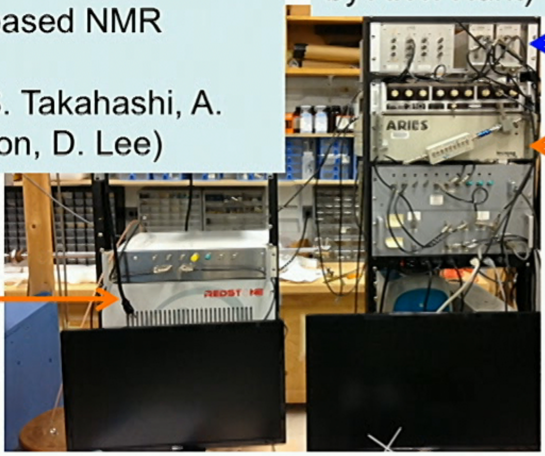


W. He, Y.S. Lee, M. Fujita et al. (Stanford/Tohoku 2017)
Also see Croft (PRB 2014) & Thumpy (PRB 2014)

T. Imai and K. Hirota (1999)

We have been finally vindicated(!!) and charge order exists even in superconducting $La_{1.88}Sr_{0.12}CuO_4$ etc. (although new comers don't even know the raging battle in ~1999).

But a question remains: why did charge order led to those NMR anomalies?
Let's revisit using modern NMR techniques.



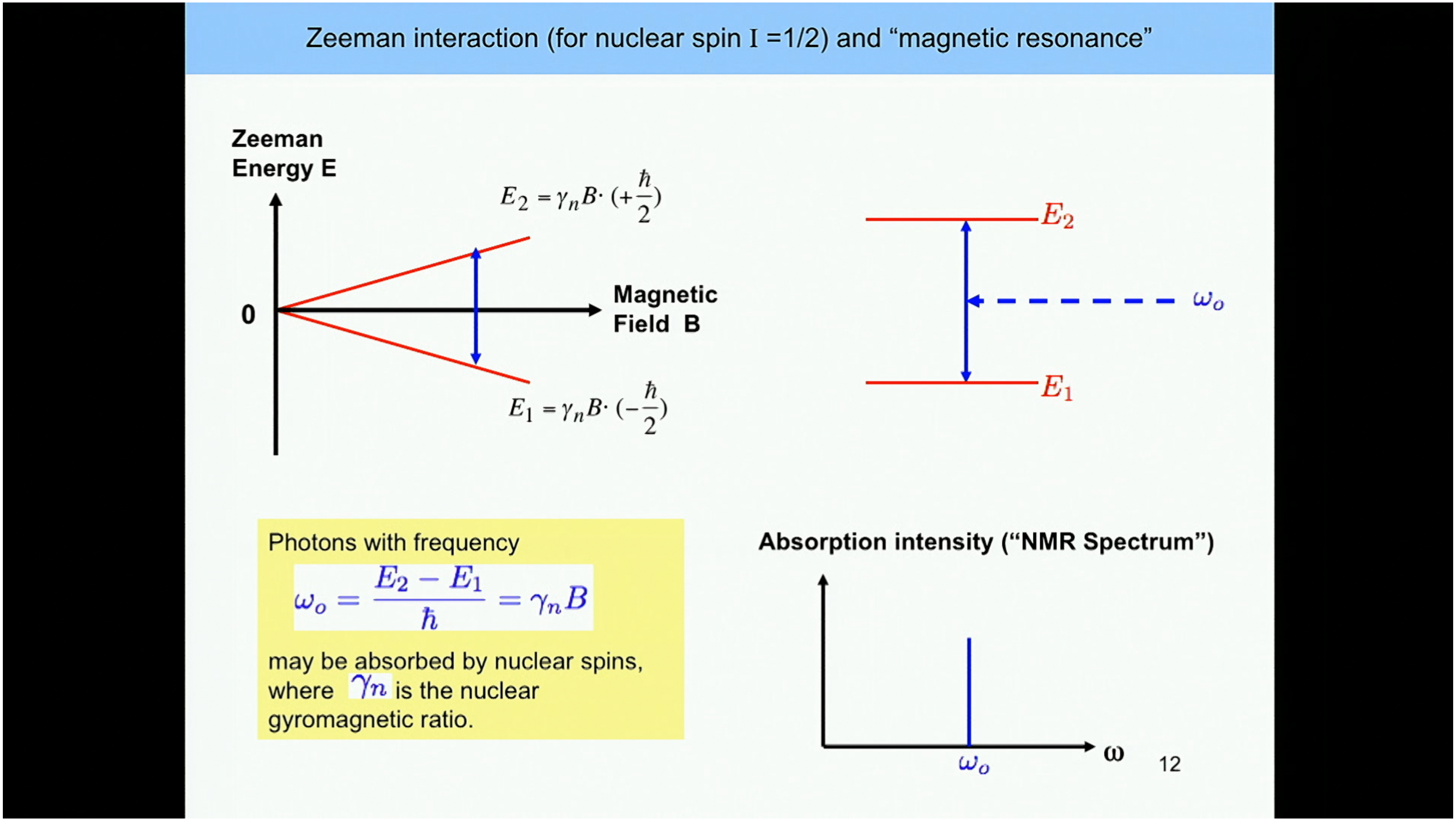
Old "Aries"-based NMR spectrometer (ca.1996, set up by A.W. Hunt)

New "Redstone"-based NMR spectrometer
(2016, set up by S. Takahashi, A. Arseneault, A. Acton, D. Lee)

Homemade analog video amplifiers

"Aries" =
(12 bits averager that requires signal boost with analog video amplifiers). Operating system is Apple G3 or earlier.

"Redstone" =
(all-in-one digital "black box" with 24 bits averager)



Zeeman interaction (for nuclear spin I =1/2) and “magnetic resonance”

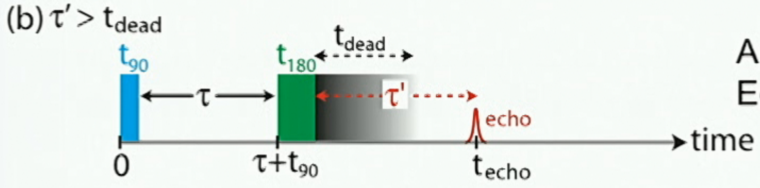
Photons with frequency

$$\omega_o = \frac{E_2 - E_1}{\hbar} = \gamma_n B$$

may be absorbed by nuclear spins, where γ_n is the nuclear gyromagnetic ratio.

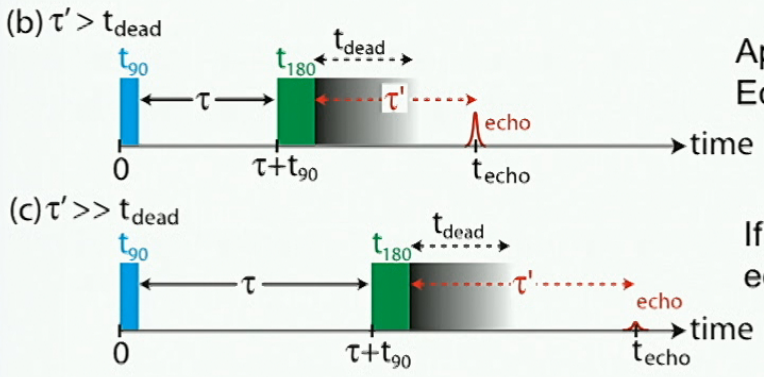
Absorption intensity (“NMR Spectrum”)

How do we detect NMR spin-echo signals?



Apply 90 & 180 degree RF pulses, separated by τ.
Echo appears $\tau' = \tau + t_{180}/\pi$ after we turn off 180.

How do we detect NMR spin-echo signals?



Apply 90 & 180 degree RF pulses, separated by τ. Echo appears $\tau' = \tau + t_{180}/\pi$ after we turn off 180.

If $\tau' >> T_2$ (the transverse relaxation time), the echo becomes small.

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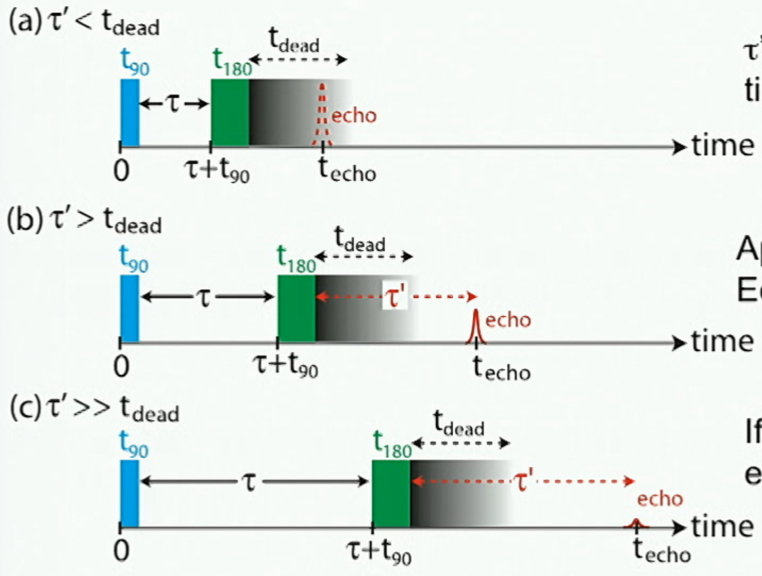

τ' must be longer than the spectrometer dead-time, $t_{dead} \sim 2\mu s$, to observe the echo.

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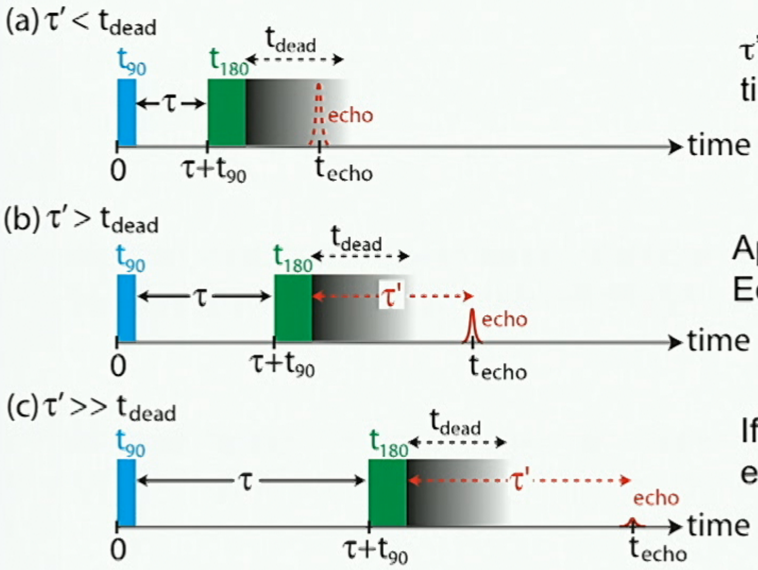

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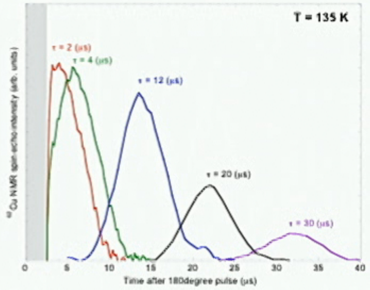
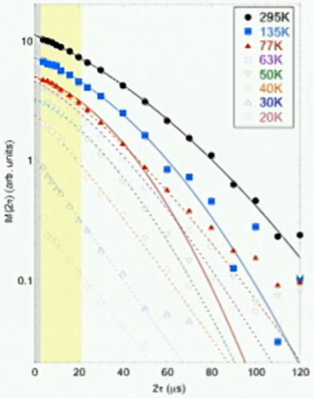


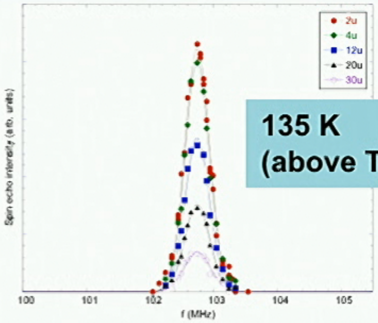


$t_{dead} \sim 12\ \mu s$ for Aries (1999)

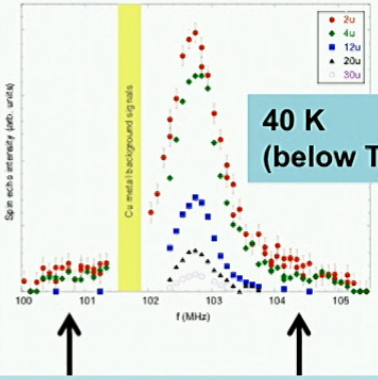
$t_{dead} \sim 2\ \mu s$ for Redstone (2017)

We can detect fast phenomena with newer NMR spectrometers

^{63}Cu NMR lineshapes of $La_{1.885}Sr_{0.115}CuO_4$ single crystal (9T || c-axis)



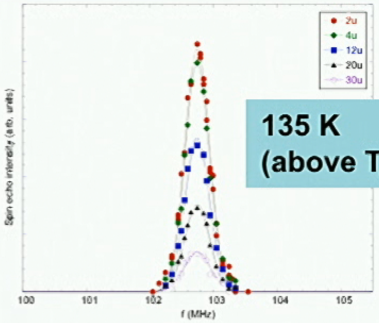
135 K
(above T_{charge}~ 80K)



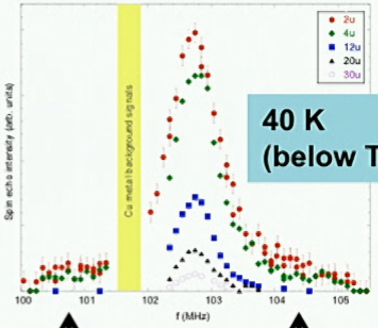
40 K
(below T_{charge}~ 80K)

New, broad wings appear in the charge ordered state below T_{charge} = 80K if we use very short τ = 2 or 4 μs. Our old NMR spectrometers used in the 1990's had analog video-amplifiers with t_{dead} ~ 12 μs, and we were unable to detect these very fast signals.

^{63}Cu NMR lineshapes of $La_{1.885}Sr_{0.115}CuO_4$ single crystal (9T || c-axis)



135 K
(above T_{charge}~ 80K)



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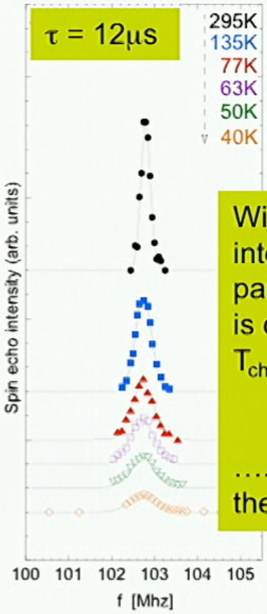
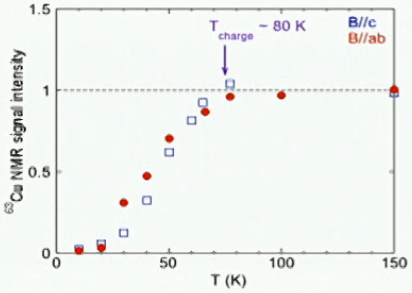


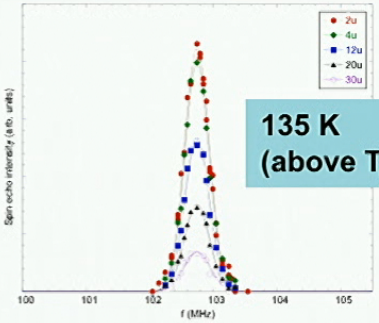
With fixed τ =12 μs, the integrated intensity of the paramagnetic NMR signal is conserved down to T_{charge}~80K, then….

…..gradually wiped out in the charge ordered state.

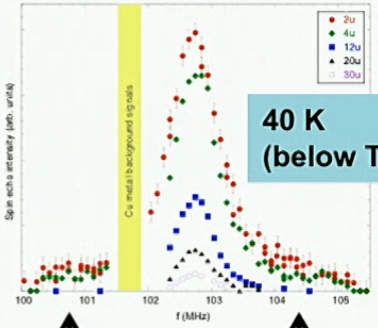


18

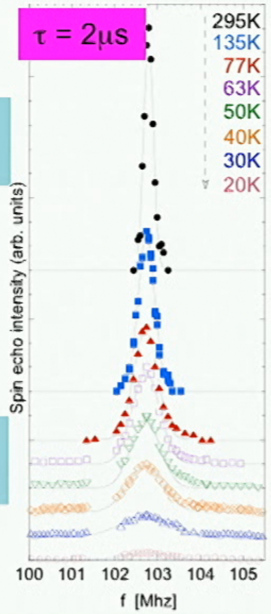
^{63}Cu NMR lineshapes of $La_{1.885}Sr_{0.115}CuO_4$ single crystal (9T || c-axis)

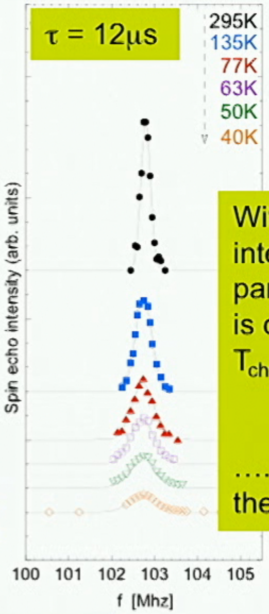


135 K
(above T_{charge}~ 80K)



40 K
(below T_{charge}~ 80K)





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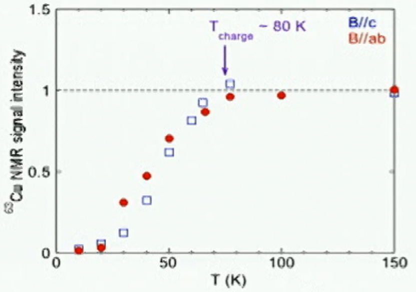
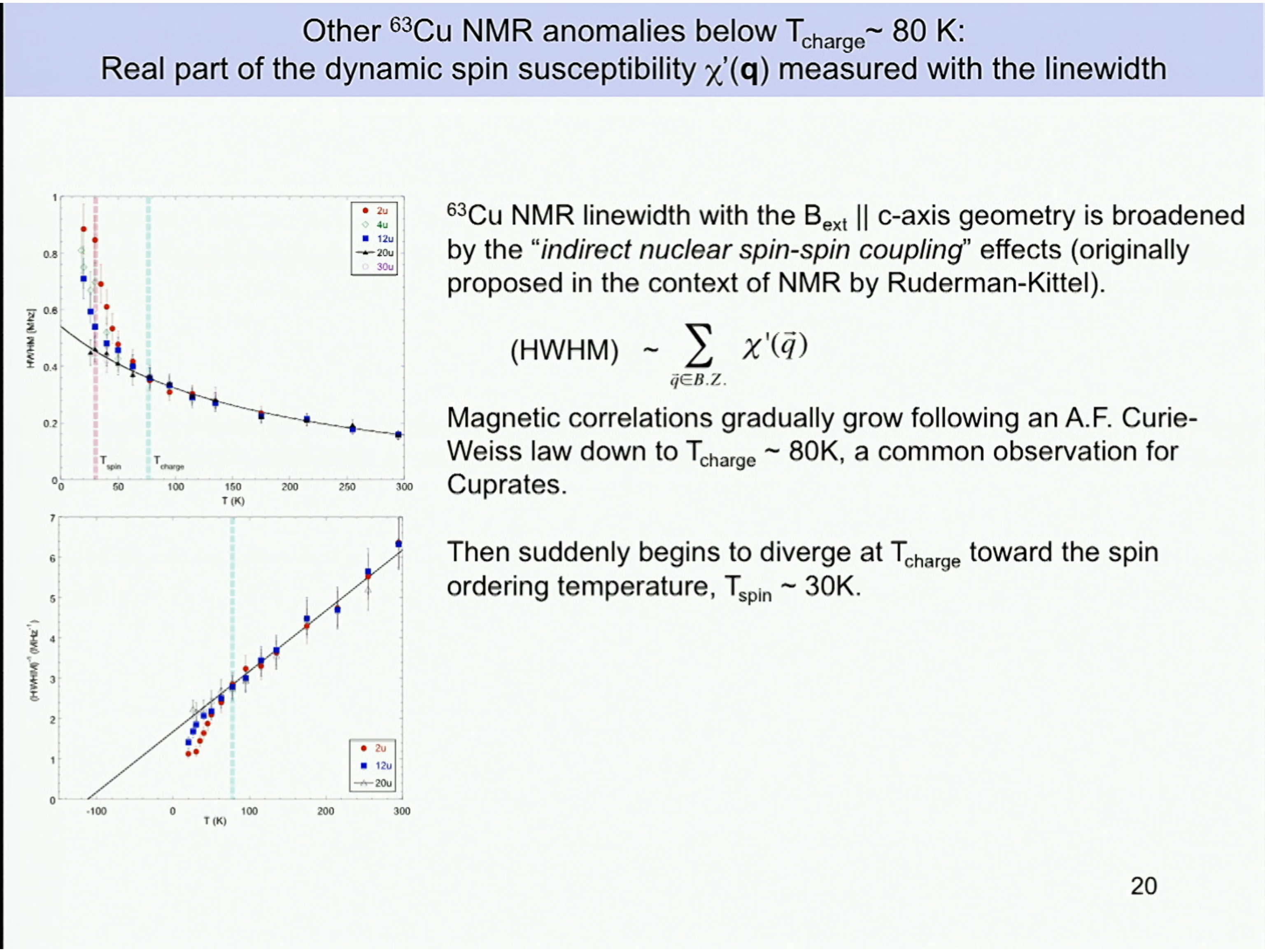


With fixed τ =2 μs, the missing spectral weight shifts to the "wing" parts.

New, broad wings appear in the char
below T_{charge} = 80K if we use very short τ = 2 or 4 μs. Our old NMR spectrometers used in the 1990's had analog video-amplifiers with t_{dead} ~ 12 μs, and we were unable to detect these very fast signals.



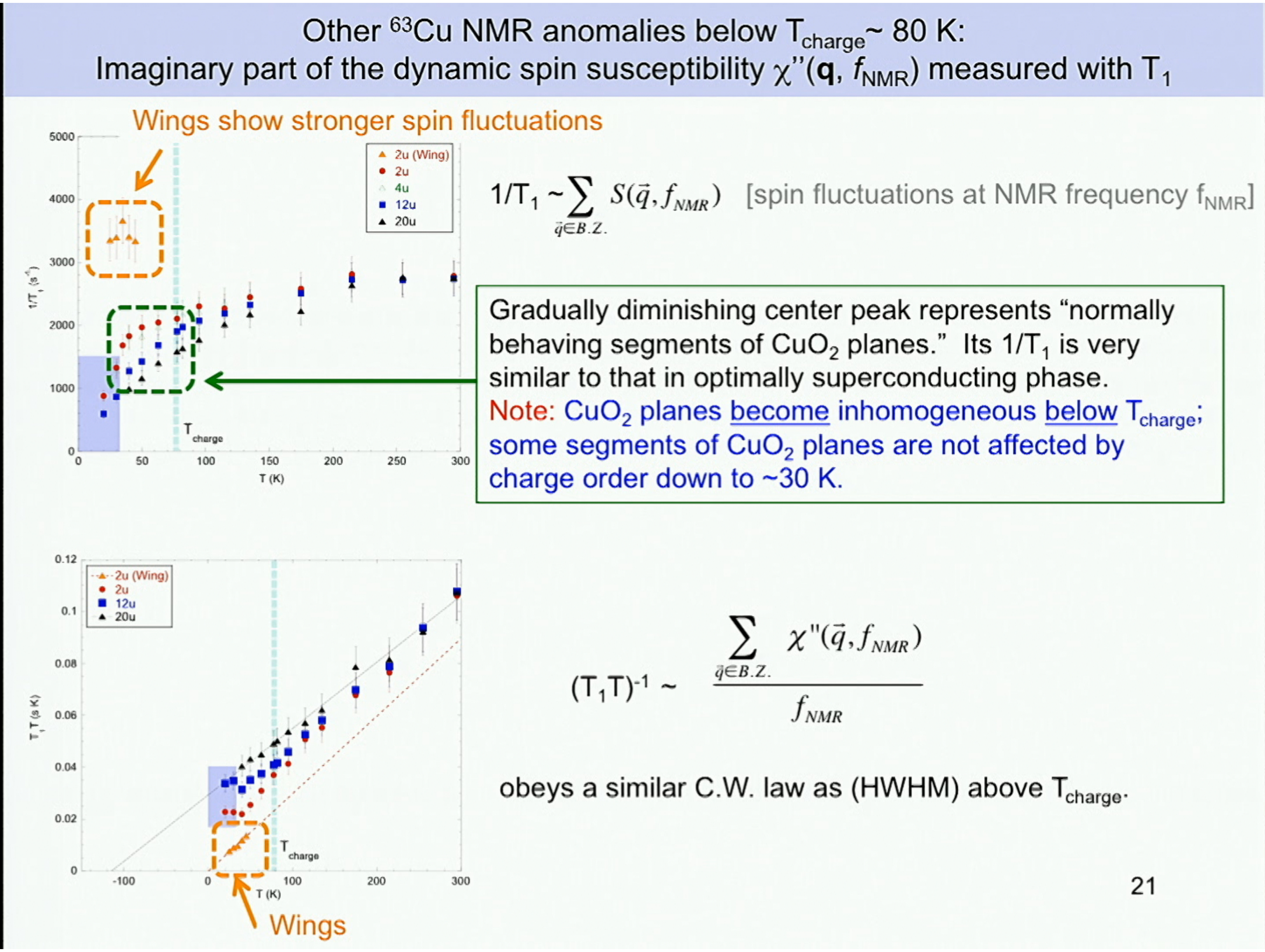
Other ^{63}Cu NMR anomalies below T_{charge}~ 80 K:
Real part of the dynamic spin susceptibility $\chi'(\mathbf{q})$ measured with the linewidth

^{63}Cu NMR linewidth with the B_{ext} || c-axis geometry is broadened by the "*indirect nuclear spin-spin coupling*" effects (originally proposed in the context of NMR by Ruderman-Kittel).

$$(\text{HWHM}) \sim \sum_{\vec{q}\in B.Z.} \chi'(\vec{q})$$

Magnetic correlations gradually grow following an A.F. Curie-Weiss law down to T_{charge} ~ 80K, a common observation for Cuprates.

Then suddenly begins to diverge at T_{charge} toward the spin ordering temperature, T_{spin} ~ 30K.



Other ^{63}Cu NMR anomalies below T_{charge} ~ 80 K:
Imaginary part of the dynamic spin susceptibility $\chi''(\mathbf{q}, f_{NMR})$ measured with T_1

Wings show stronger spin fluctuations

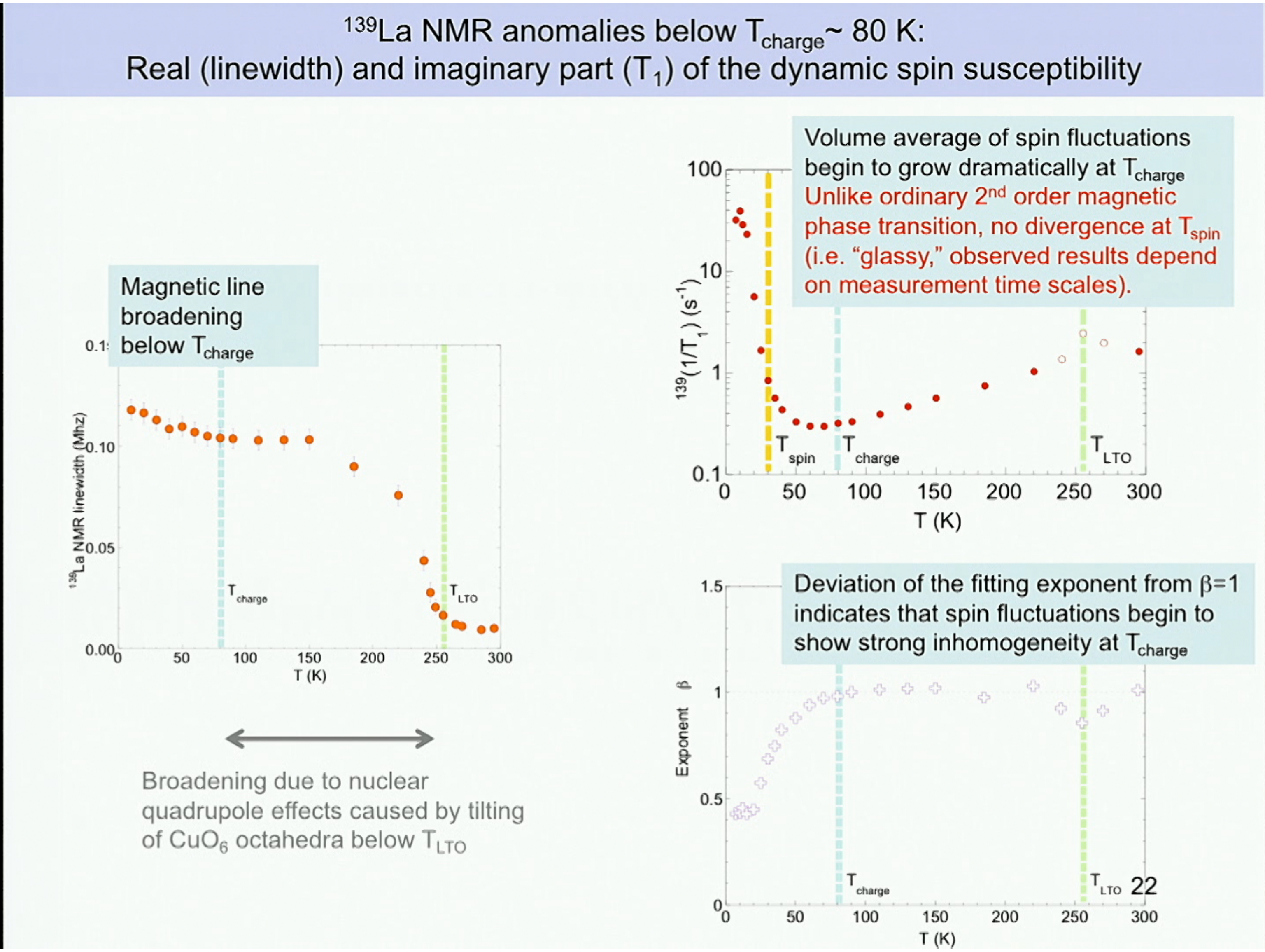
$$1/T_1 \sim \sum_{\vec{q}\in B.Z.} S(\vec{q}, f_{NMR})$$ [spin fluctuations at NMR frequency f_{NMR}]

Gradually diminishing center peak represents “normally behaving segments of CuO_2 planes.” Its $1/T_1$ is very similar to that in optimally superconducting phase.
Note: CuO_2 planes become inhomogeneous below T_{charge}; some segments of CuO_2 planes are not affected by charge order down to ~30 K.

$$(T_1T)^{-1} \sim \frac{\sum_{\vec{q}\in B.Z.} \chi''(\vec{q}, f_{NMR})}{f_{NMR}}$$

obeys a similar C.W. law as (HWHM) above T_{charge}.

Wings



^{139}La NMR anomalies below T_{charge}~ 80 K: Real (linewidth) and imaginary part (T_1) of the dynamic spin susceptibility

Magnetic line broadening below T_{charge}

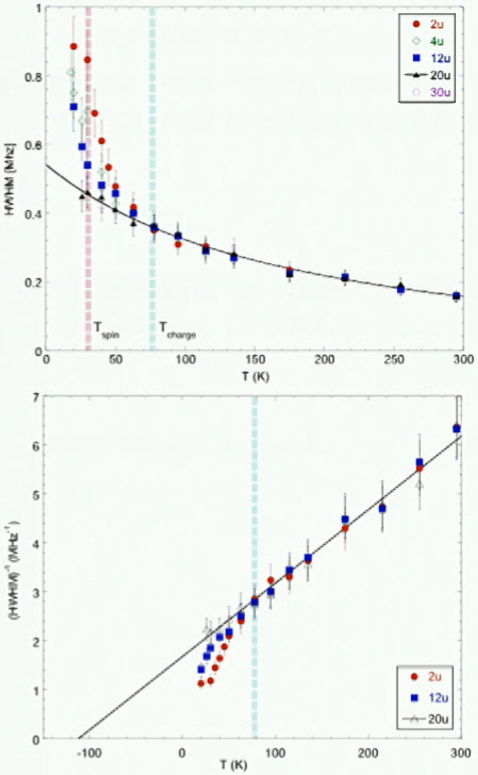
Broadening due to nuclear quadrupole effects caused by tilting of CuO_6 octahedra below T_{LTO}

Volume average of spin fluctuations begin to grow dramatically at T_{charge}

Unlike ordinary 2nd order magnetic phase transition, no divergence at T_{spin} (i.e. “glassy,” observed results depend on measurement time scales).

Deviation of the fitting exponent from β=1 indicates that spin fluctuations begin to show strong inhomogeneity at T_{charge}

Other ^{63}Cu NMR anomalies below T_{charge}~ 80 K: Real part of the dynamic spin susceptibility $\chi'(\mathbf{q})$ measured with the linewidth



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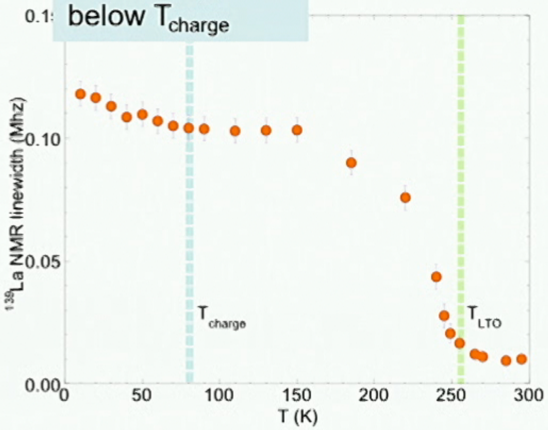

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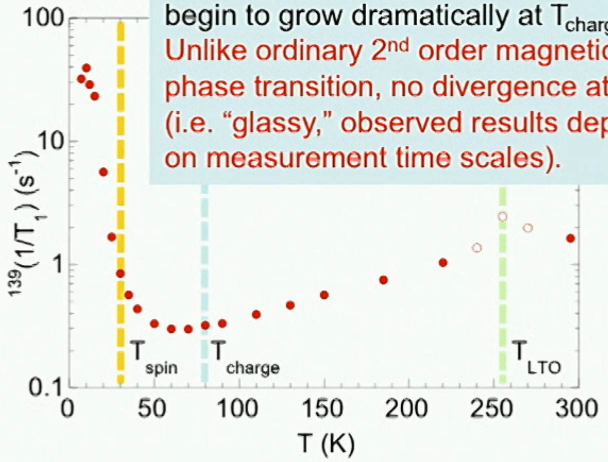
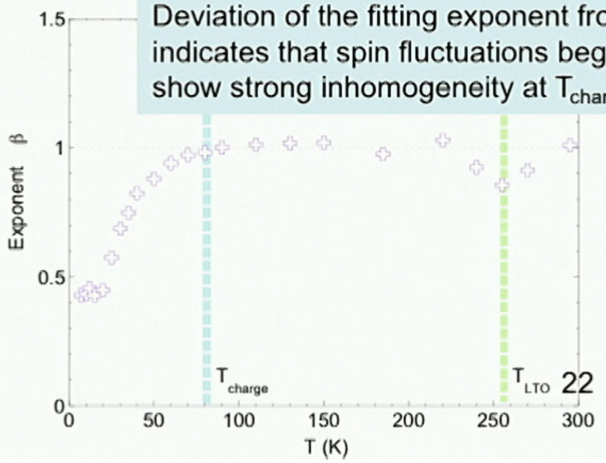


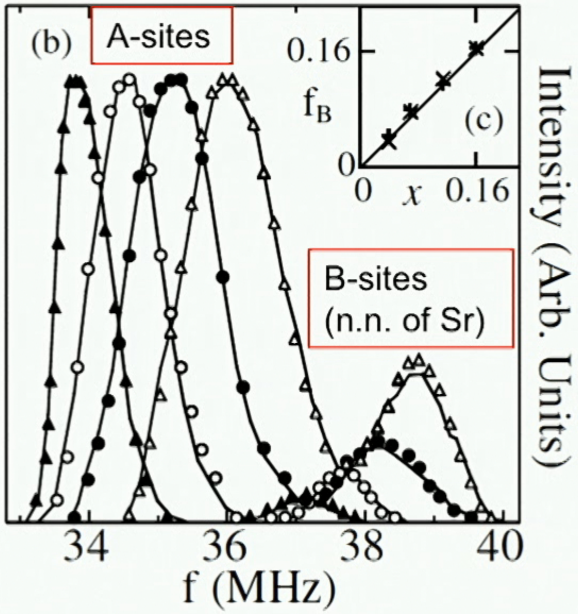
Volume average of spin fluctuations begin to grow dramatically at T_{charge}
Unlike ordinary 2nd order magnetic phase transition, no divergence at T_{spin} (i.e. "glassy," observed results depend on measurement time scales).



Deviation of the fitting exponent from β=1 indicates that spin fluctuations begin to show strong inhomogeneity at T_{charge}

How much does charge density modulate below T_{charge}? ---- Small !

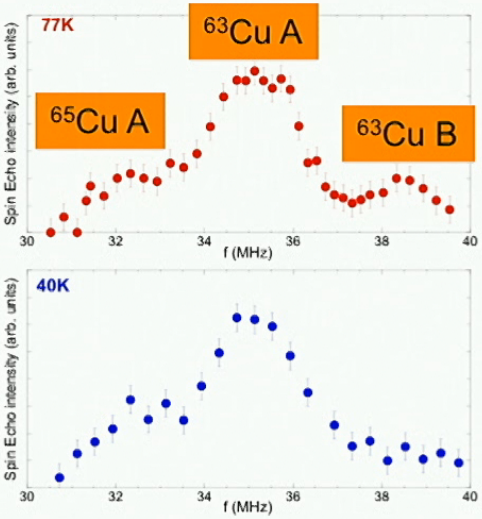
^{63}Cu NQR lineshapes for ^{63}Cu isotope enriched powders with x = 4%, 7%, 11%, 16%



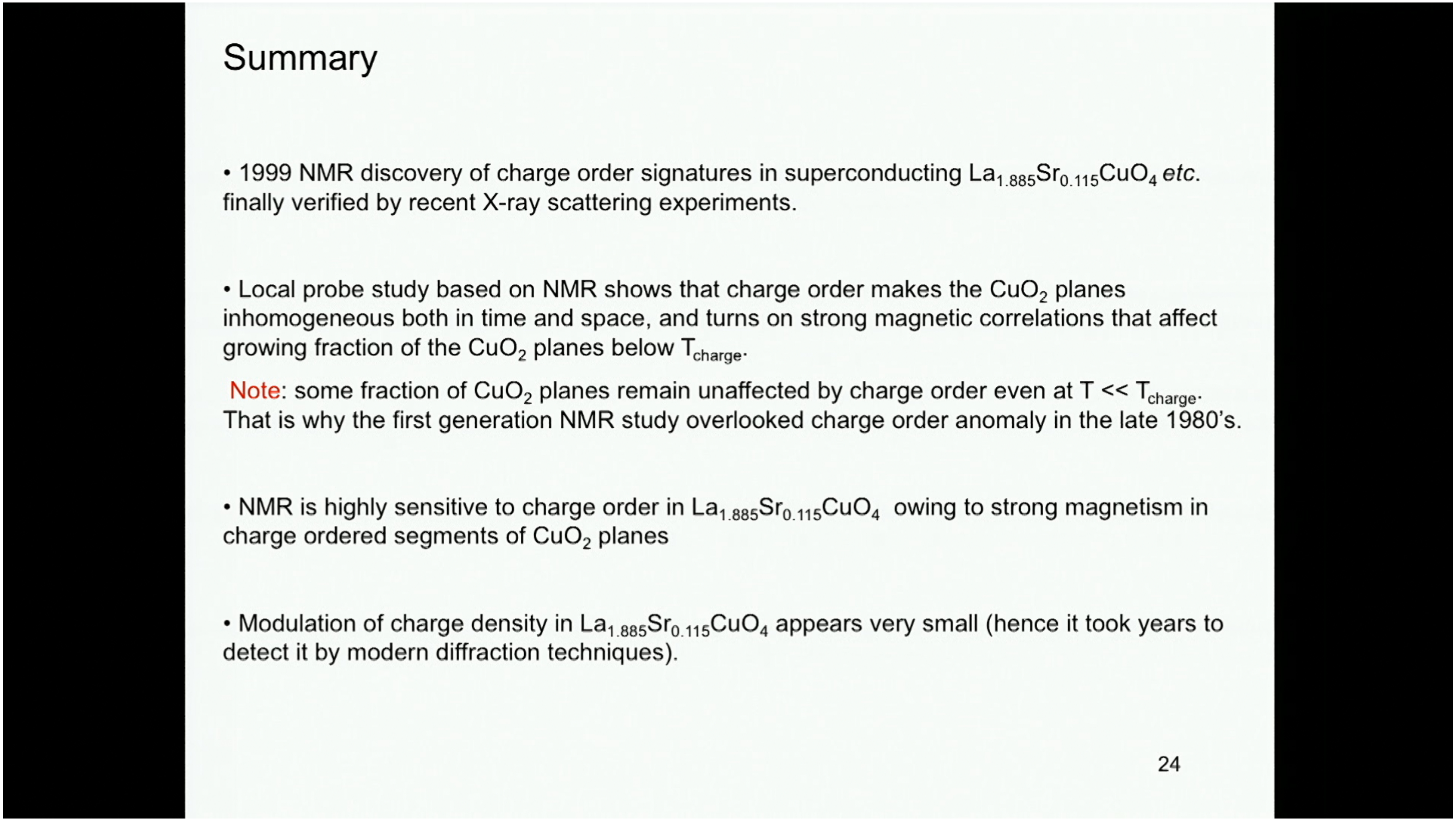
^{63}Cu NQR frequency is sensitive to the hole concentration and its distribution

Singer, Hunt, T.I., PRL 88 (2001) 047602

^{63,65}Cu NQR lineshapes for $La_{1.885}Sr_{0.115}CuO_4$ single crystal measured with τ = 4 μs



Practically no changes in ^{63,65}Cu NQR lineshapes below T_{charge}



Summary

- 1999 NMR discovery of charge order signatures in superconducting $La_{1.885}Sr_{0.115}CuO_4$ *etc.* finally verified by recent X-ray scattering experiments.

- Local probe study based on NMR shows that charge order makes the CuO_2 planes inhomogeneous both in time and space, and turns on strong magnetic correlations that affect growing fraction of the CuO_2 planes below T_{charge}.

  Note: some fraction of CuO_2 planes remain unaffected by charge order even at $T << T_{charge}$. That is why the first generation NMR study overlooked charge order anomaly in the late 1980's.

- NMR is highly sensitive to charge order in $La_{1.885}Sr_{0.115}CuO_4$ owing to strong magnetism in charge ordered segments of CuO_2 planes

- Modulation of charge density in $La_{1.885}Sr_{0.115}CuO_4$ appears very small (hence it took years to detect it by modern diffraction techniques).