Scattering Using Hard X-Rays: Coherent and Incoherent

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Why would brighter sources be useful?

- Interesting effects often associated with very weak peaks/diffuse scattering (10^{-8} to 10^{-10} of a Bragg reflection)
- To distinguish from impurity phases need extremely pure crystals---very tiny crystals and high resolution.
- High absorption means higher energies (40-100 Kev) desirable.
- For many highly correlated electron sytems, only tiny crystals are available.
- Dynamics using coherent beams.

What other equipment would be desirable?

- High Magnetic Fields (upto 20 Tesla)
- Very Low Temperatures (down to mK)
- Large, efficient Area Detectors.

Examples:

- Novel Heavy Fermion Compounds (Brian Maple UCSD)
- CMR Manganites
- High-Tc Superconductors

Filled skutterudites: MT_4X_{12}

M —	alkaline earth	Ca, Sr, Ba
	lanthanide	La, Ce, Pr, Nd, Sm, Eu, Yb
	actinide	Th, U
T —	transition metal	Fe, Ru, Os
X —	pnictogen	P, As, Sb

Variety of strongly correlated electron ground states, phenomena

- Superconductivity ($LaFe_4P_{12}$, $LaRu_4Sb_{12}$)
- Ferromagnetism (UFe_4P_{12}, $SmFe_4Sb_{12}$)
- Small "hybridization gap" semiconductivity ("Kondo insulator" behavior) ($CeFe_4P_{12}$, UFe_4P_{12})
- Intermediate valence/heavy fermion behavior ($CeFe_4Sb_{12}$, $YbFe_4Sb_{12}$)
- Metal-insulator transition ($PrRu_4P_{12}$)
- Non-Fermi liquid behavior ($CeRu_4Sb_{12}$)
- Heavy fermion superconductivity ($PrOs_4Sb_{12}$)

Potential for thermoelectric applications

Crystal structure of the filled skutterudites MT_4X_{12}

Filled skutterudites: derived from binary skutterudites TX_3

(T = Co, Rh, Ir; X = P, As, Sb)

Prototype $CoAs_3$: discovered in Skutterud, Norway

M cations — bcc sublattice

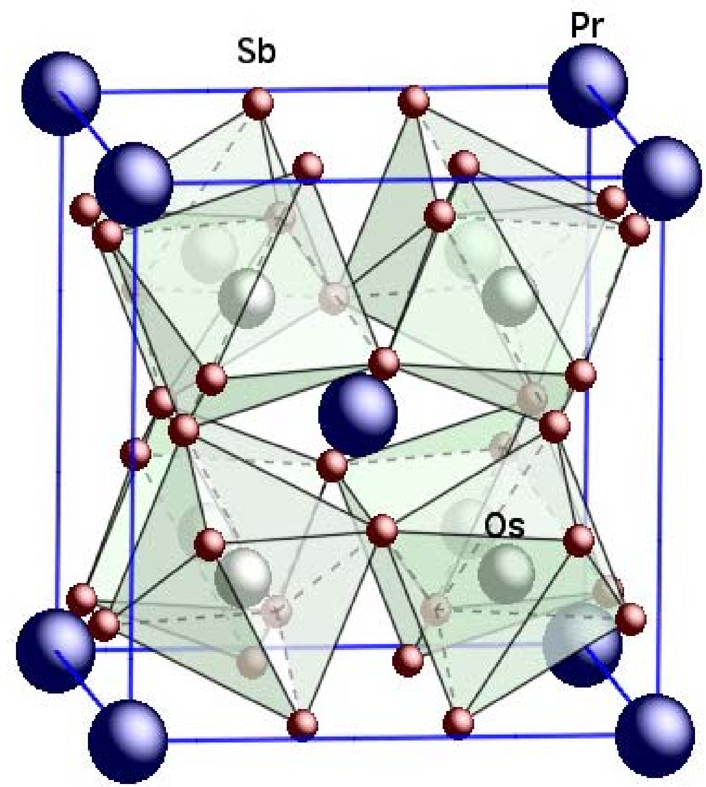
T cations — sc sublattice

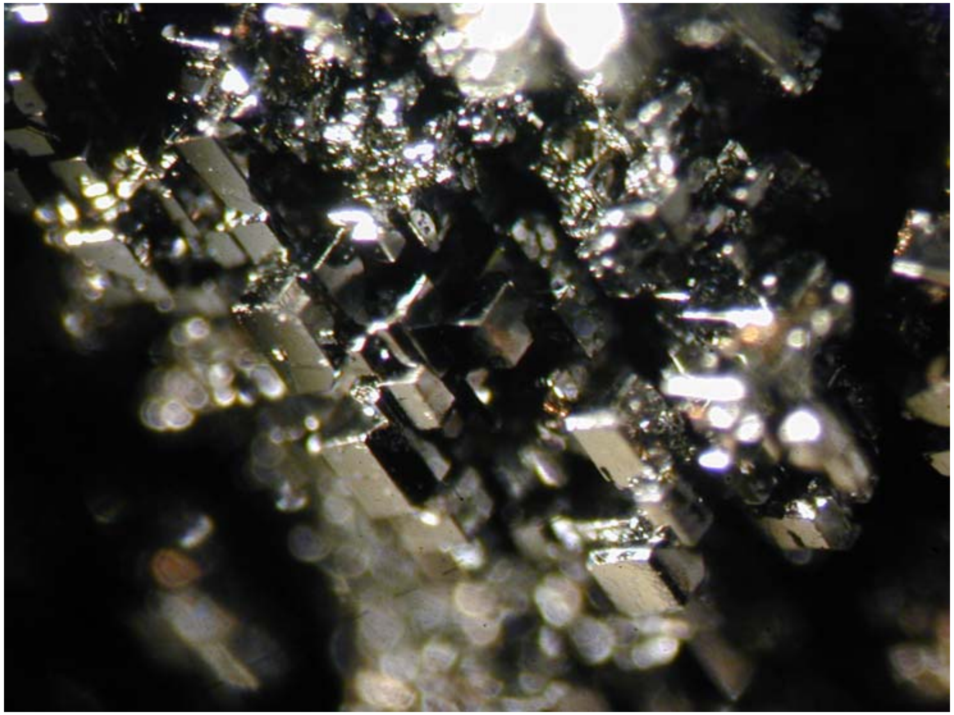
X anions — distorted corner sharing octahedra centered by T cation

bcc structure (*Im-3*)

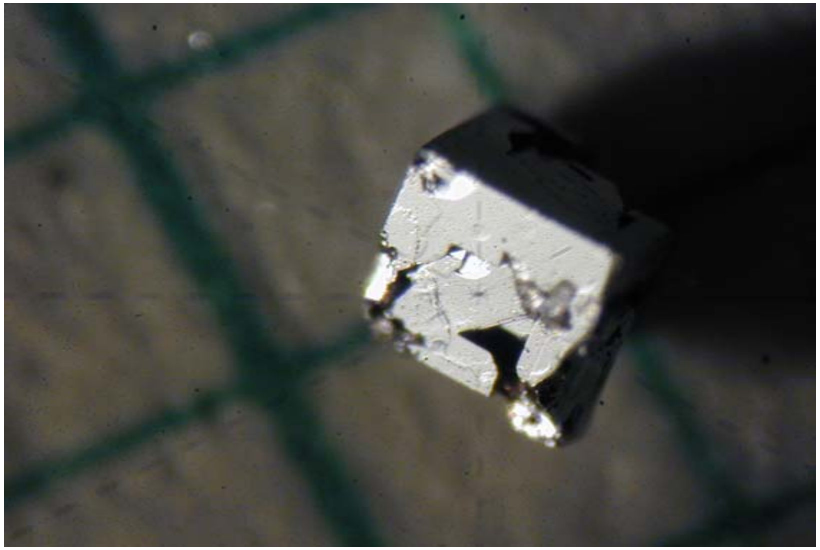
a = 9.3068 Å

W. Jeitschko & D. J. Braun '77





$PrOs_4Sb_{12}$ crystals



Why is $PrOs_4Sb_{12}$ interesting?
And, what does it have to do with quantum criticality?

- Nonmagnetic heavy Fermi liquid ($\gamma \approx 500$ mJ/mol-K^2; $m^* \approx 50\ m_e$)
- Unconventional superconductivity (different than that of Ce, U-based compounds)
- $PrOs_4Sb_{12}$: first Pr-based heavy fermion superconductor (all others: Ce, U-based)
- Formation of heavy Fermi liquid (and, possibly, superconductivity) may
  involve electric quadrupole fluctuations, rather than magnetic dipole fluctuations
- Pr^{3+} energy level scheme in cubic CEF:

  In cubic CEF, Pr^{3+} J = 4 Hund's rule multiplet

  $\Rightarrow \Gamma_1$ singlet, Γ_3 nonmagnetic doublet (quadrupole moment), Γ_4 & Γ_5 triplets

  Analysis of $\chi(T)$:

  Ground state: Γ_1 singlet or Γ_3 doublet

  1st excited state: Γ_5 triplet ($\Delta \approx 10$ K)

  2nd & 3rd excited states: Γ_4, Γ_1 or Γ_3 ($\Delta > \sim 10^2$ K)
- Our experiments $\Rightarrow \Gamma_3$ ground state (other experiments $\Rightarrow \Gamma_1$ ground state)

  Hybridization between Pr^{3+} localized 4f states & conduction electron states

  $\Rightarrow$ stage set for quadrupolar Kondo effect (2-channel, spin-1/2 Kondo effect with NFL behavior) $\Rightarrow$ quadrupolar Kondo lattice $\Rightarrow$ heavy Fermi liquid? $\Rightarrow$SC?
- High field ordered phase (HFOP) – quadrupolar order?
- Near quadrupolar quantum critical point (QCP)?
- Analogous to occurrence of SC in heavy fermion compounds in vicinity of AFM QCP,
  accessed by pressure; e.g., $CeIn_3$, $CePd_2Si_2$

Diffuse Scattering Studies of Layered Manganites

- Branton Campbell ANL/BYU
- Lida Vasiliu-Doloc NIST/NIU/***
- Ray Osborn ANL
- Stefan Rosenkranz ANL
- Joel Mesot ANL
- John Mitchell ANL
- Oliver Seeck ANL/Julich
- Jeff Lynn NIST
- Zahir Islam ANL
- Dimitri Argyriou ANL/HMI

CMR Materials exhibit many types of competing order.

- Charge Order
- Spin Order
- Orbital Order
- Lattice Modulations

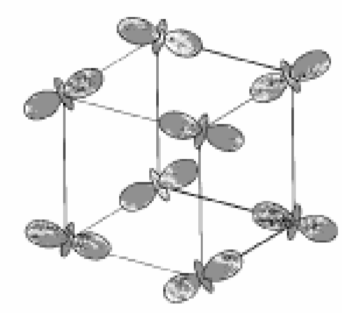
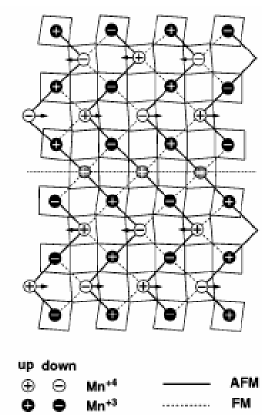
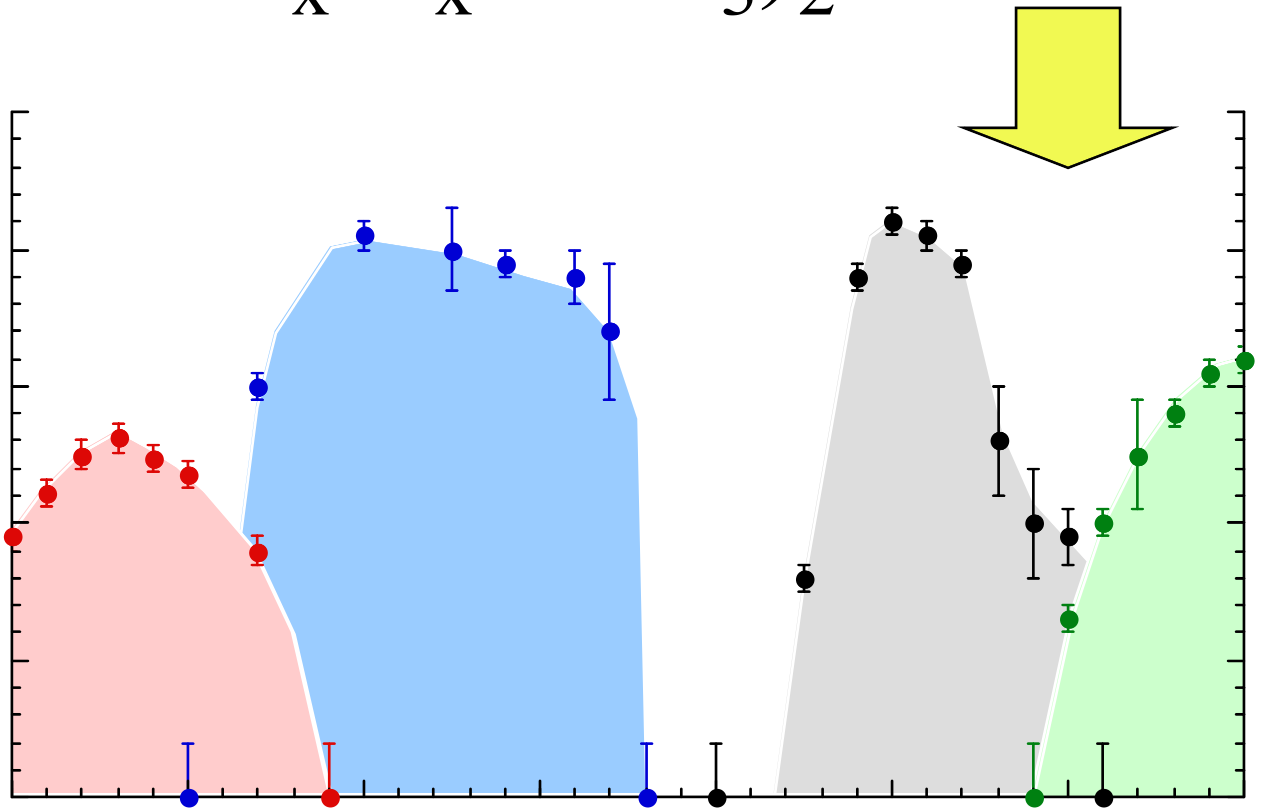


FIG. 1. The $(3x^2-r^2/3y^2-r^2)$-type orbital ordering.

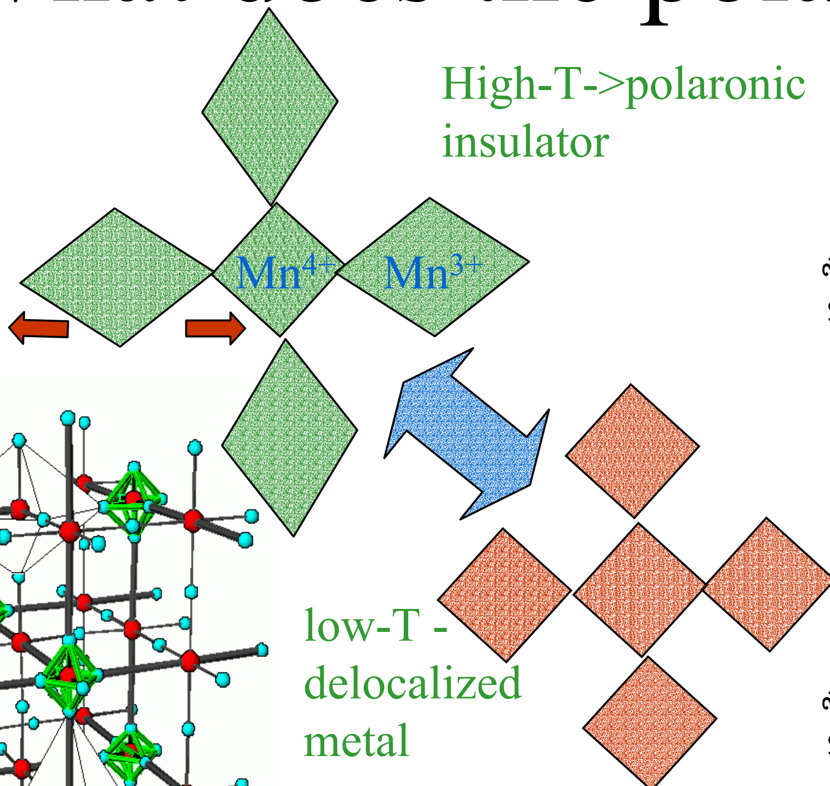


$La_{0.5}Ca_{0.5}MnO_3$
From Radaelli et al. (1997)

Phase Diagram of $SrO \bullet (La_{1-x}Sr_xMnO_3)_2$



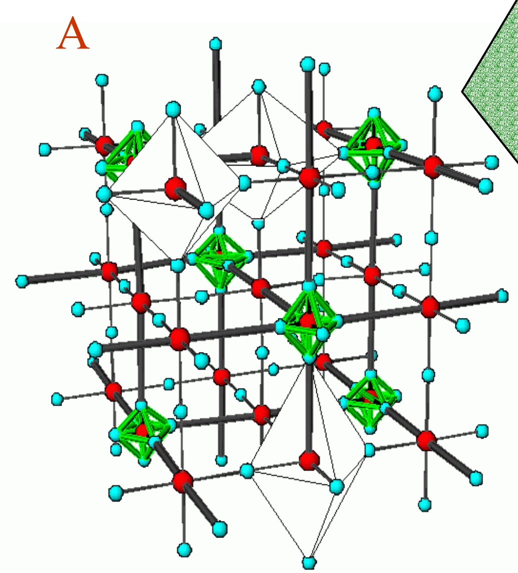
What does the polaron look like?

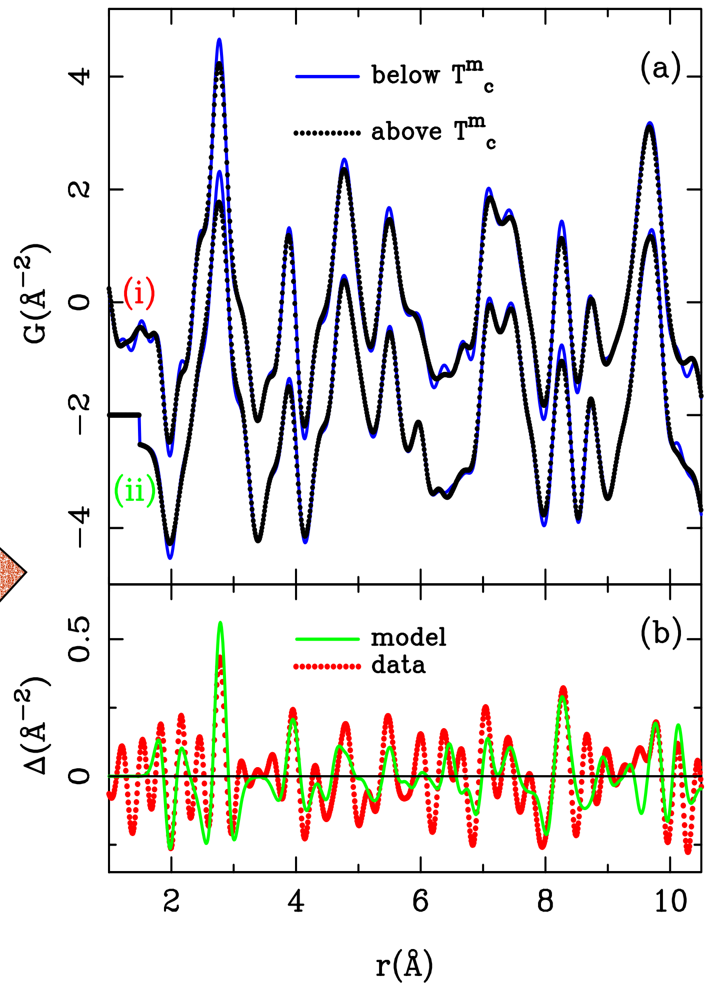


High-T->polaronic insulator

low-T - delocalized metal

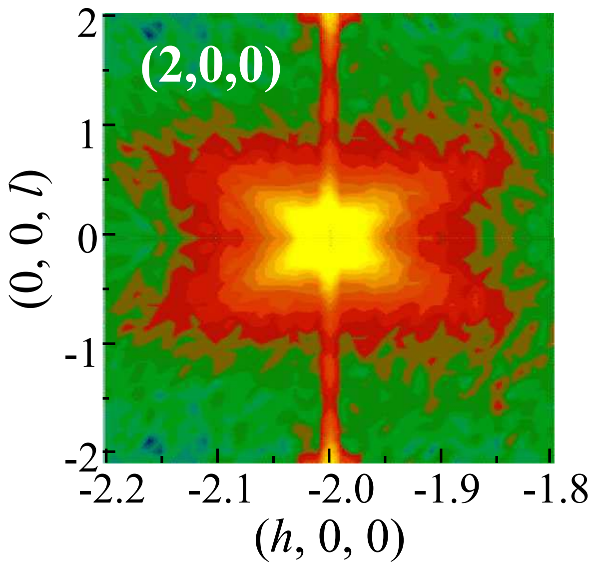
δ=0.24 A

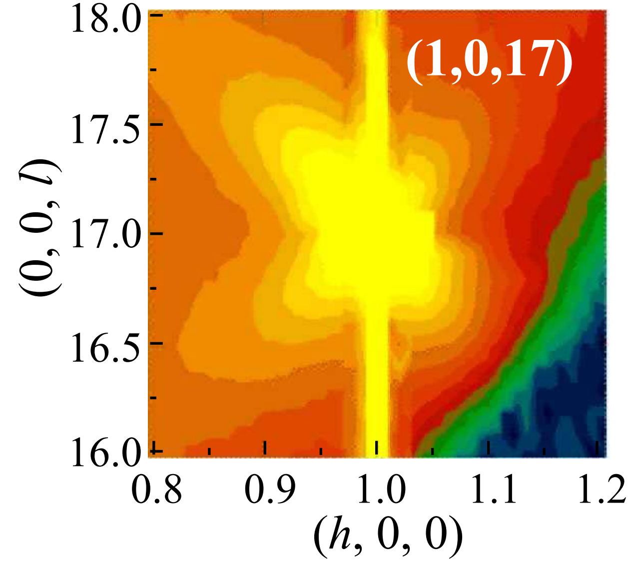


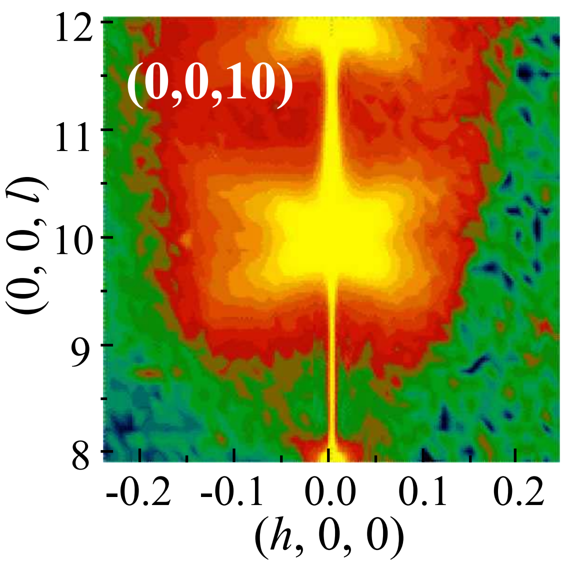


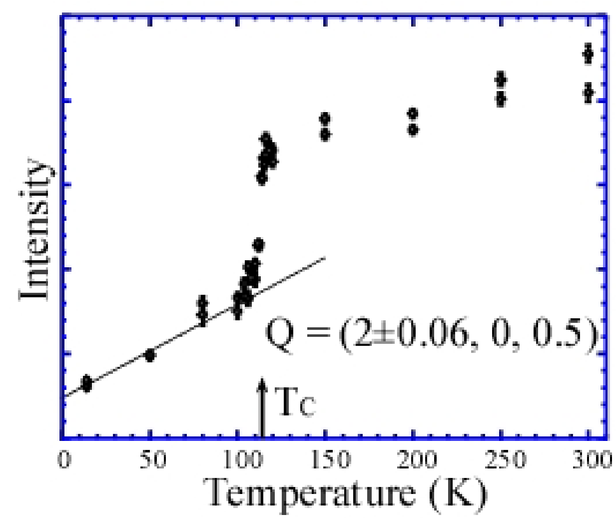
S.J.L. Billinge *et al*, *Phys. Rev. Lett*. **77**, 715 (1996); S. J. L. Billinge, *et al., Phys. Rev. B* **62**, 1203 (2000)]

Polarons via single-crystal diffuse scattering



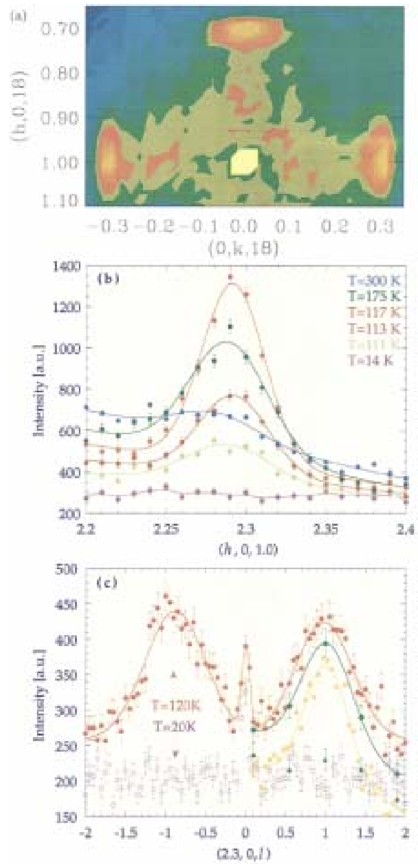




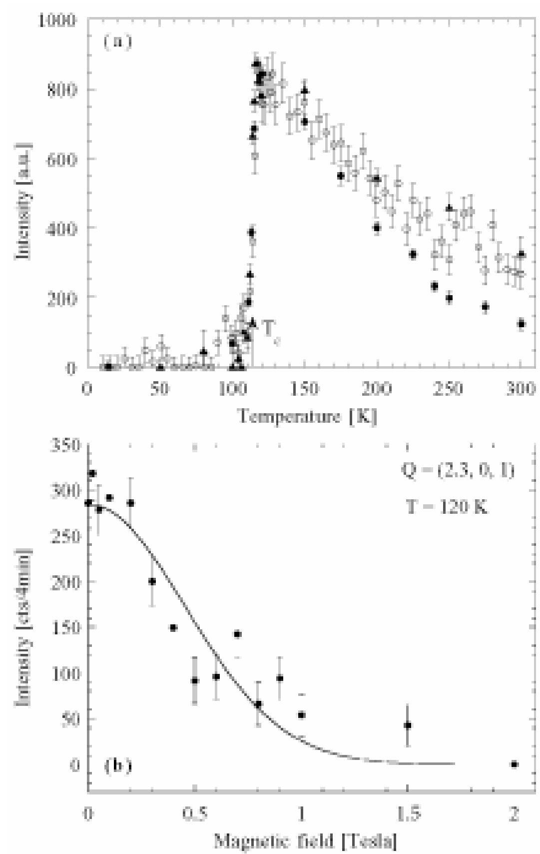


L. Vasiliu-Doloc *et al.*, PRL **83**, 4393 (1999).

Polarons show stripe-like short range order.

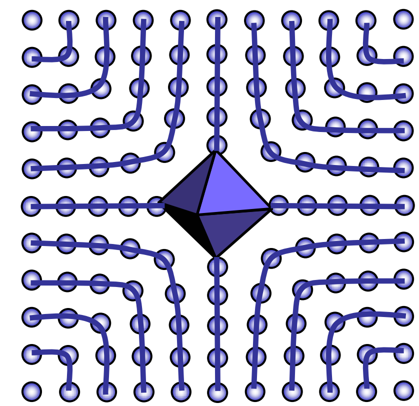


Polarons collapse in metallic phase (<Tc)



$$I_{POL}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \sum_{\alpha,\beta,\gamma,\delta} Q_\beta Q_\delta \left(\sum_{j,j'} \frac{\varepsilon_{\alpha,\mathbf{q},j}\varepsilon^*_{\beta,\mathbf{q},j}\varepsilon^*_{\gamma,\mathbf{q},j'}\varepsilon_{\delta,\mathbf{q},j'}}{q^4 v^2_{\mathbf{q},j} v^2_{\mathbf{q},j'}} \right) \sum_{m,n} \Im_{m,\alpha} \Im_{n,\gamma} e^{i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)}$$

$$I_{TDS}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \left(\frac{kT}{2M} \right) \sum_{\beta,\delta} Q_\beta Q_\delta \sum_{j} \frac{\varepsilon^*_{\beta,\mathbf{q},j}\varepsilon_{\delta,\mathbf{q},j}}{q^2 v^2_{\mathbf{q},j}}$$



$$u_{m,\alpha} = \sum_{\beta,\mathbf{q},j} \frac{\varepsilon^*_{\beta,\mathbf{q},j}\varepsilon_{\alpha,\mathbf{q},j}}{q^2 v^2_{\mathbf{q},j}} \sum_{n} \Im_{n,\beta} e^{i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)}$$

Measure 6 independent phonon velocities (3-axis INS).

Determine elastic constants (C_{11},C_{12},C_{13},C_{33},C_{44},C_{66}).

Calculate eigenvectors/eigenvalues of continuum DM.

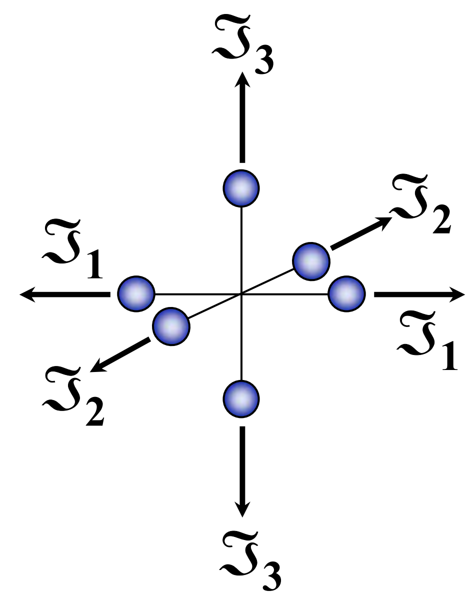
Calculate diffuse scattering (quadratic in the forces).

Fit the forces against the experimental data.

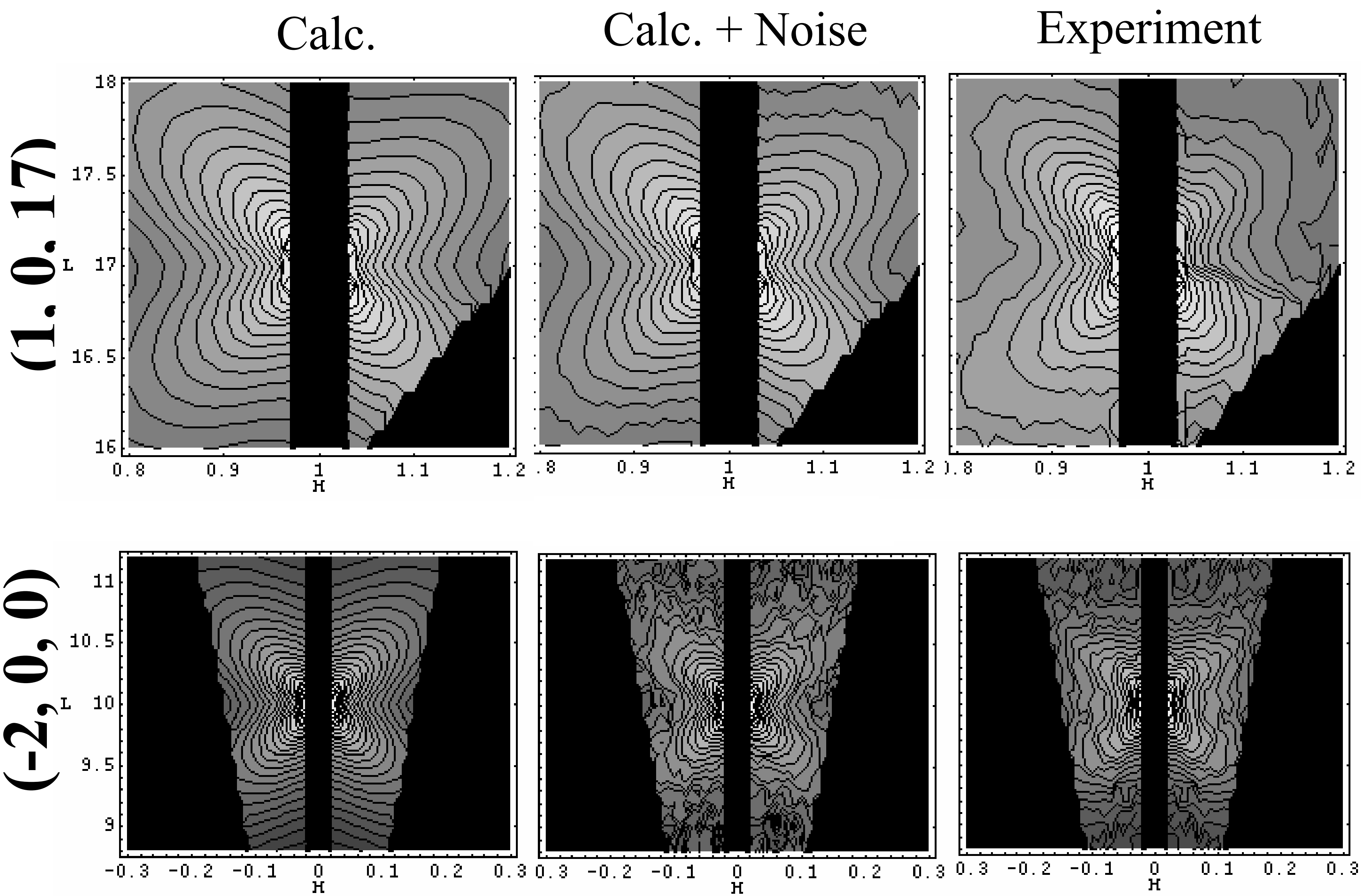
Integrate the displacement expression.

Determine temperature evolution of local structure.

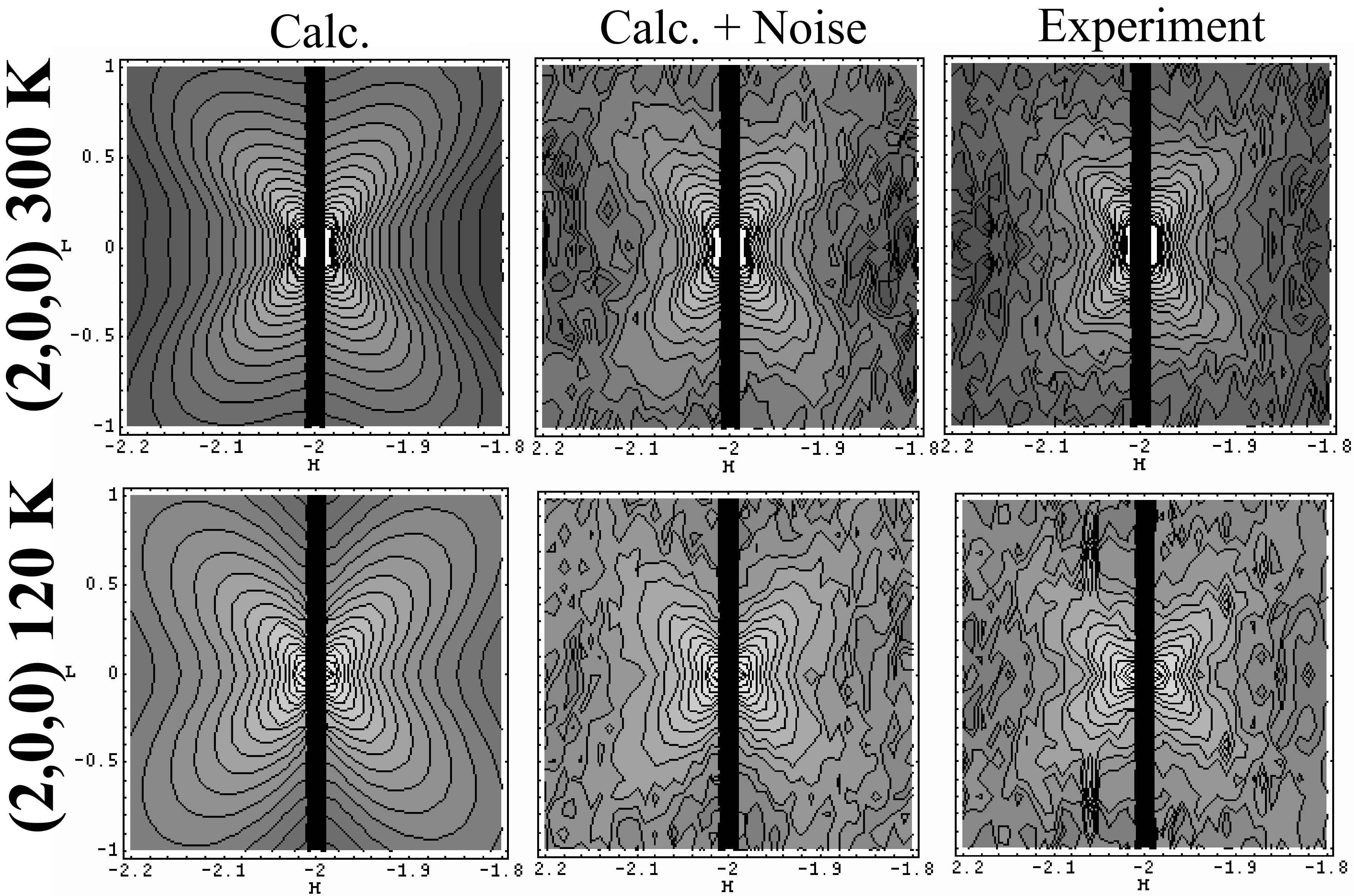
B.J.Campbell et al., Phys. Rev. B 67, 020409R (2003)



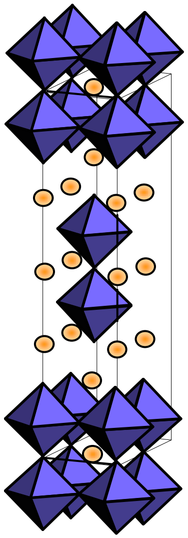
Experiment vs. Calculation (300 K)



New orbital polarization near T_C

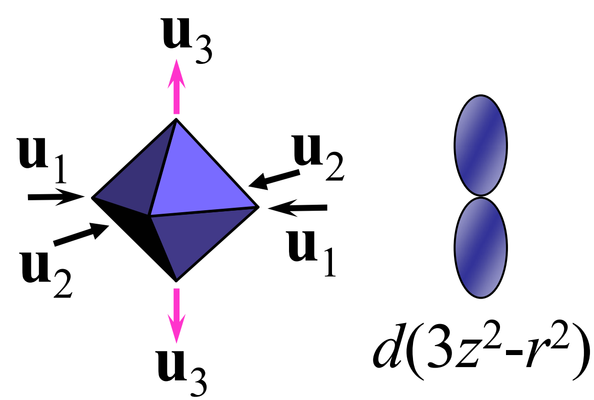


JT polarons: A 3D local structure model

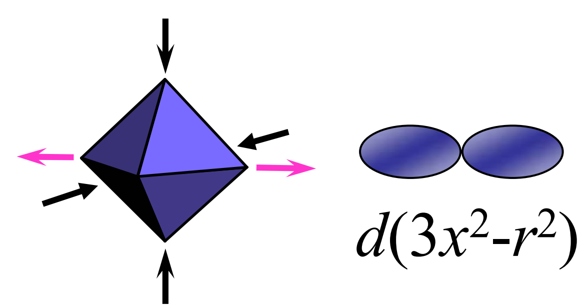


$$\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = a\sqrt{\frac{kT}{2Mv_0^2\, x(1-x)}} \begin{bmatrix} 0.444 & -0.119 & -0.126 \\ -0.119 & 0.444 & -0.126 \\ -0.126 & -0.126 & 0.429 \end{bmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix}$$

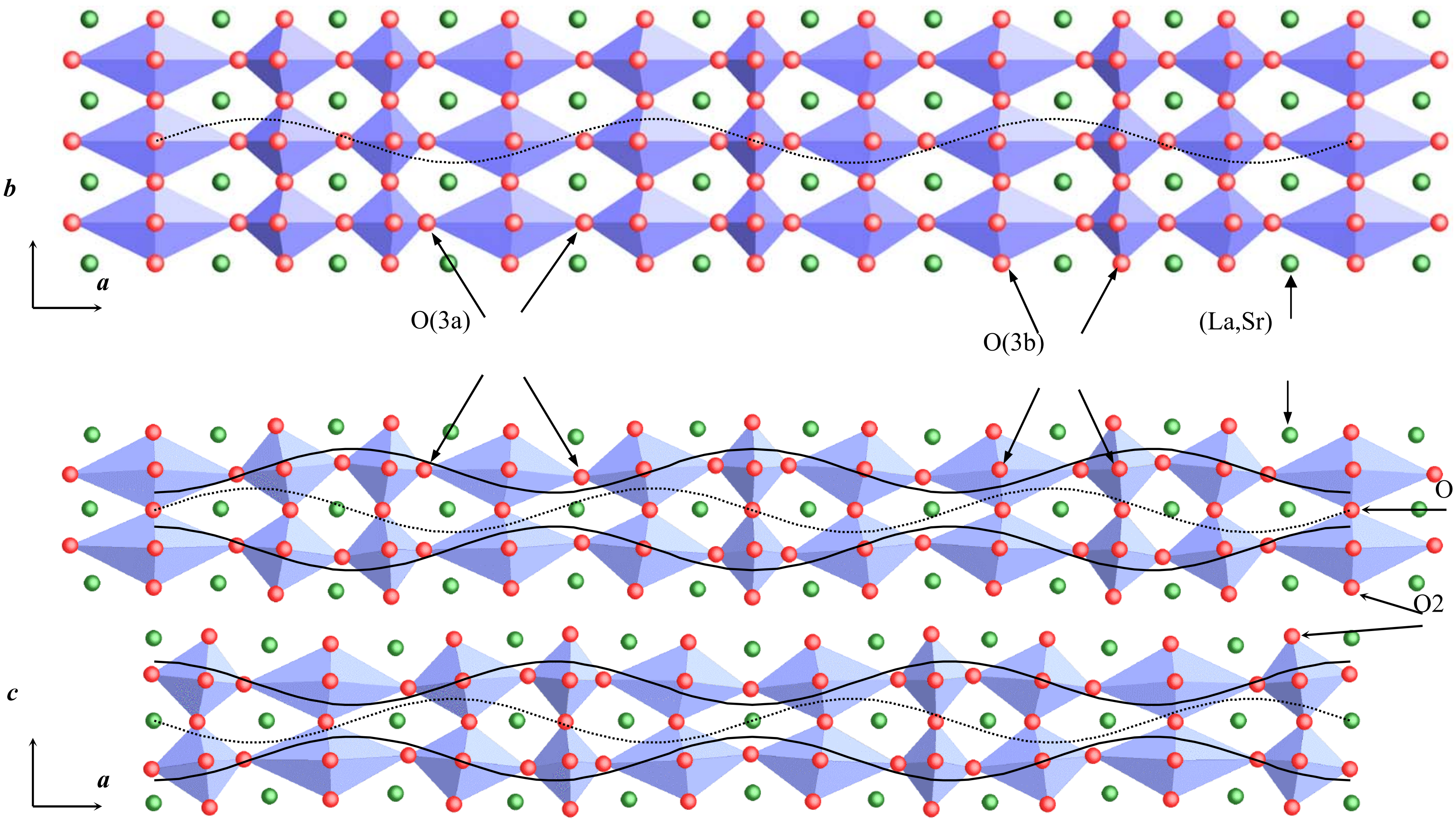
$$\begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \begin{pmatrix} 0.6 \\ 0.6 \\ 3.0 \end{pmatrix} \text{ at } 300\,\text{K} \Rightarrow \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} -0.0120 \\ -0.0120 \\ 0.0744 \end{pmatrix} \text{Å}$$



$$\begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \begin{pmatrix} 4.5 \\ 0 \\ 0 \end{pmatrix} \text{ at } 120\,\text{K} \Rightarrow \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} 0.0828 \\ -0.0222 \\ -0.0234 \end{pmatrix} \text{Å}$$



B.J.Campbell et al., Phys. Rev. B 65, 014427 (2001)



Lattice Modulations and Distortions in $YBa_2Cu_3O_{6+x}$

Zahirul Islam	ANL
Daniel Haskel	ANL
Jonathan Lang	ANL
George Srajer	ANL
Dean Haeffner	ANL
Boyd Veal	ANL
D. R. Lee	ANL
Herb Mook	ORNL
Si Moss	U. Houston
Peter Wochner	MPI Stuttgart

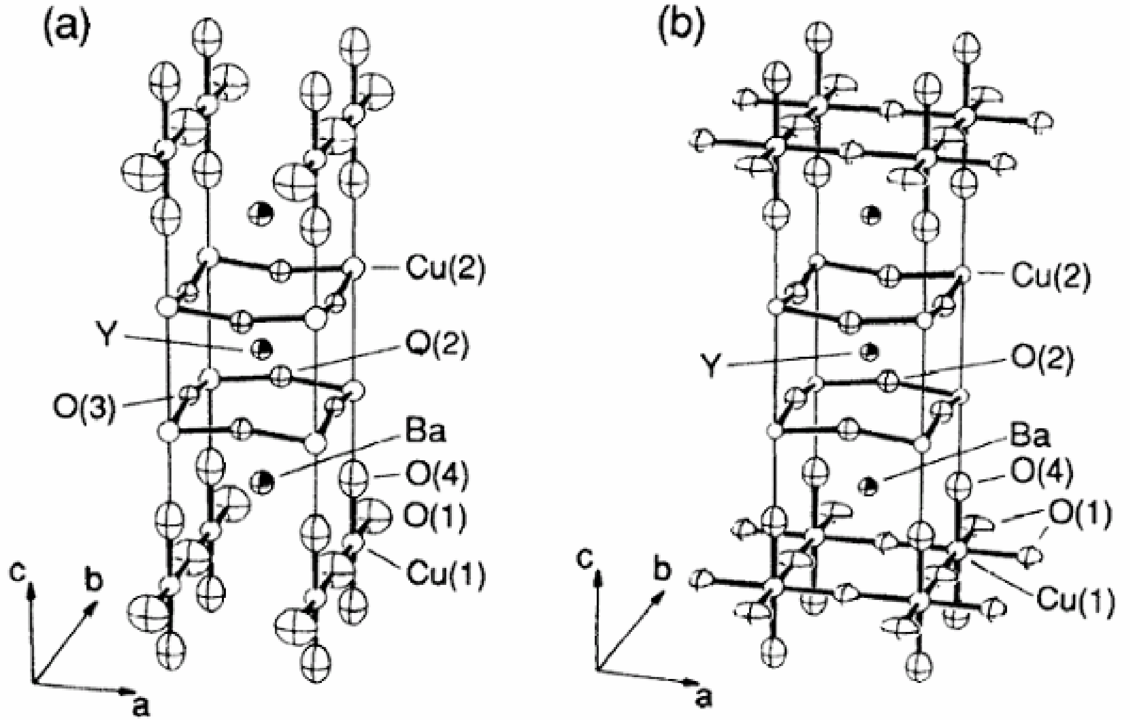
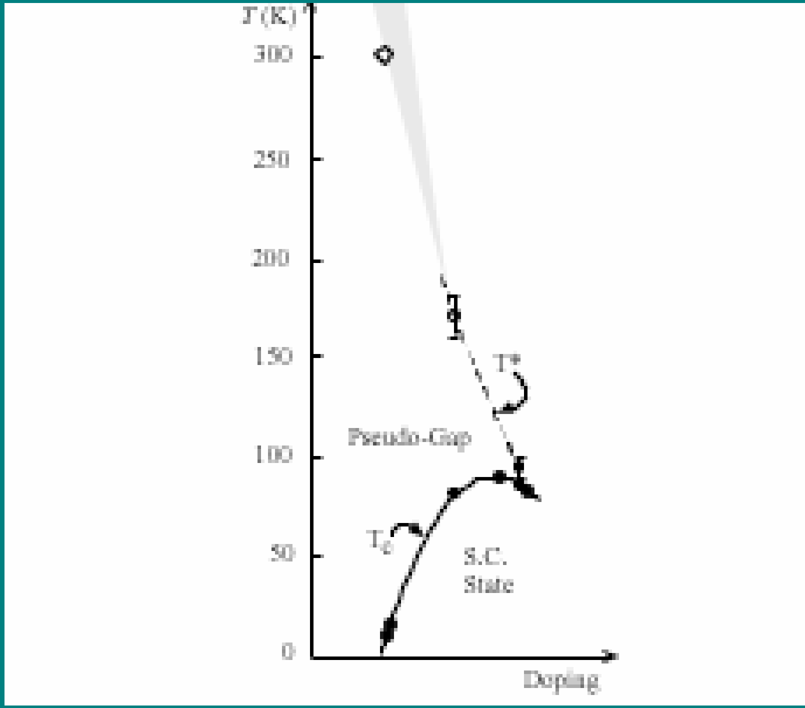


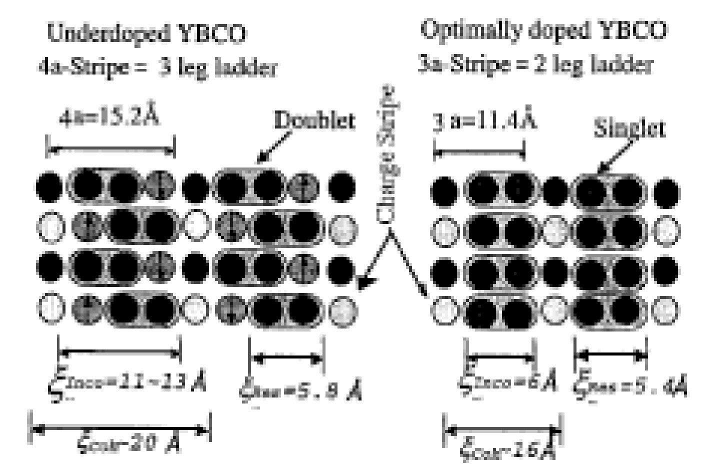
FIG. 1. (a) Orthorhombic and (b) tetragonal structures of $YBa_2Cu_3O_{7-\delta}$. In the tetragonal structure (b) the different atom symbol for the O(1) site is used to indicate that this site is not fully occupied.

A/F and S/C….What else?

- Pseudogap (Campuzzano et al. 1996; Rossat-Mignod et al. 1993; Basov et al. 1995,2002)
- Stripes (Tranquada et al. 1996; Zimmerman et al. 1998; Kapitulnik et al. 2002; Emery et al. 1999; Zaanen 1999)
- Incommensurate Spin Excitations (Mook et al. 1999; Arai et al. 2000; Yamada et al. 1999)
- Orbital Magnetism (Varma 2001; Chakravarty et al. 20010

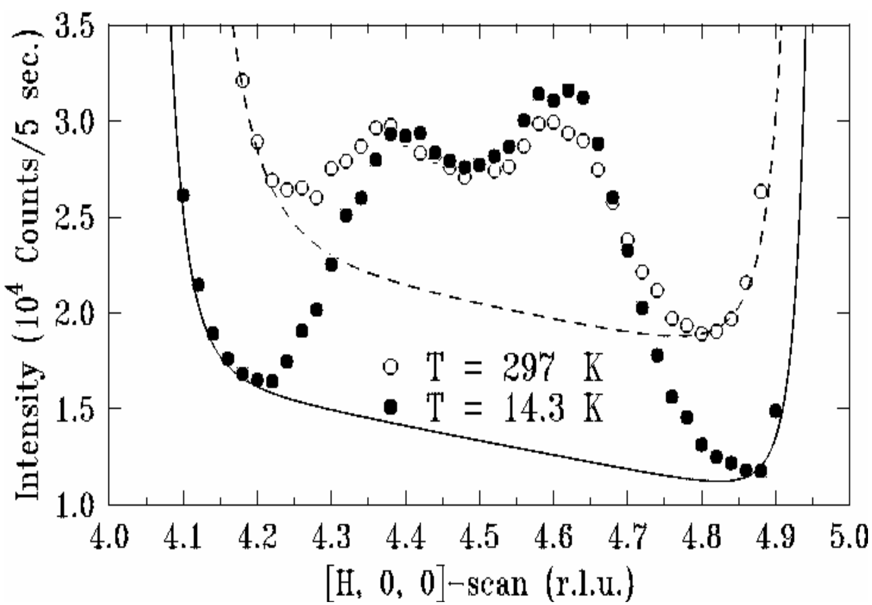


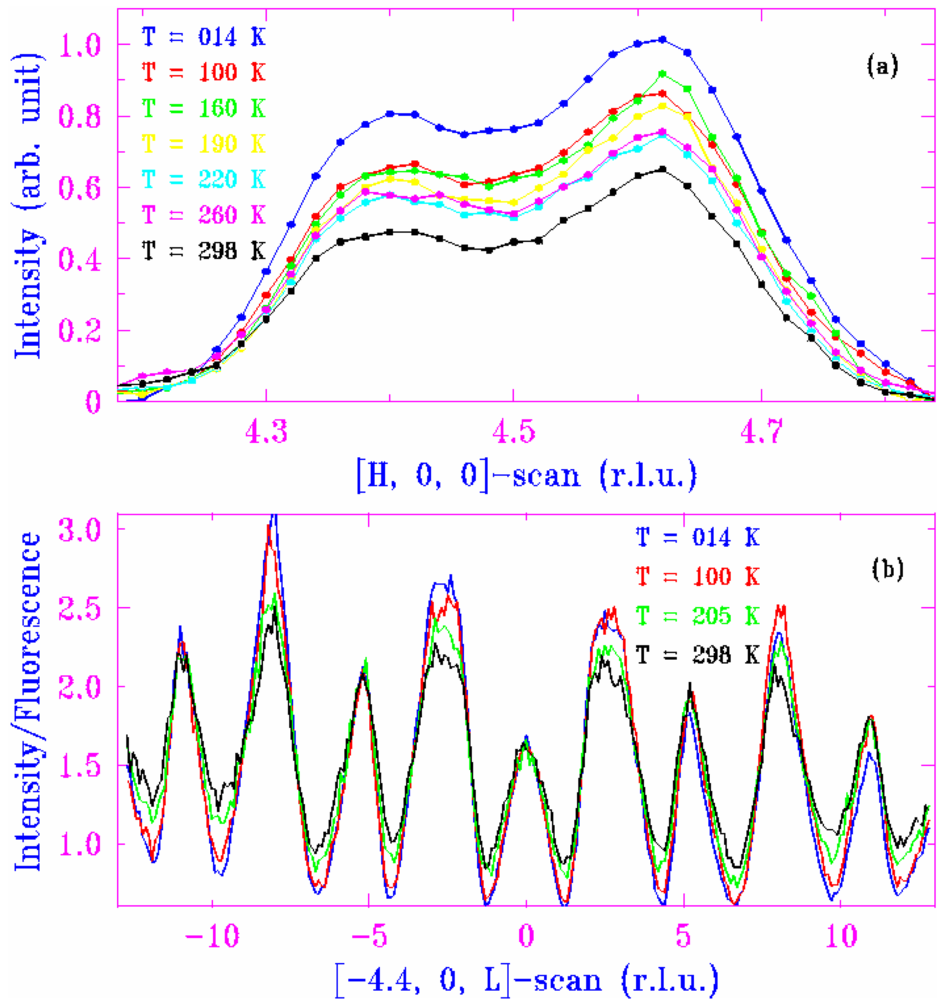
Schematic of Proposed Possible Stripe Phases.



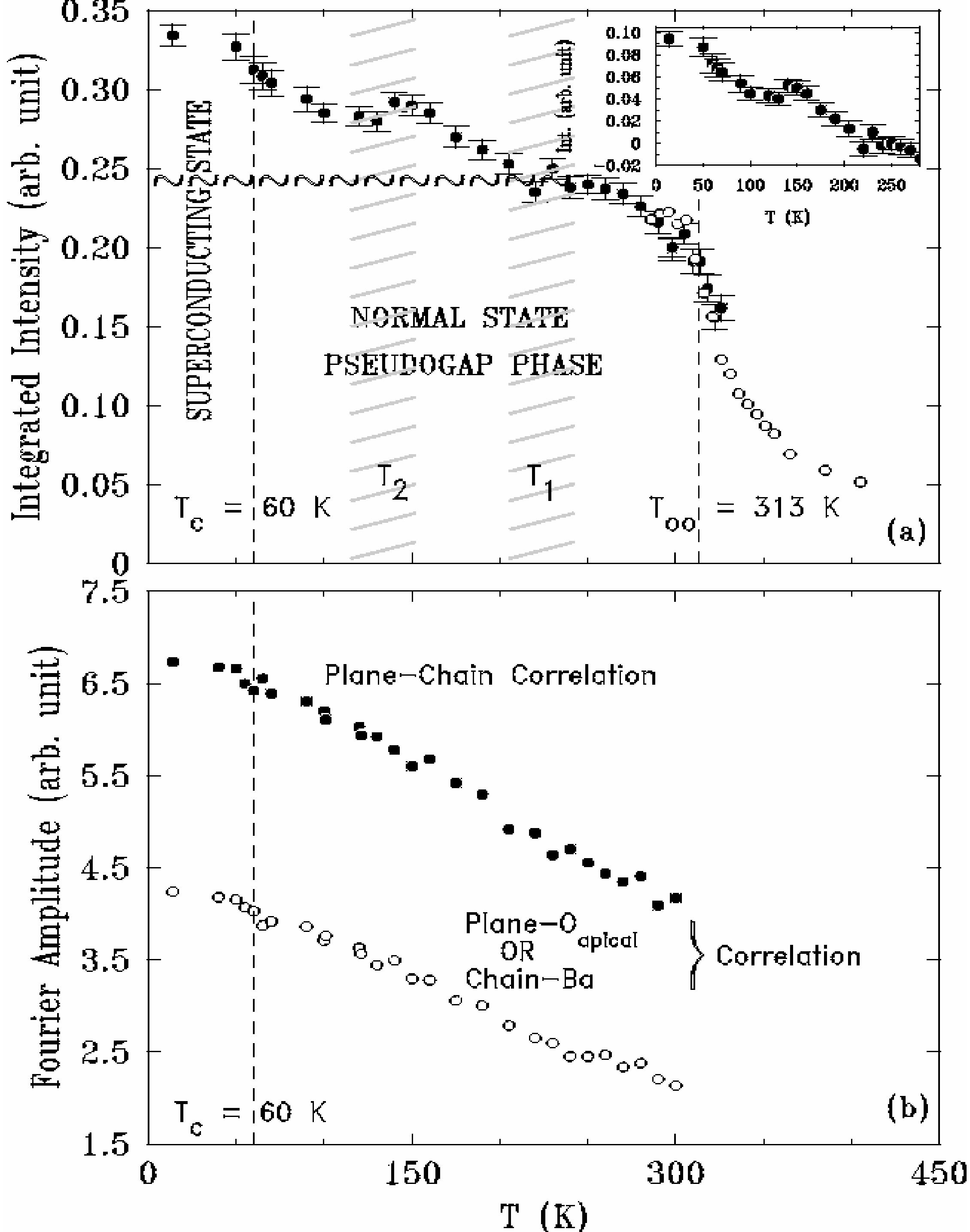
(Arai,Endoh, Tajima and Bennington (2000))

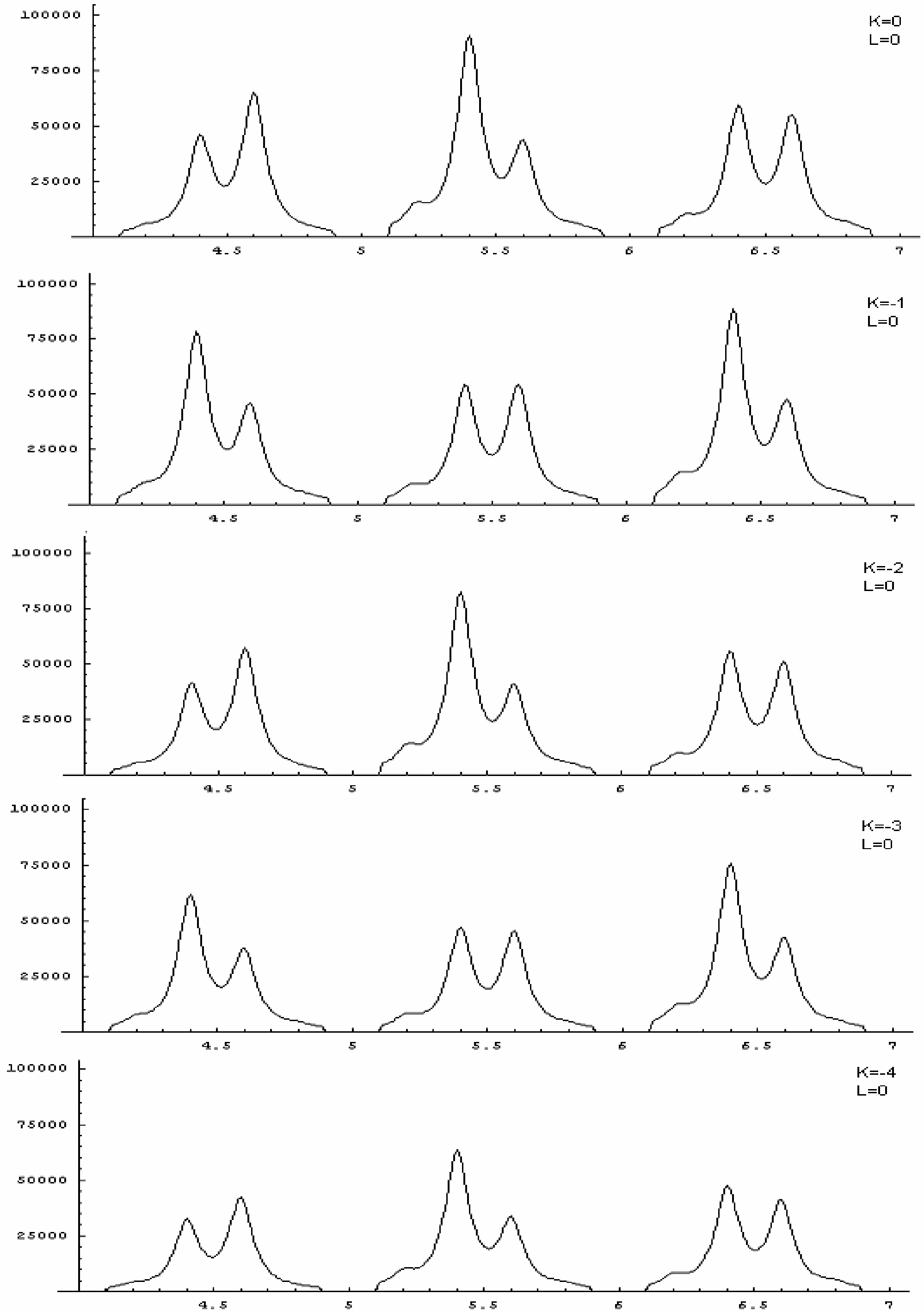
Using 36 KeV X-Rays to look for Lattice Modulations in $YBa_2Cu_3O_{6.63}$ (T_c=60K) (Z.Islam *et al.*, Phys. Rev. B **66**, 092501 (2002))

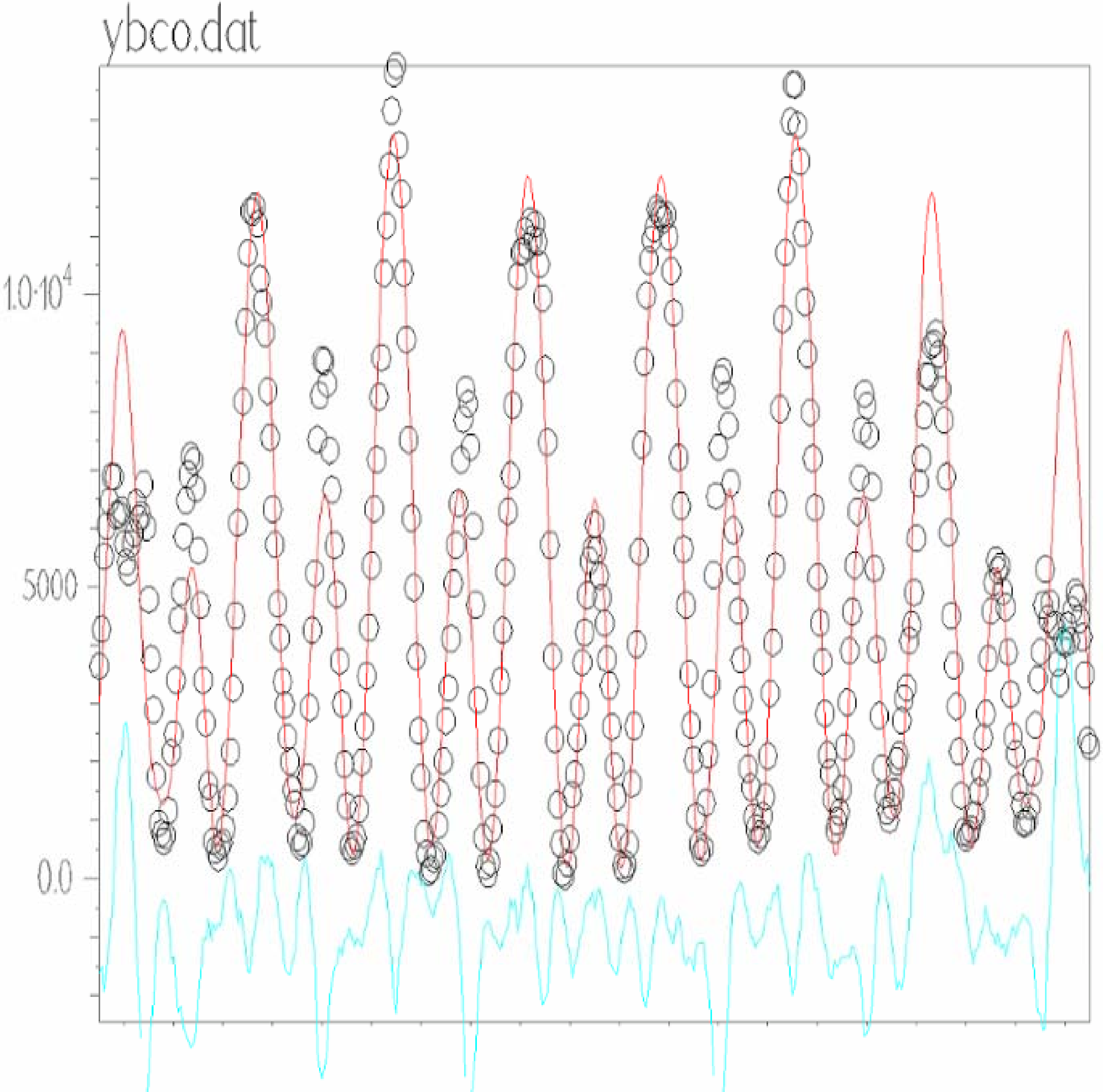




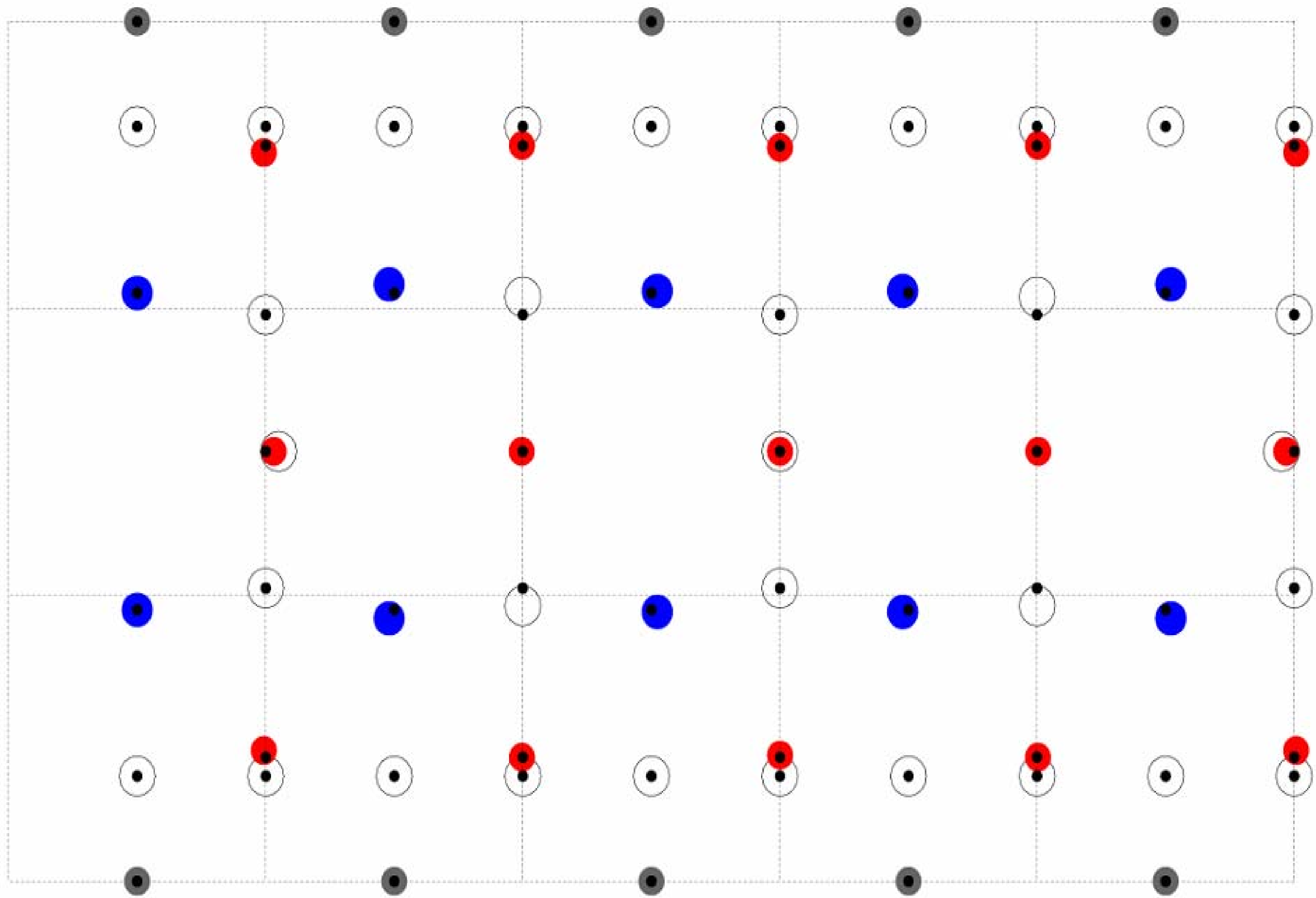
Temperature Dependence

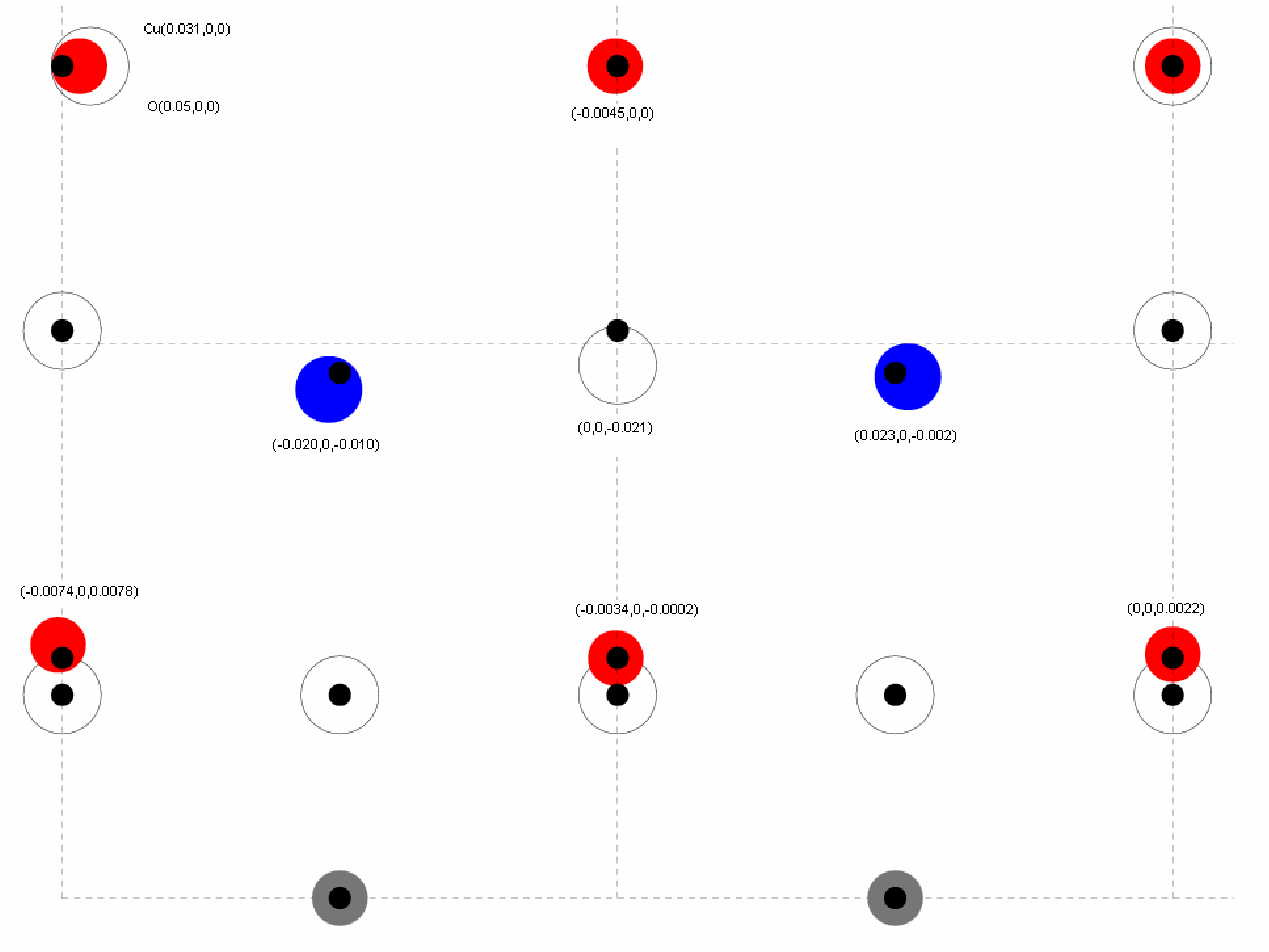



100000
75000
50000
25000
K=0
L=0
4.5
5
5.5
6
6.5
7
K=-1
L=0
K=-2
L=0
K=-3
L=0
K=-4
L=0

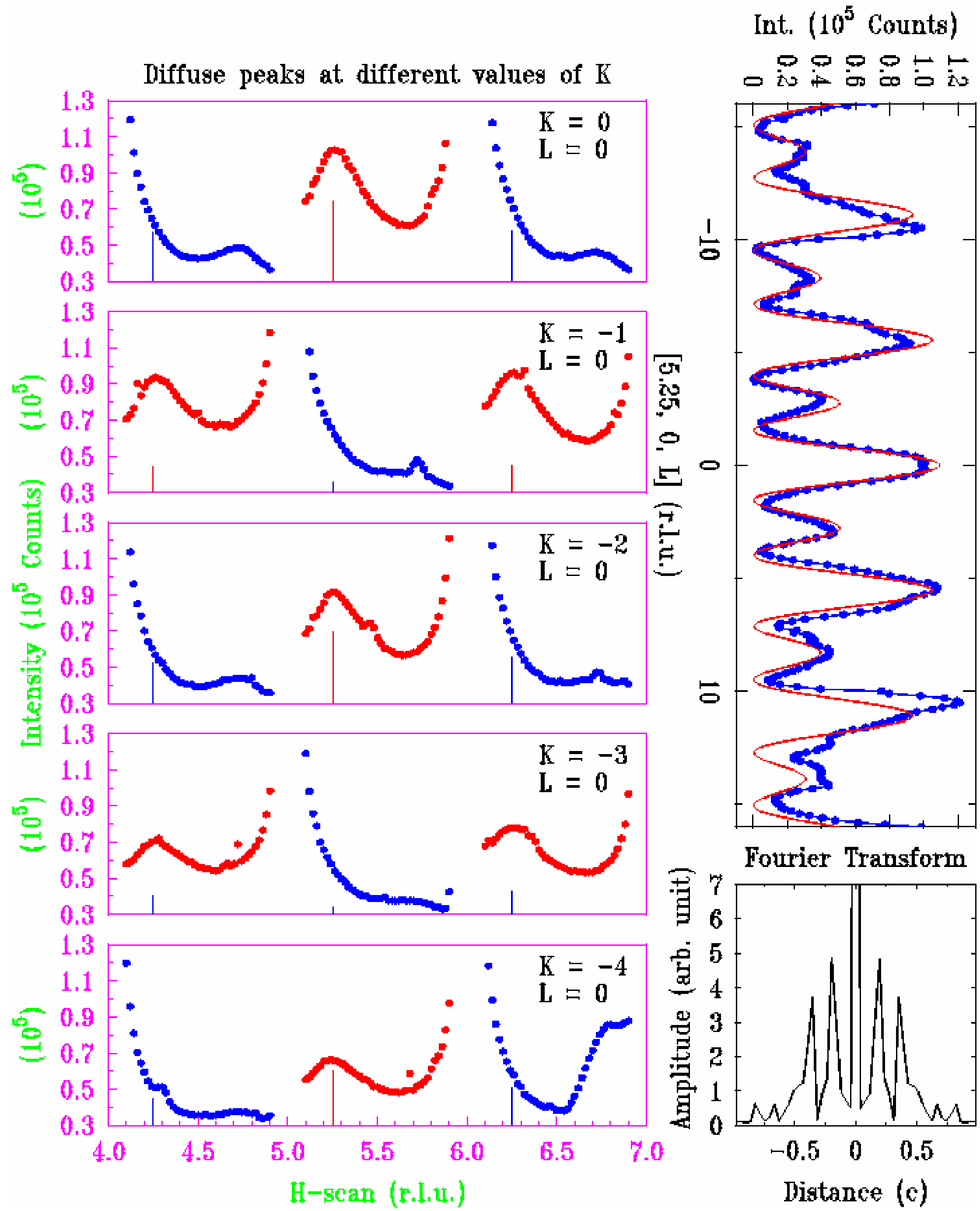


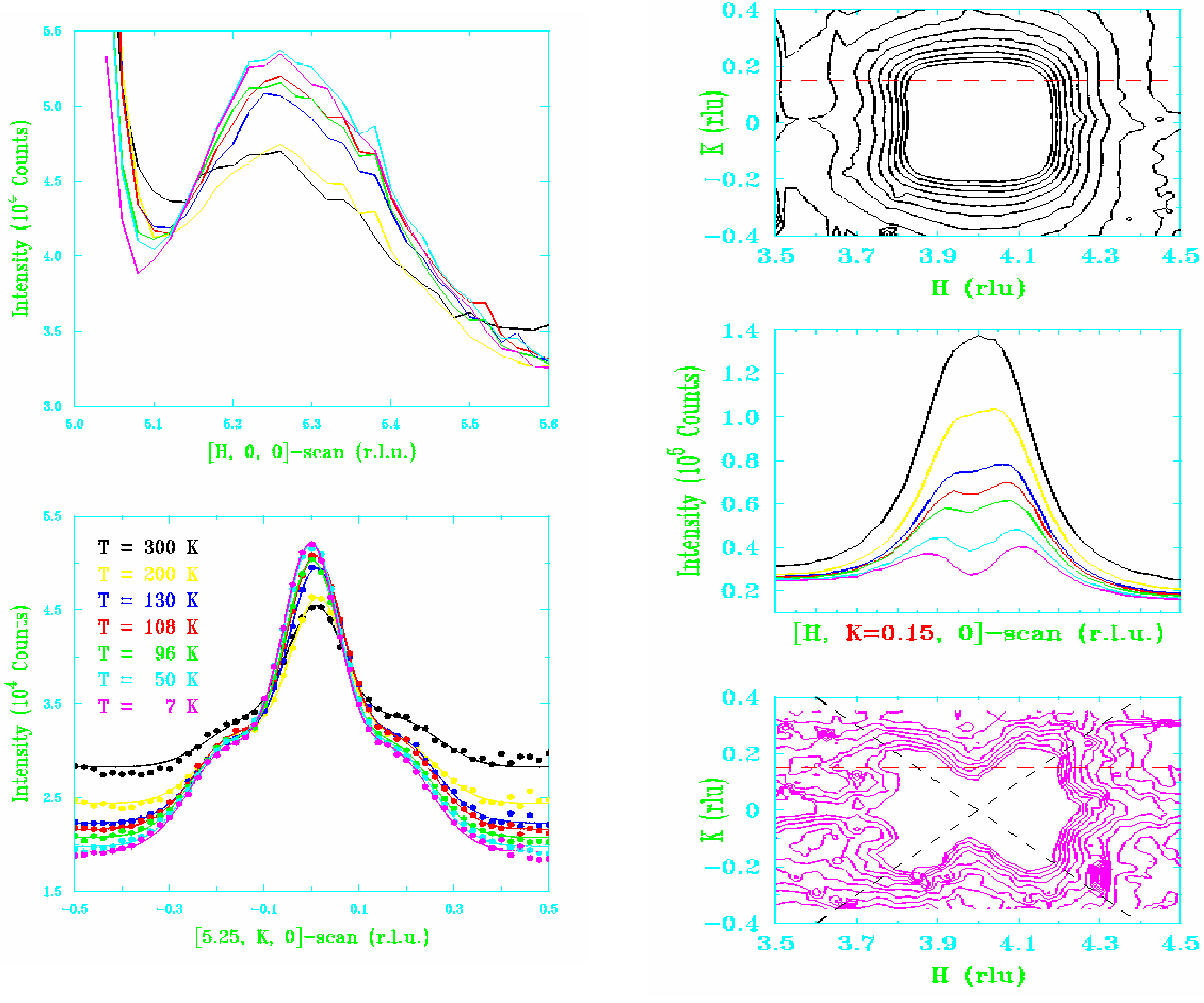
ybco.dat
1.0·10^4
5000
0.0



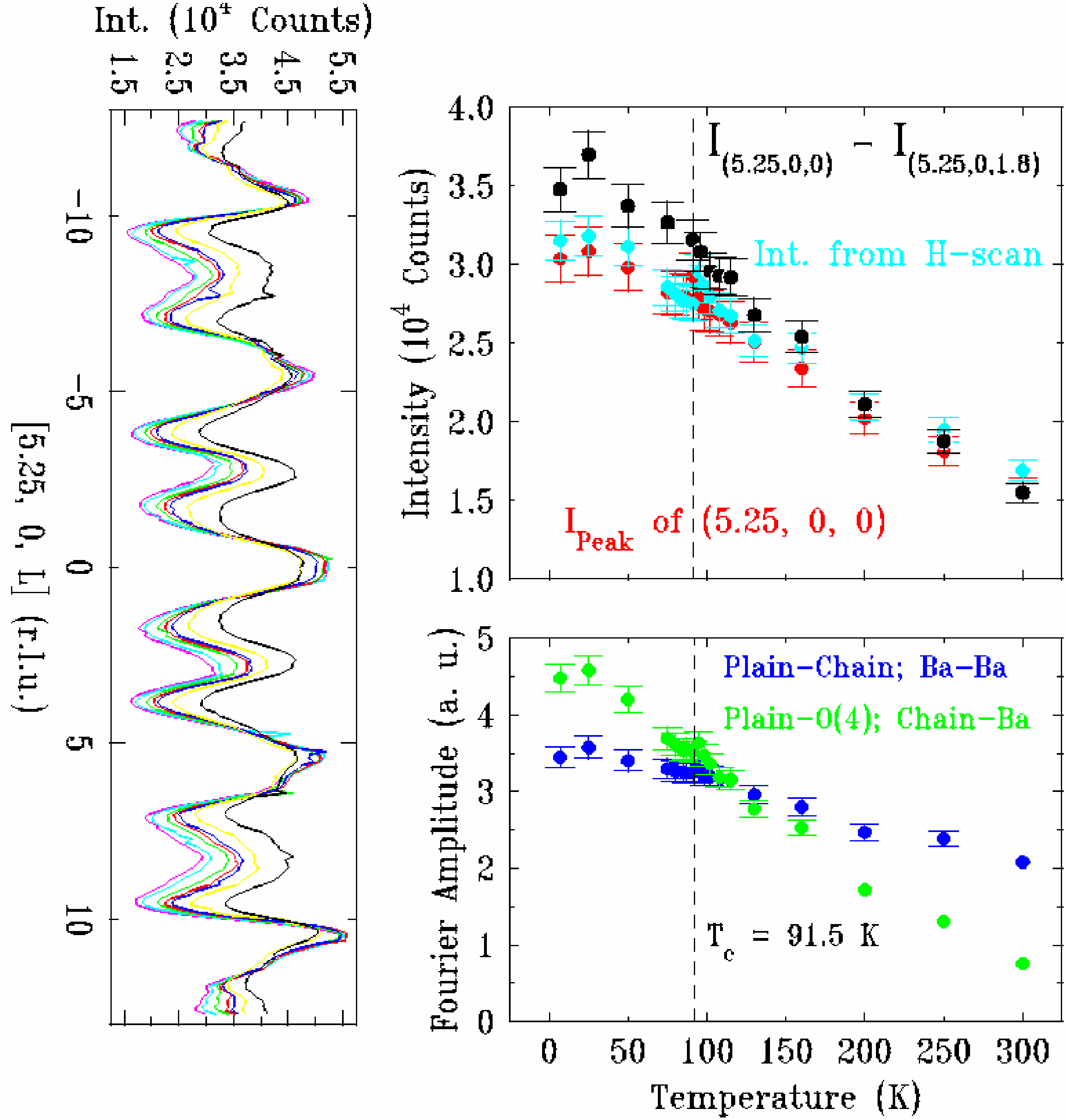

Cu(0.031,0,0)
O(0.05,0,0)
(-0.0045,0,0)
(-0.020,0,-0.010)
(0,0,-0.021)
(0.023,0,-0.002)
(-0.0074,0,0.0078)
(-0.0034,0,-0.0002)
(0,0,0.0022)

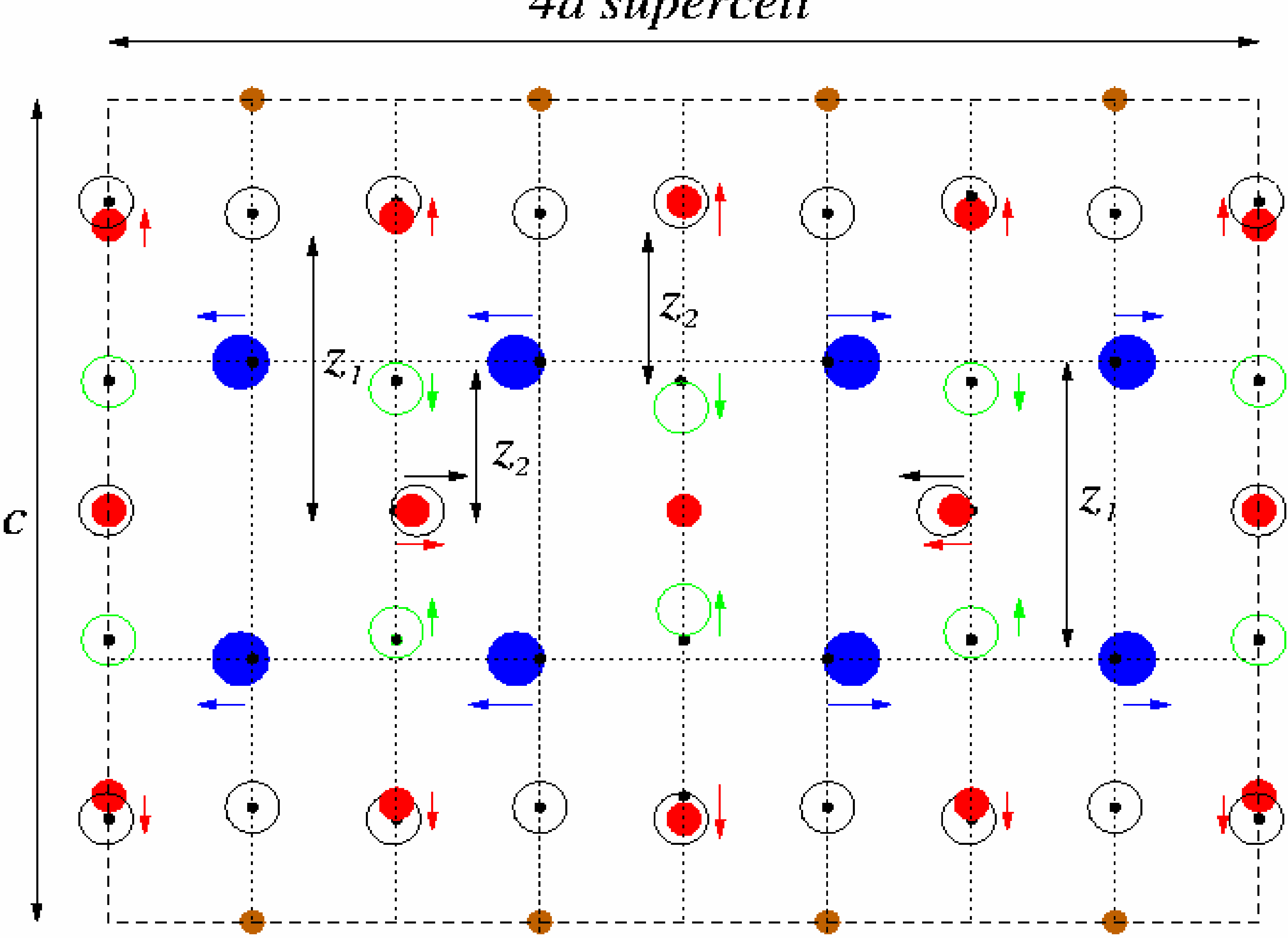
$YBa_2Cu_3O_{6.92}$
(T_c=91.5K)





Intensity (10^4 Counts)
[H, 0, 0]-scan (r.l.u.)
T = 300 K
T = 200 K
T = 130 K
T = 108 K
T = 96 K
T = 50 K
T = 7 K
[5.25, K, 0]-scan (r.l.u.)
K (rlu)
H (rlu)
Intensity (10^5 Counts)
[H, K=0.15, 0]-scan (r.l.u.)


Int. (10^4 Counts)
1.5 2.5 3.5 4.5 5.5
[5.25, 0, L] (r.l.u.)
−10 −5 0 5 10
$I_{(5.25,0,0)} - I_{(5.25,0,1.8)}$
Int. from H-scan
I_{Peak} of (5.25, 0, 0)
Intensity (10^4 Counts)
4.0 3.5 3.0 2.5 2.0 1.5 1.0
Plain-Chain; Ba-Ba
Plain-O(4); Chain-Ba
T_c = 91.5 K
Fourier Amplitude (a. u.)
5 4 3 2 1 0
0 50 100 150 200 250 300
Temperature (K)


4a supercell
c
Z_1
Z_2
Z_2
Z_1

Other things to look for:

- Evidence for orbital currents--various ordered phases.
- Evidence for surface currents in high-T_c films.
- Magnetic modulations which are related to lattice modulations.

What could we do with

Coherent Beams of X-Rays?

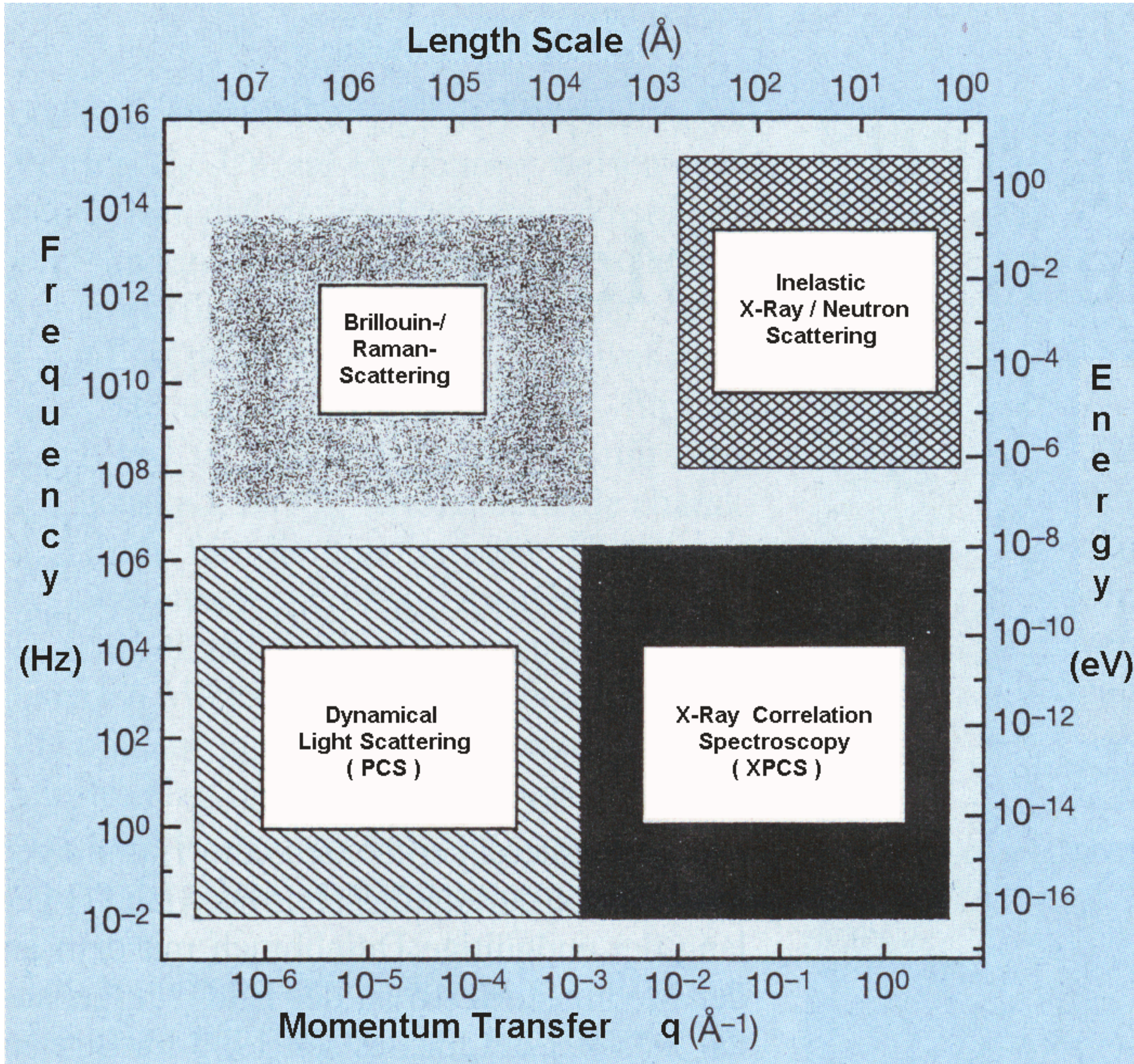
Coherence ⇒ *DYNAMICS !*

X-Ray Photon
Correlation
Spectroscopy
XPCS

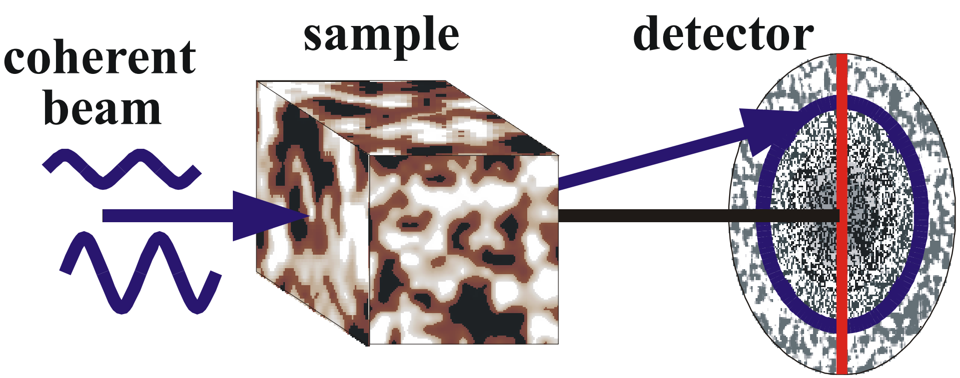
„Speckle Fluctuations“

$$g_2(\tau) = \frac{\langle I(t+\tau)I(t)\rangle_t}{\langle I(t)\rangle_t^2}$$

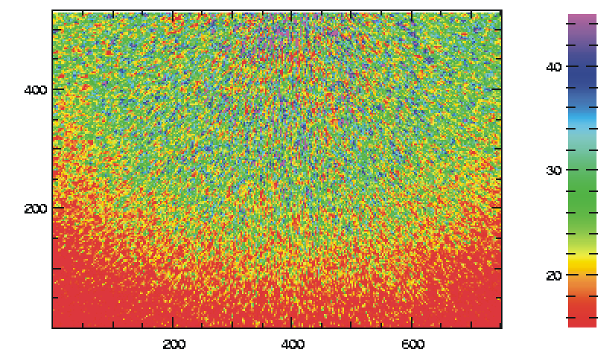
G. Grübel; Phys. Bl. *54*, 1036 (1998)

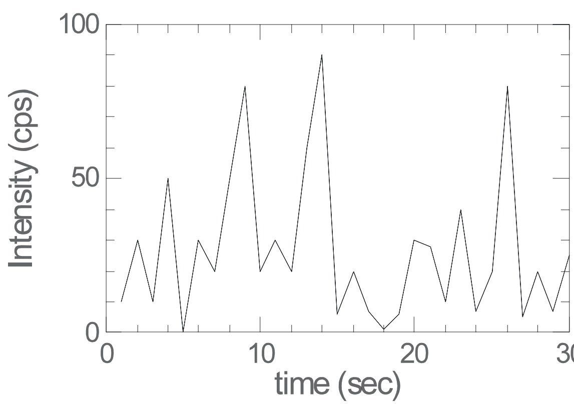


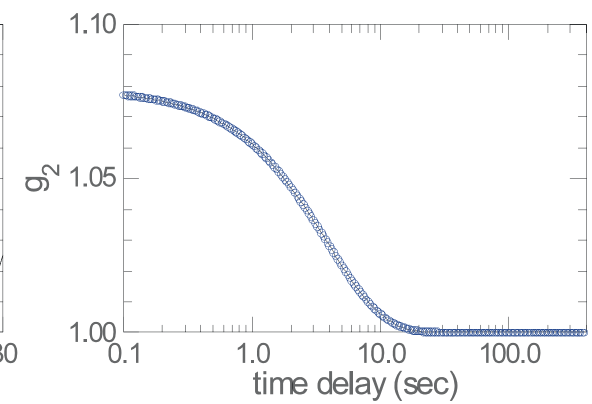
Photon Correlation Spectroscopy



X-ray speckle pattern from a static silica aerogel







$$g_2(\boldsymbol{q},t) = \frac{\langle I(\boldsymbol{q},t')I(\boldsymbol{q},t'+t)\rangle}{\langle I(\boldsymbol{q},t')\rangle^2}$$

$$g_2(t) = 1 + \beta \exp(-2\Gamma t)$$
$$= 1 + \beta \exp(-2t/\tau)$$

β:speckle contrast