Diffuse scattering studies of lattice modulations and lattice distortions in complex oxides

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Diffuse Scattering Studies of Layered Manganites

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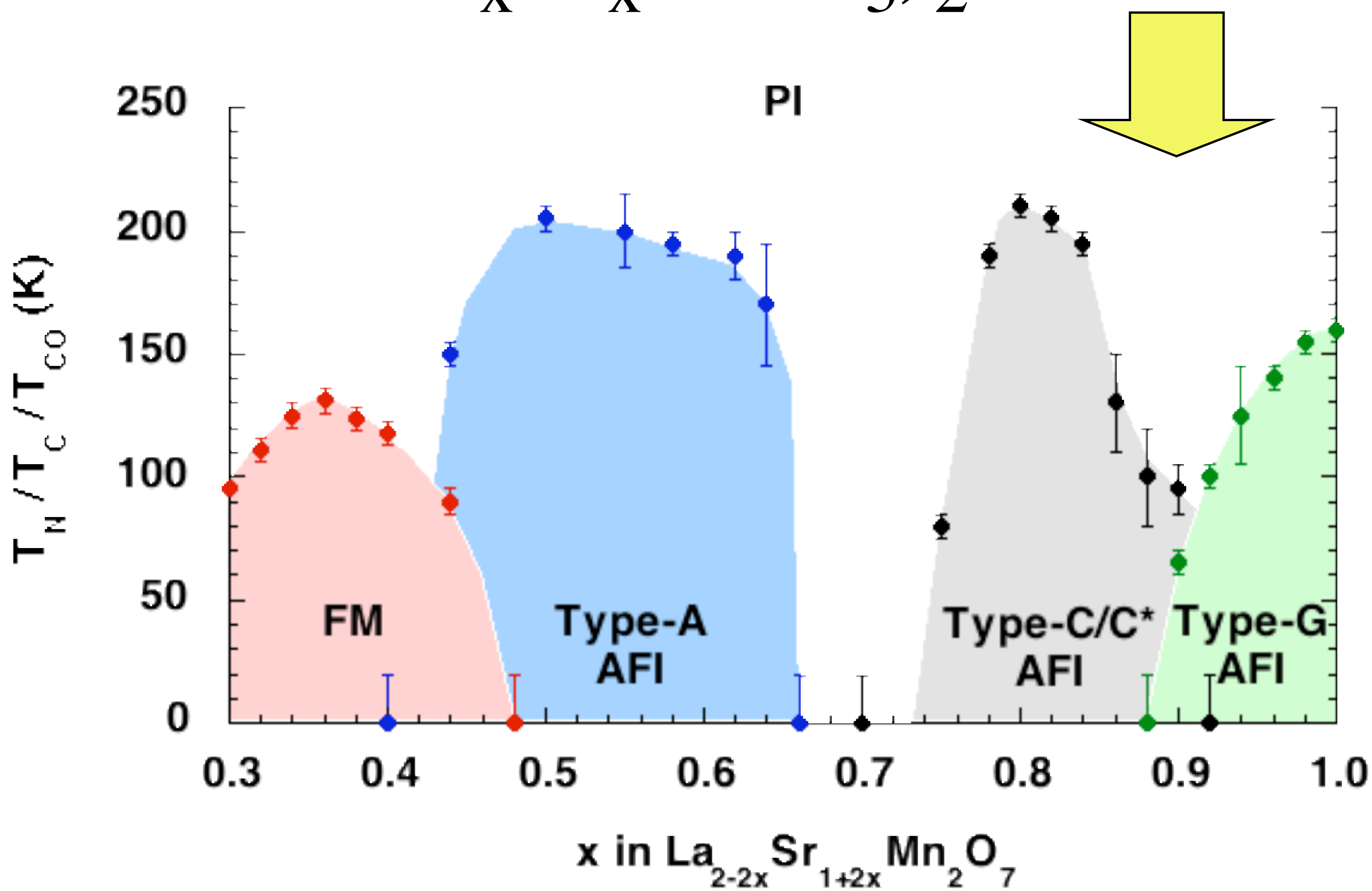
CMR Materials

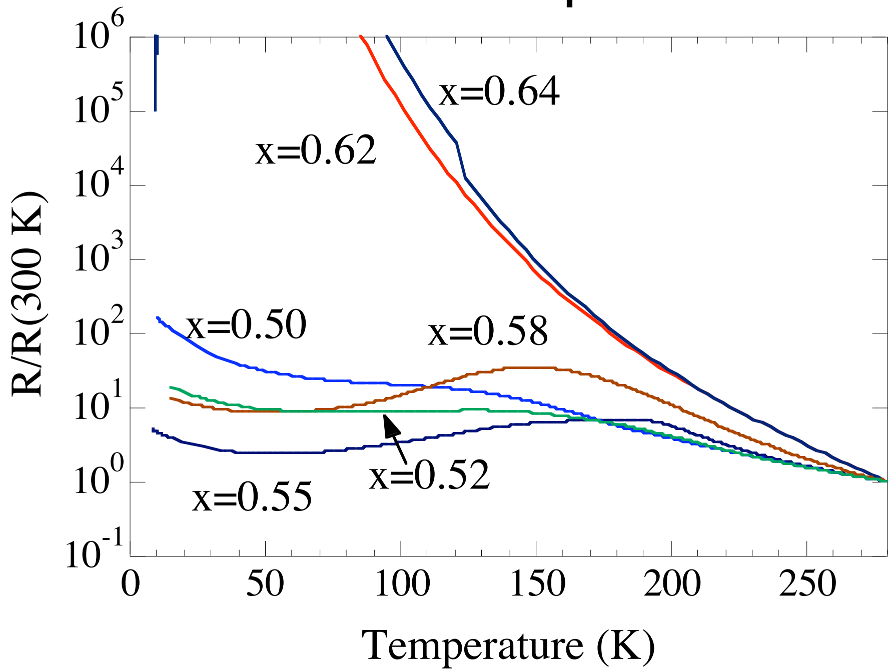
- Magnetic ordering (FM, AFM)
- Charge ordering
- Orbital ordering
- Jahn-Teller Distortions
- Polarons

Phase Diagram of SrO•(La$_{1-x}$Sr$_x$MnO$_3$)$_2$

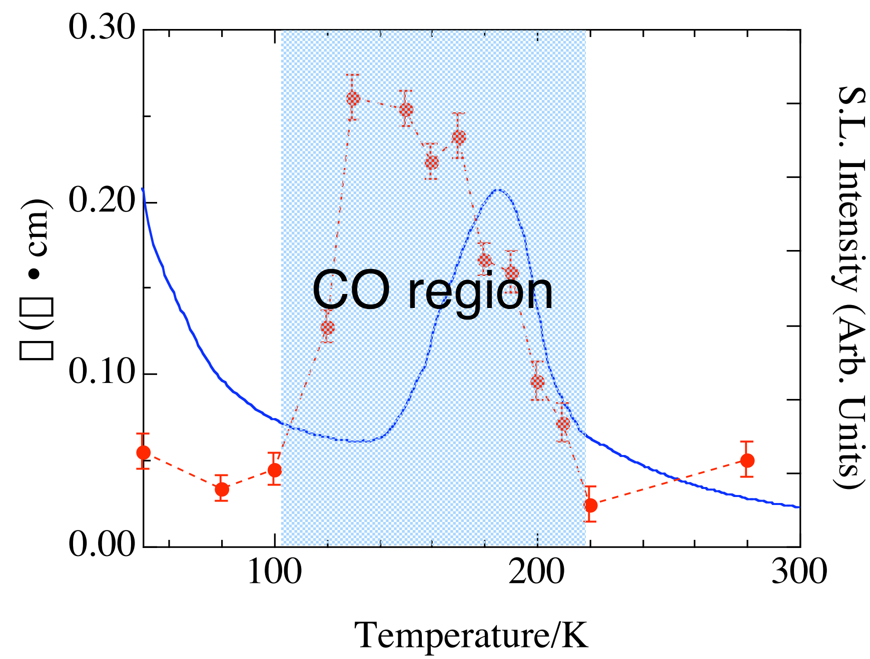


Transport Properties Abruptly Respond to Increasing Dopant Concentration

x ≥ 0.5 pellets



x=0.5 crystal

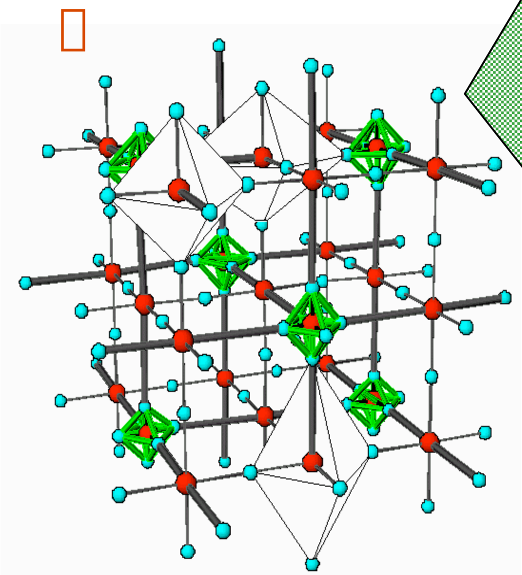


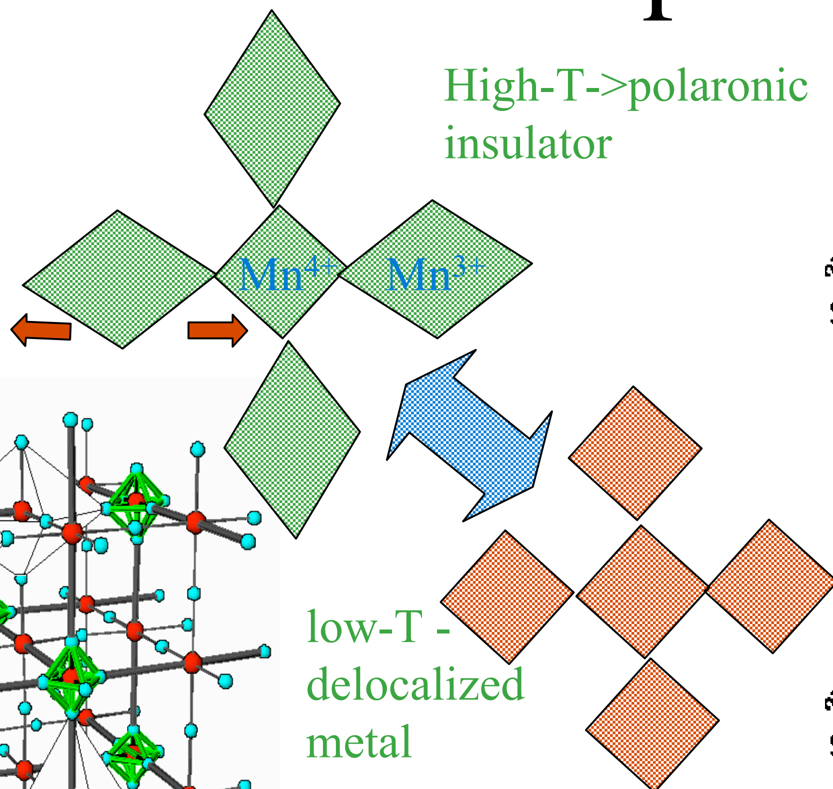
I-M transitions 0.5 ≤ x < 0.6 may indicate small region of charge-ordering, but no direct evidence

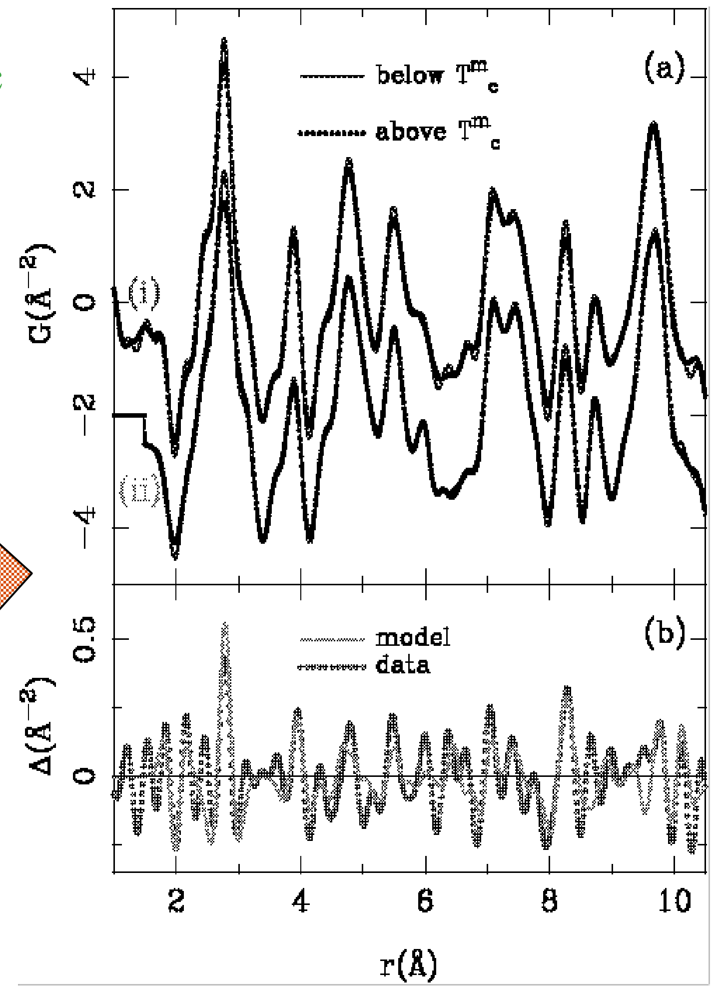
FM metals: K.E. Gray, V24.001, Thurs. 2:30 p.m.

What does the polaron look like?

□=0.24
□

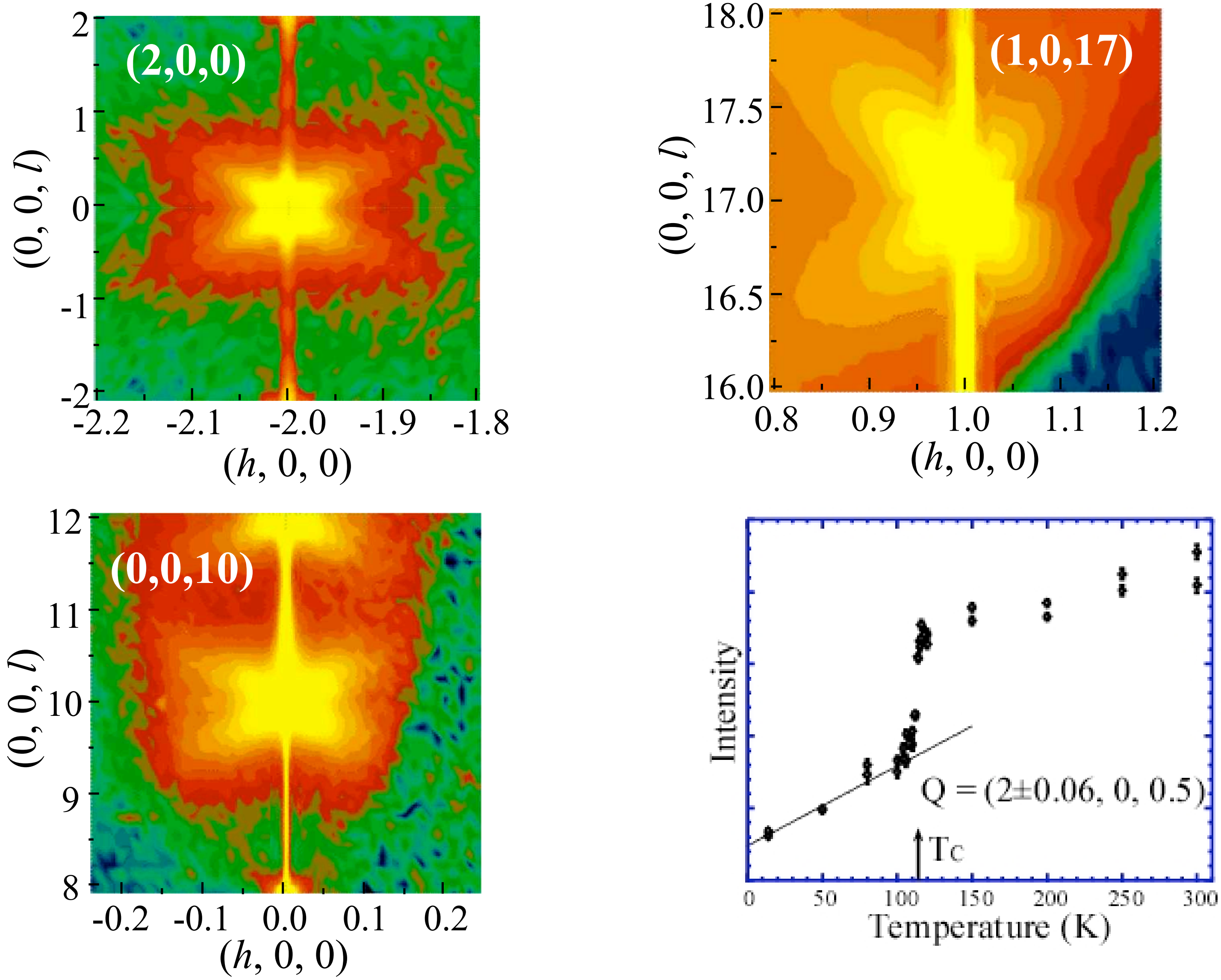






S.J.L. Billinge *et al*, *Phys. Rev. Lett*. **77**, 715 (1996); S. J. L. Billinge, *et al.*, *Phys. Rev. B* **62**, 1203 (2000)]

Polarons via single-crystal diffuse scattering



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

$$(1)\quad n(\mathbf{r}) = \sum_{m} f_m \delta(\mathbf{r} - \mathbf{R}_m - \mathbf{u}_m)$$

$$(2)\quad n(\mathbf{Q}) = \sum_{m} f_m e^{i\mathbf{Q}\cdot\mathbf{R}_m}$$

$$(3)\quad I(\mathbf{Q}) = \left\langle \left| n(\mathbf{Q}) \right|^2 \right\rangle = \sum_{m,n} f_m f_n \, d_{mn} \, e^{i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)}$$

$$(4)\quad d_{mn} = \left\langle e^{i\mathbf{Q}\cdot(\mathbf{u}_m - \mathbf{u}_n)} \right\rangle \approx e^{-W_m} e^{-W_n} e^{\left\langle (\mathbf{Q}\cdot\mathbf{u}_m)(\mathbf{Q}\cdot\mathbf{u}_n) \right\rangle}$$

$$\text{where} \quad e^{-W_m} \equiv e^{-\frac{1}{2}\left\langle \left| \mathbf{Q}\cdot\mathbf{u}_m \right|^2 \right\rangle} \quad \{\text{Debye Waller factor}\}$$

$$(5)\quad I(\mathbf{Q}) = \sum_{m,n} f_m f_n e^{i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} e^{-W_m} e^{-W_n} \left(1 + \left\langle (\mathbf{Q}\cdot\mathbf{u}_m)(\mathbf{Q}\cdot\mathbf{u}_n) \right\rangle + \ldots \right)$$

$$= \qquad I_B(\mathbf{Q}) \quad + \quad I_D(\mathbf{Q})$$

$$(6)\quad I_D(\mathbf{Q}) = \sum_{m,n} e^{i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} f_m f_n e^{-W_m} e^{-W_n} \left\langle (\mathbf{Q}\cdot\mathbf{u}_m)(\mathbf{Q}\cdot\mathbf{u}_n) \right\rangle$$

$$(7)\quad u_{m,\alpha} = \sum_{\mathbf{q},j} A(\mathbf{q},j)\,\varepsilon_{m,\alpha}(\mathbf{q},j)\, e^{i\mathbf{q}\cdot\mathbf{R}_m} \qquad \{\text{frozen phonon expansion}\}$$

$$(8)\quad F_{m,\alpha} = -\sum_{m,n,\beta} \Phi_{m,n,\alpha,\beta}\, u_{m,\beta} \qquad \{\text{force balance}\}$$

$$(9)\quad \sum_{\mathbf{q}',j',m,n,\alpha,\beta} \varepsilon^*_{n,\alpha}(\mathbf{q}',j')\, e^{-i\mathbf{q}'\cdot\mathbf{R}_n}\, \Phi_{m,n,\alpha,\beta}\, \varepsilon_{m,\beta}(\mathbf{q},j)\, e^{i\mathbf{q}\cdot\mathbf{R}_m} = N\,\omega^2(\mathbf{q},j)$$

{dynamical matrix}

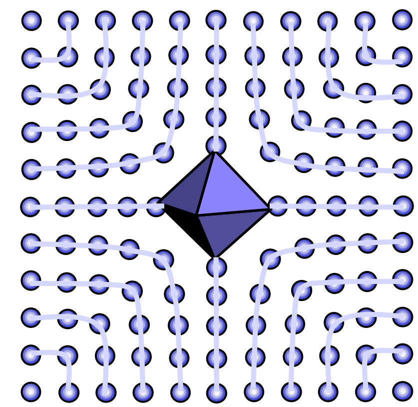
$$(10)\quad A(\mathbf{q},j) = \frac{1}{N\,\omega^2(\mathbf{q},j)} \sum_{n,\alpha} F_{n,\alpha}\, \varepsilon^*_{n,\alpha}(\mathbf{q},j)\, e^{-i\mathbf{q}\cdot\mathbf{R}_n}$$

$$(11)\quad u_{m,\alpha} = \sum_{\mathbf{q},j} \frac{1}{N\,\omega^2(\mathbf{q},j)} \sum_{n,\beta} \varepsilon^*_{n,\beta}(\mathbf{q},j)\, e^{-i\mathbf{q}\cdot\mathbf{R}_n}\, F_{n,\beta}\, \varepsilon_{m,\alpha}(\mathbf{q},j)\, e^{i\mathbf{q}\cdot\mathbf{R}_m}$$

$$= \sum_{\beta,\mathbf{q},j} \frac{\varepsilon^*_{\beta,\mathbf{q},j}\, \varepsilon_{\alpha,\mathbf{q},j}}{q^2 v^2_{\mathbf{q},j}} \sum_n F_{n,\beta}\, e^{i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} \qquad \{\text{elastic continuum}\}$$

$$I_{POL}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \square_{\square,\square,\square,\square} Q_\square Q_\square \square \square_{j,j'} \frac{\square_{\square,\mathbf{q},j}\square^*_{\square,\mathbf{q},j}\square^*_{\square,\mathbf{q},j'}\square_{\square,\mathbf{q},j'}}{q^4 v^2_{\mathbf{q},j} v^2_{\mathbf{q},j'}} \square \square_{m,n} \square_{m,\square}\square_{n,\square} e^{i\mathbf{q}\cdot(\mathbf{R}_m \square \mathbf{R}_n)}$$

$$I_{TDS}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \square \frac{kT}{2M} \square \square_{\square,\square} Q_\square Q_\square \square_j \frac{\square^*_{\square,\mathbf{q},j}\square_{\square,\mathbf{q},j}}{q^2 v^2_{\mathbf{q},j}}$$



$$u_{m,\square} = \square_{\square,\mathbf{q},j} \frac{\square^*_{\square,\mathbf{q},j}\square_{\square,\mathbf{q},j}}{q^2 v^2_{\mathbf{q},j}} \square_n \square_{n,\square} e^{i\mathbf{q}\cdot(\mathbf{R}_m \square \mathbf{R}_n)}$$

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

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

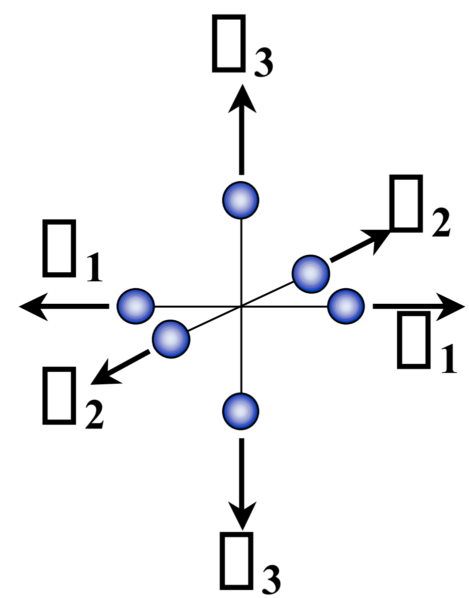
Calculate eigenvectors/eigenvalues of continuum DM.

Calculate diffuse scattering (quadratic in the forces).

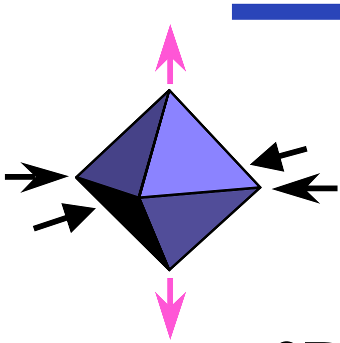
Fit the forces against the experimental data.

Integrate the displacement expression.

Determine temperature evolution of local structure.

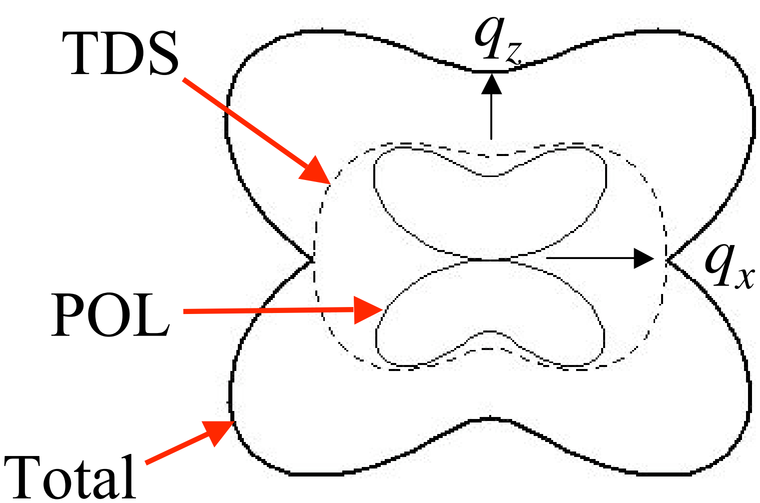


Polaronic + TDS scattering

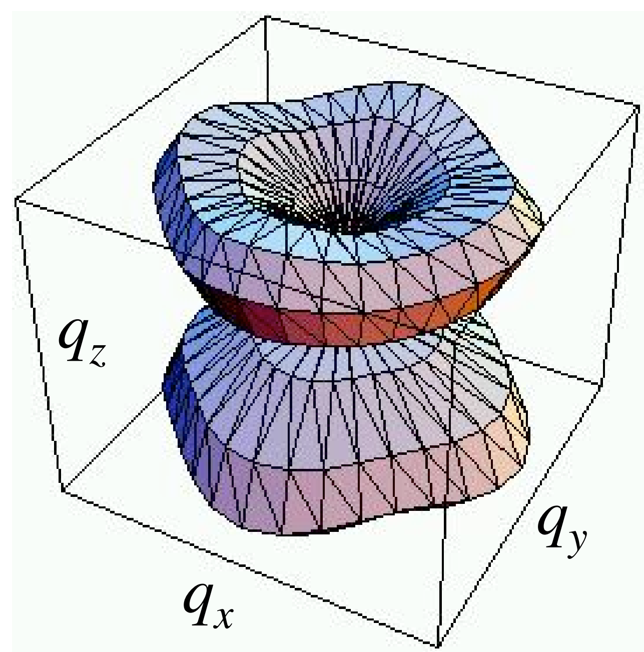


c-axis JT stretch: $I = I_{\mathrm{POLARONIC}} + I_{\mathrm{TDS}}$

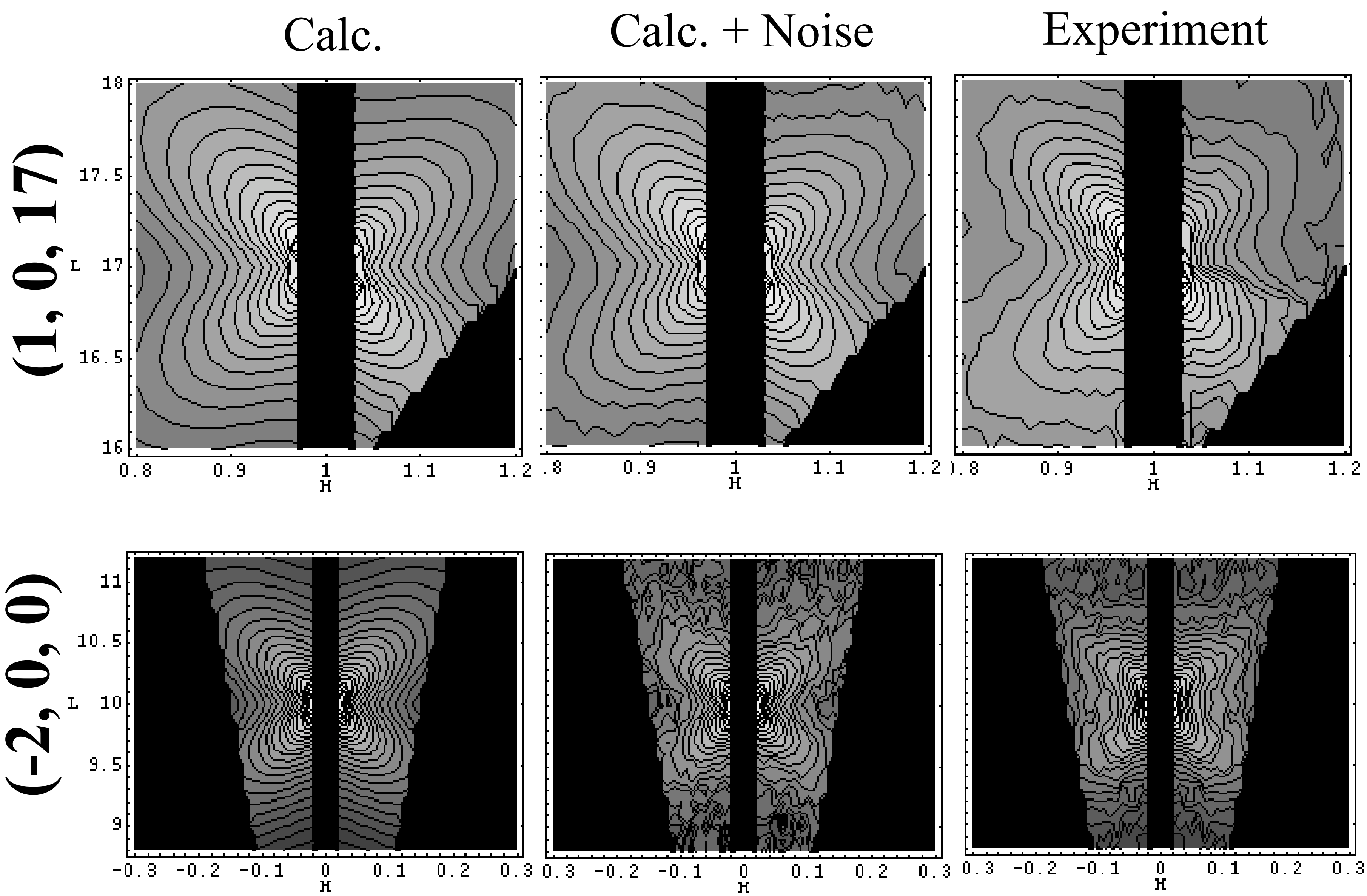
2D iso-intensity curve around (0, 0, 10). A (q_x,0,q_z) section.



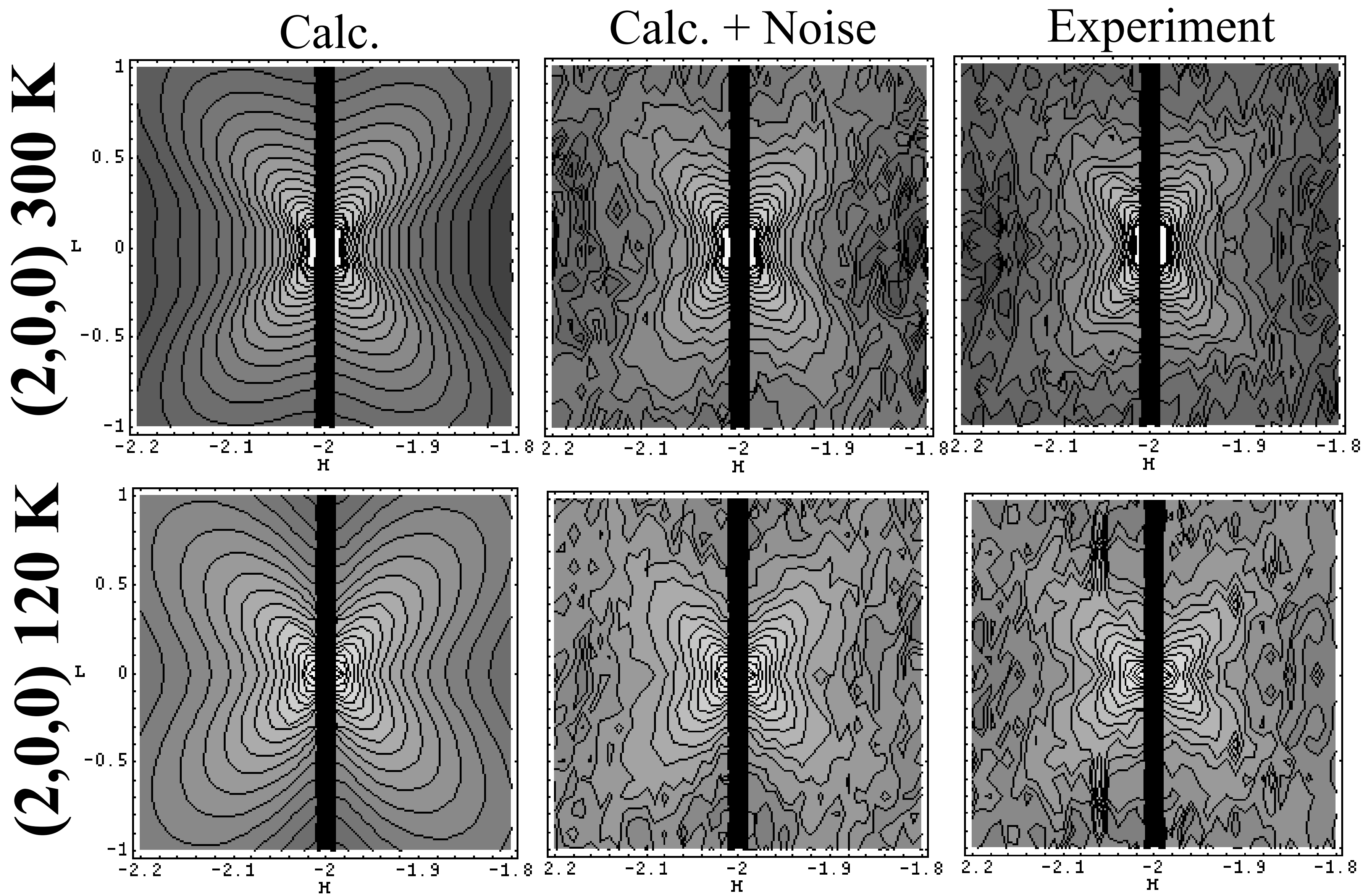
3D iso-intensity surface around (0, 0, 10).



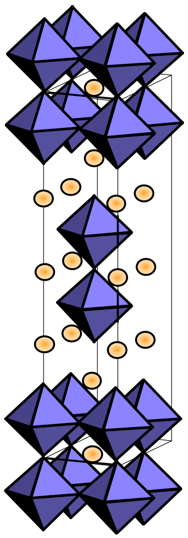
Experiment vs. Calculation (300 K)



New orbital polarization near T_C

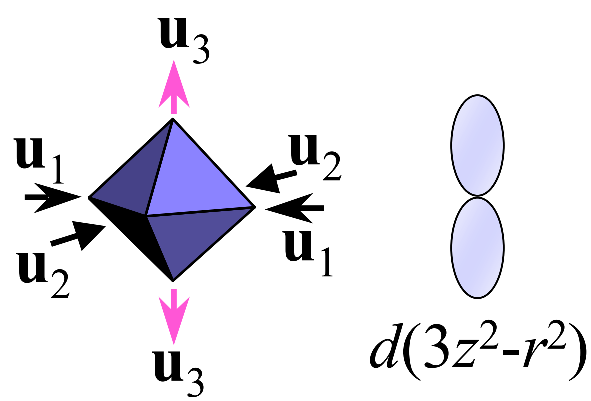


JT polarons: A 3D local structure model

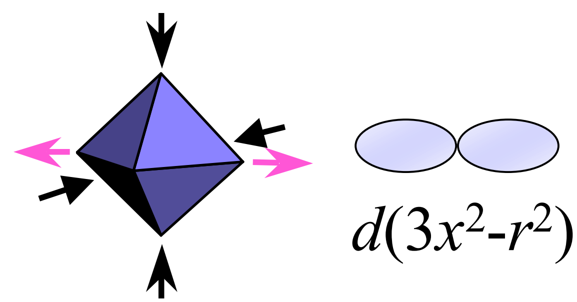


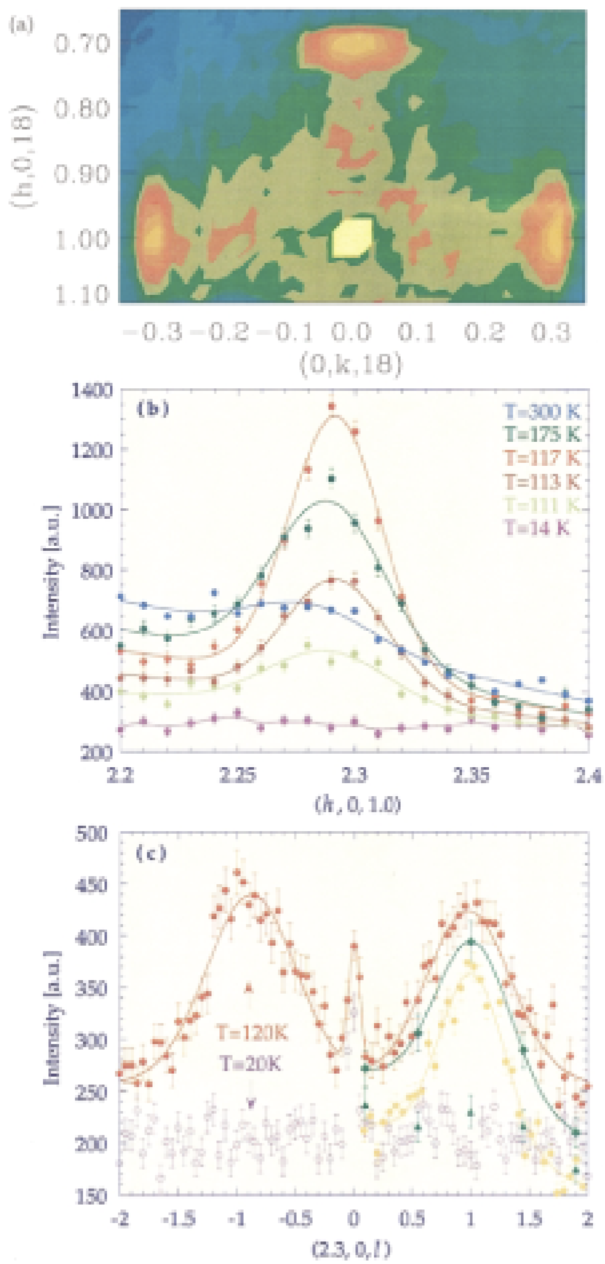
$$\begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = a\sqrt{\frac{kT}{2Mv_0^2\, x(1-x)}} \begin{bmatrix} 0.444 & -0.119 & -0.126 \\ -0.119 & 0.444 & -0.126 \\ -0.126 & -0.126 & 0.429 \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix}$$

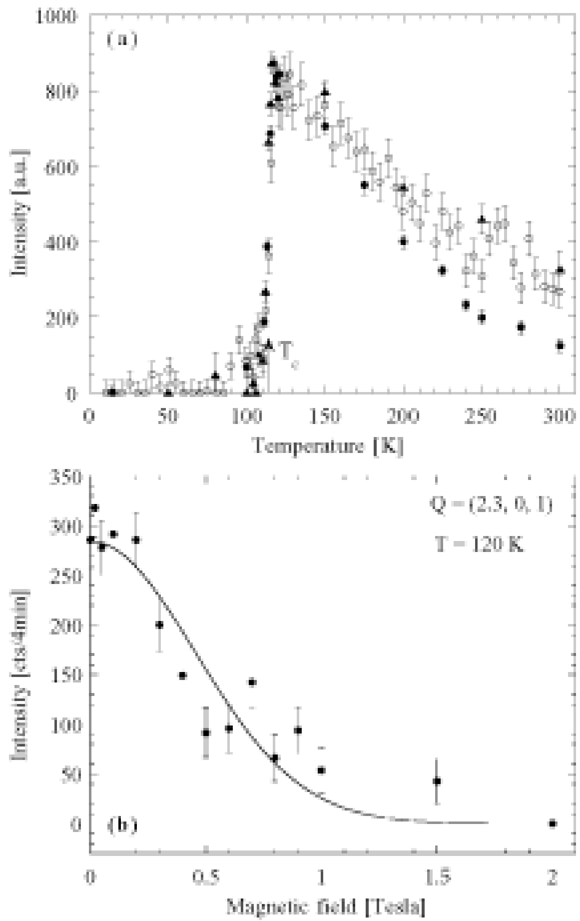
$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix} = \begin{bmatrix} 0.6 \\ 0.6 \\ 3.0 \end{bmatrix} \text{ at 300 K} \Rightarrow \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \begin{bmatrix} -0.0120 \\ -0.0120 \\ 0.0744 \end{bmatrix} \text{Å}$$



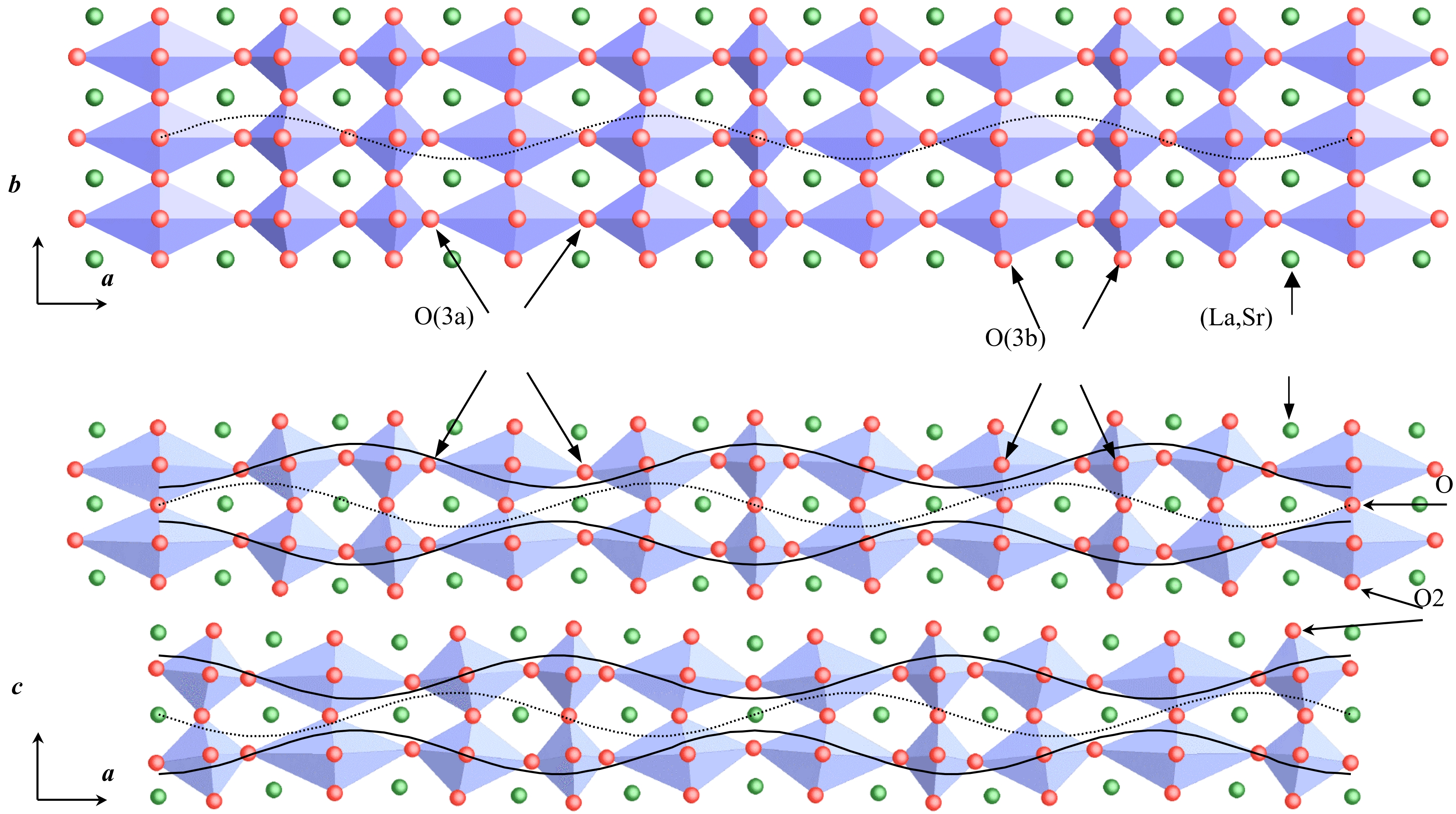
$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix} = \begin{bmatrix} 4.5 \\ 0 \\ 0 \end{bmatrix} \text{ at 120 K} \Rightarrow \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \begin{bmatrix} 0.0828 \\ -0.0222 \\ -0.0234 \end{bmatrix} \text{Å}$$




(a)
0.70
0.80
0.90
1.00
1.10
(h,0,18)
−0.3 −0.2 −0.1 0.0 0.1 0.2 0.3
(0,k,18)
(b)
T=300 K
T=175 K
T=117 K
T=113 K
T=111 K
T=14 K
Intensity [a.u.]
1400
1200
1000
800
600
400
200
2.2
2.25
2.3
2.35
2.4
(h, 0, 1.0)
(c)
T=120K
T=20K
Intensity [a.u.]
500
450
400
350
300
250
200
150
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
(2.3, 0, l)



(a)
Intensity [a.u.]
Temperature [K]
T_c
(b)
Q = (2.3, 0, 1)
T = 120 K
Intensity [cts/4min]
Magnetic field [Tesla]



b
a
O(3a)
O(3b)
(La,Sr)
O1
O2
c
a

Lattice Modulations and Distortions in YBa2Cu3O6+x

• Zahirul Islam	ANL
• Dan Haskell	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

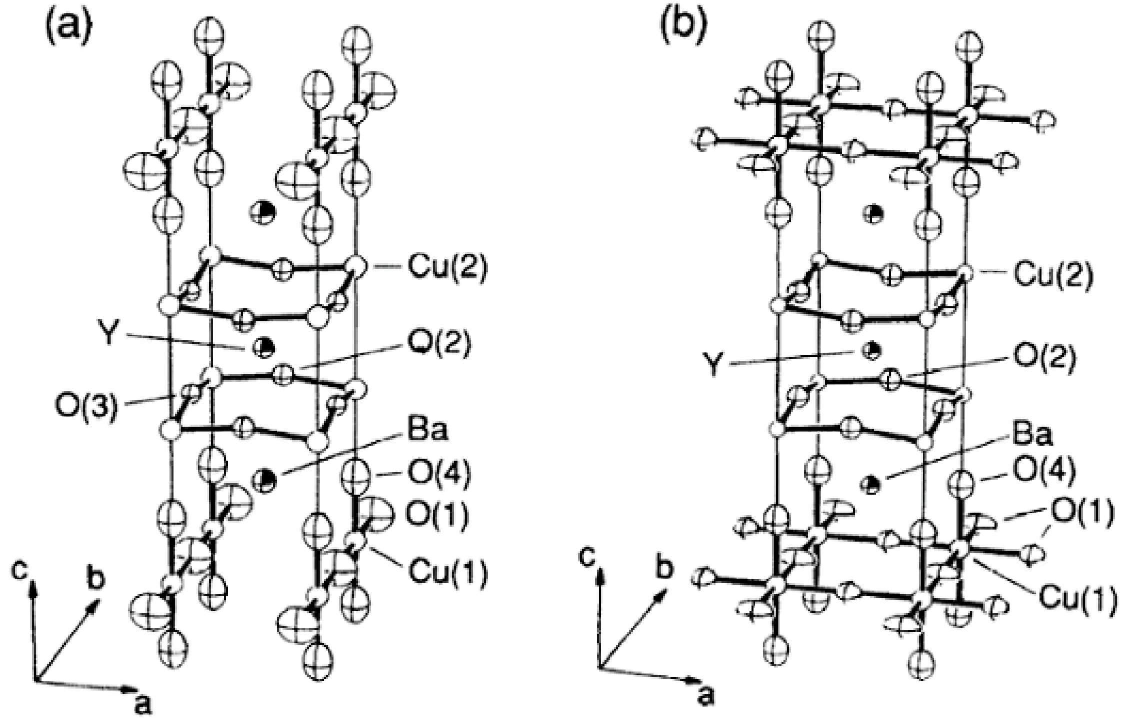
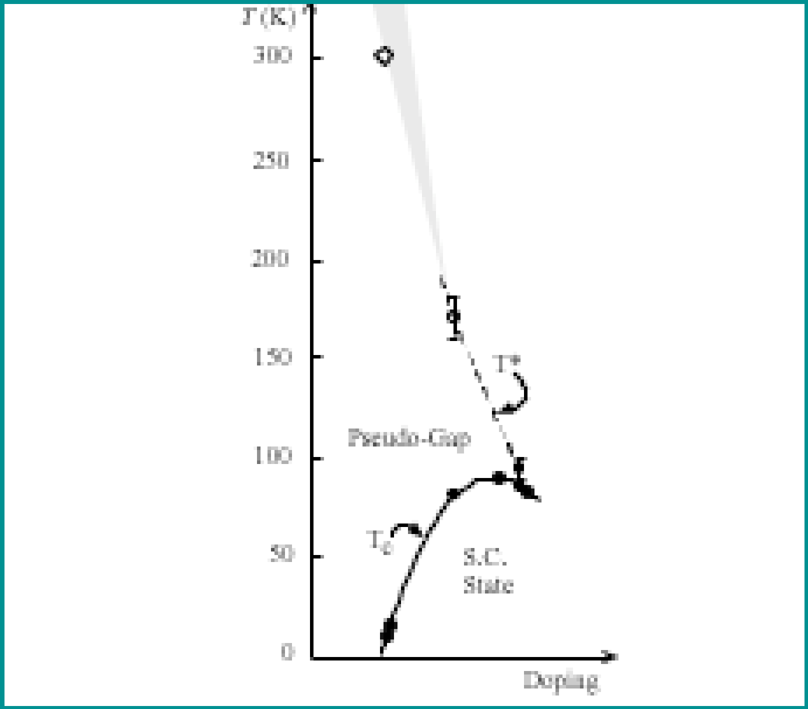


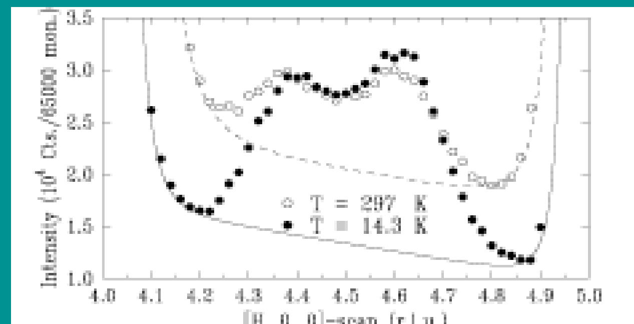
FIG. 1. (a) Orthorhombic and (b) tetragonal structures of $YBa_2Cu_3O_{7-\delta}$. In the tetragonal structure (b) the different atom symbol for the O(1) site is used to indicate that this site is not fully occupied.

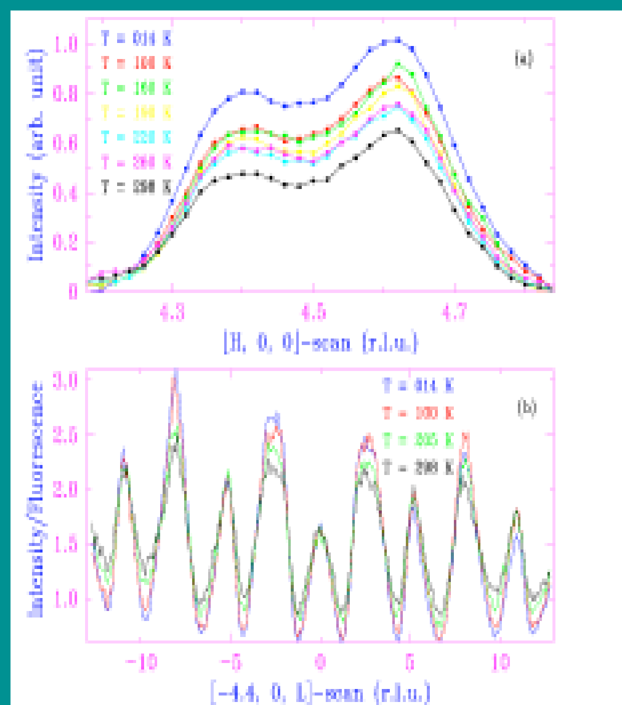
A/F and S/C….What else?

- 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

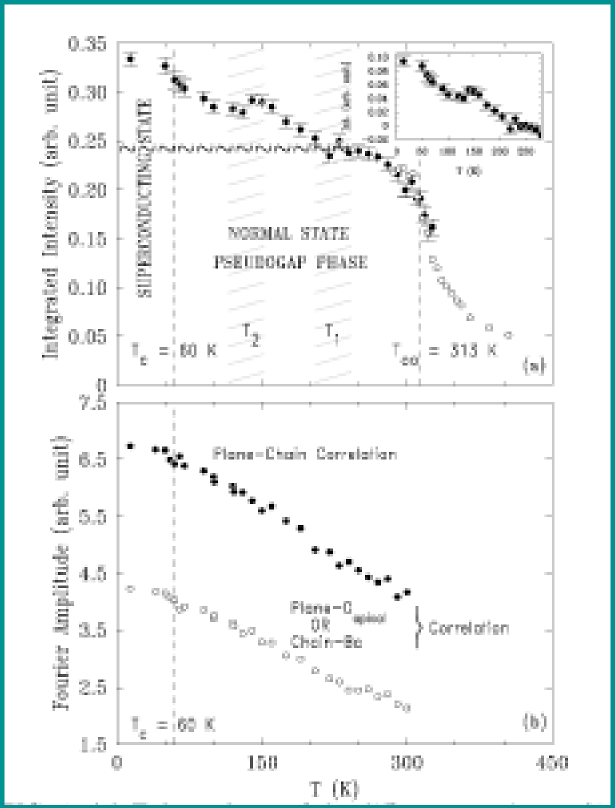


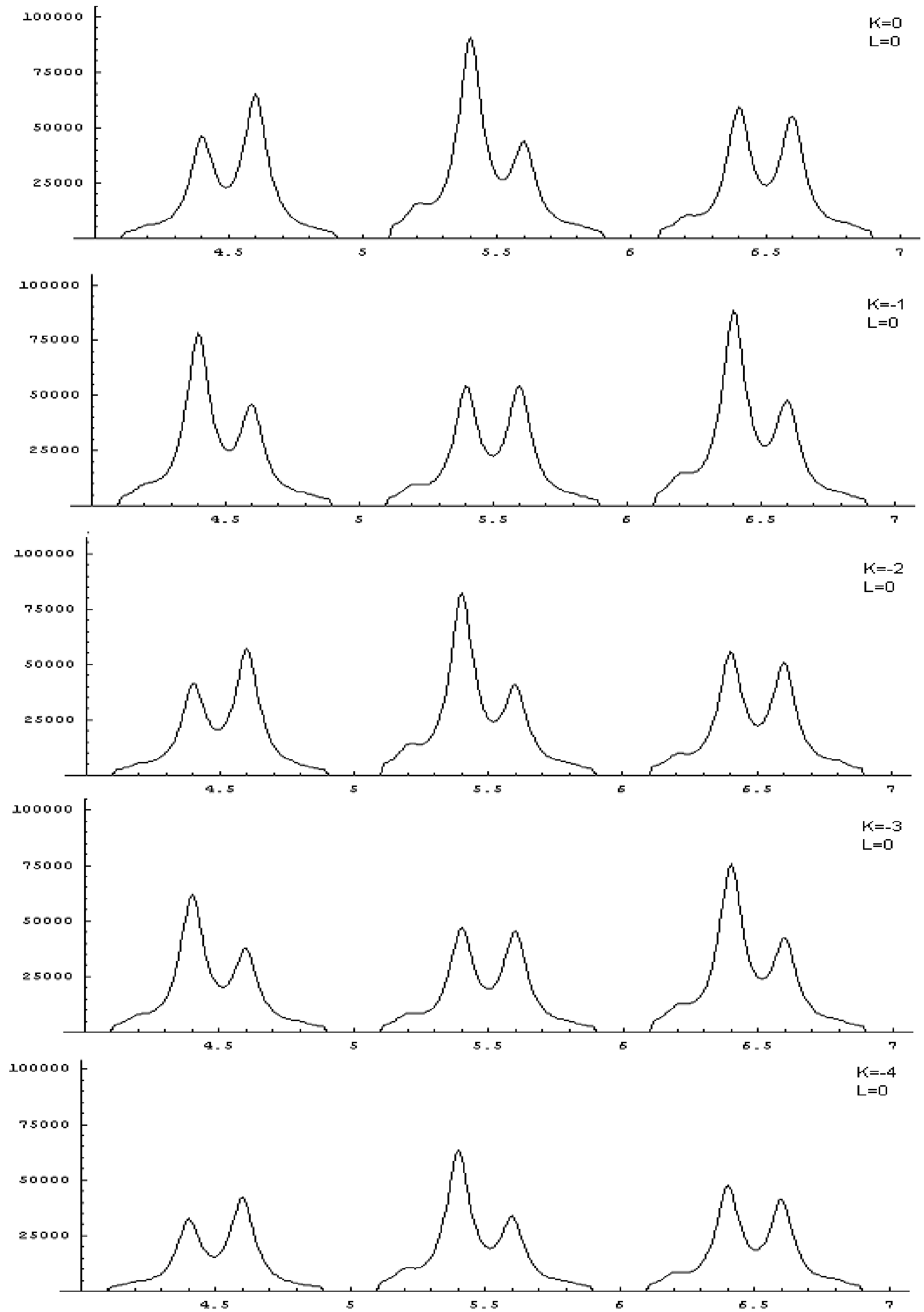
Using 65 KeV X-Rays to look for Lattice Modulations in $YBa_2Cu_3O_{6.63}$ (T_c=60K) (Z.Islam et al., Phys. Rev. B 66, 092501 (2002))



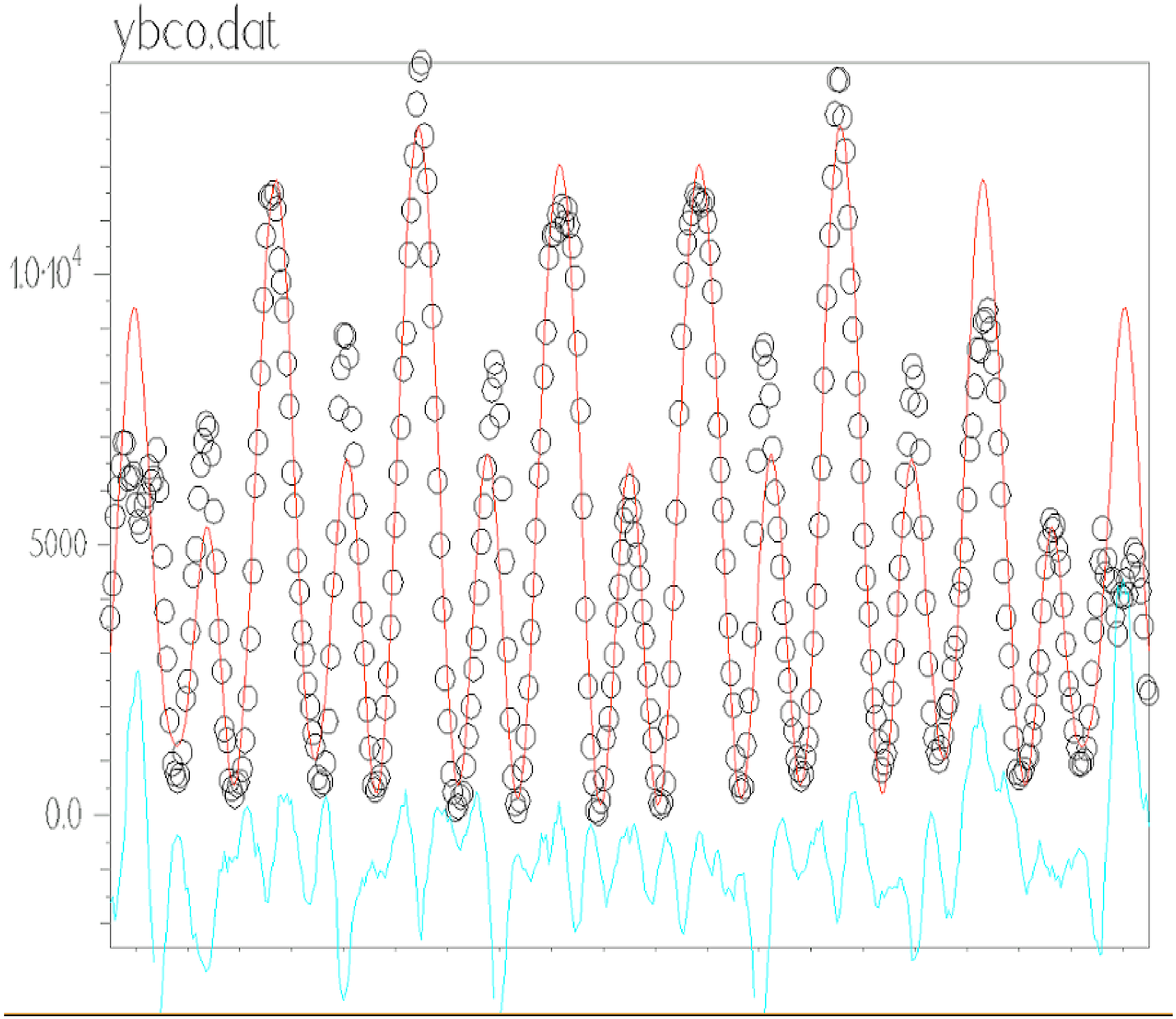


Temperature Dependence of Diffuse Peak Intensities

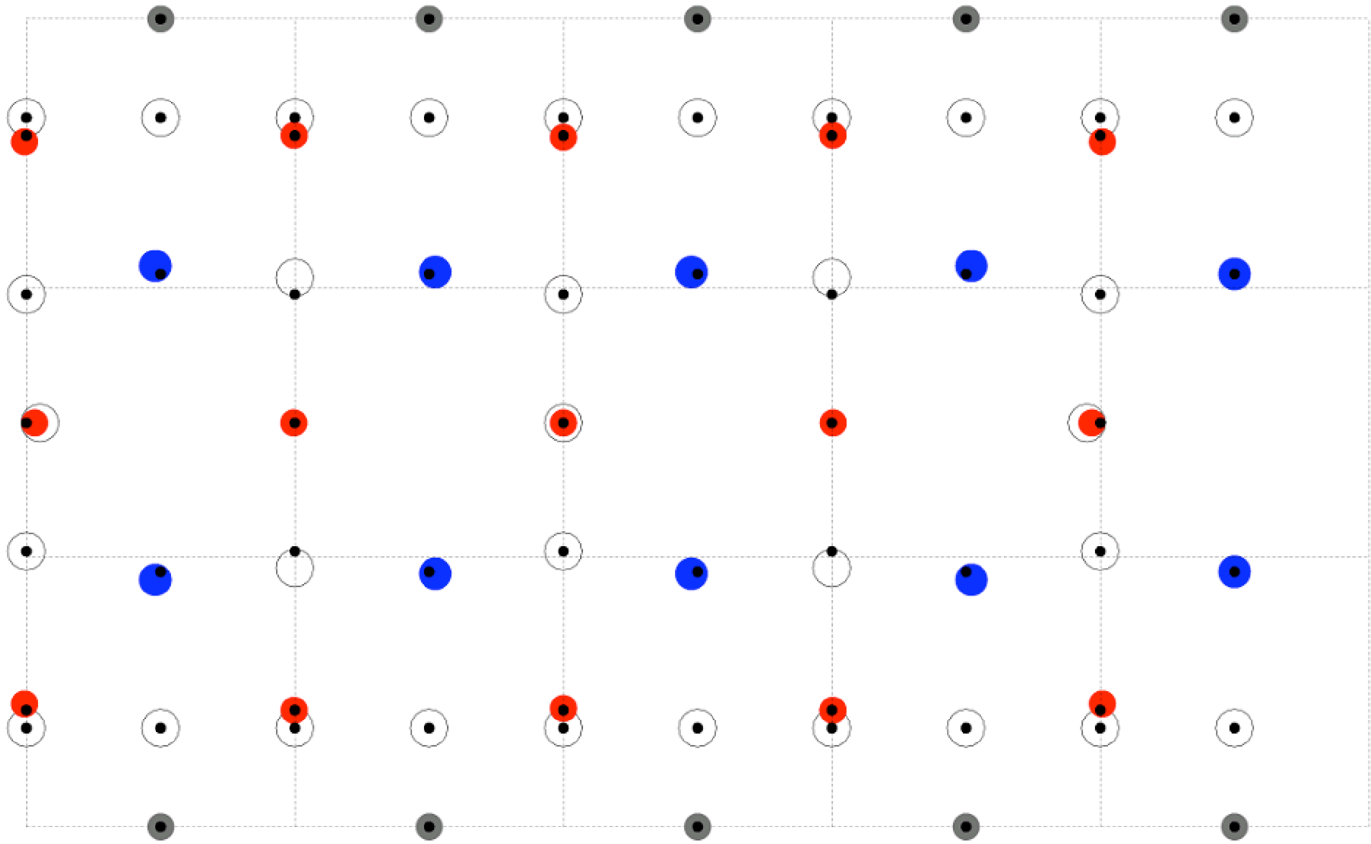


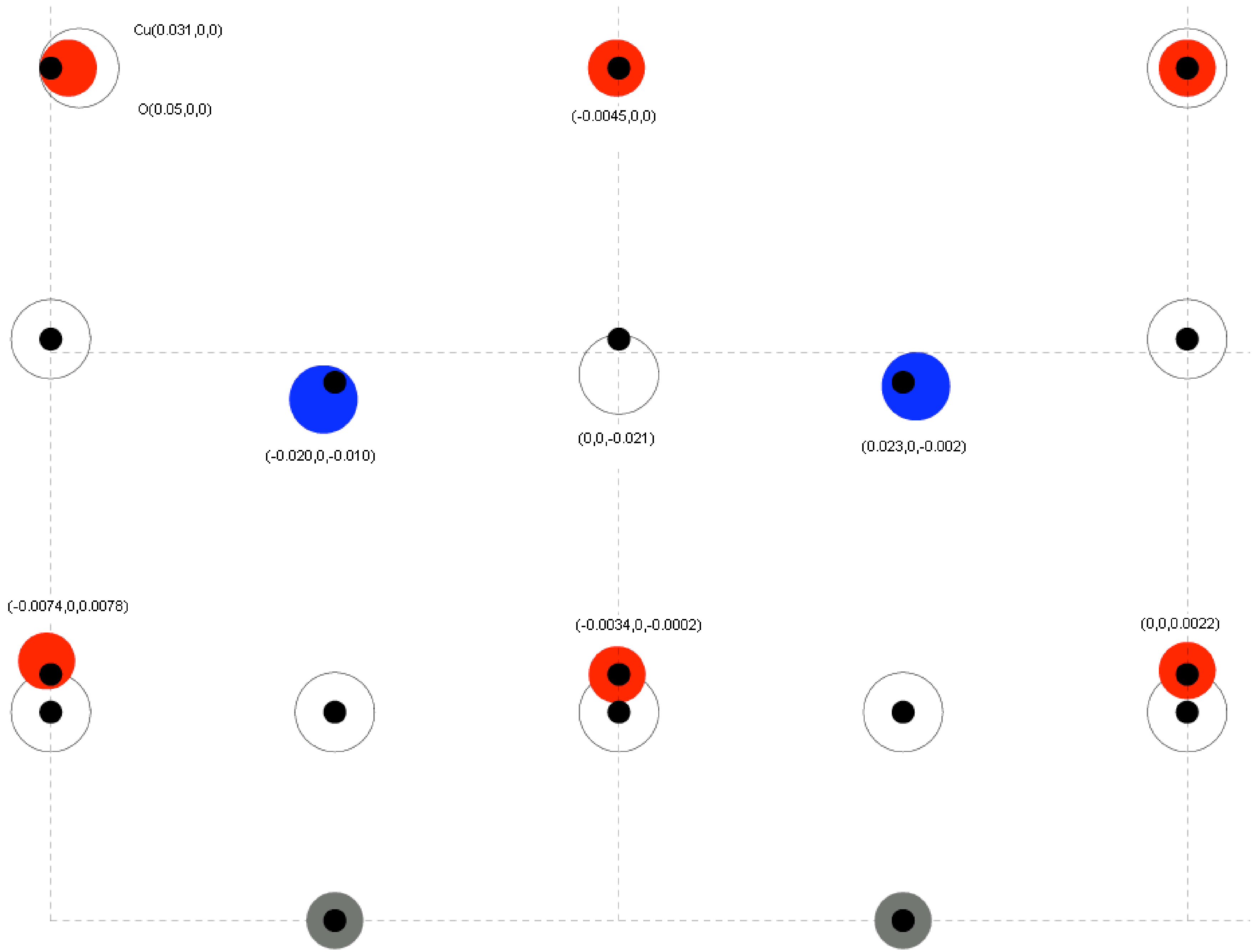


100000
75000
50000
25000
4.5
5
5.5
6
6.5
7
K=0
L=0
K=-1
L=0
K=-2
L=0
K=-3
L=0
K=-4
L=0

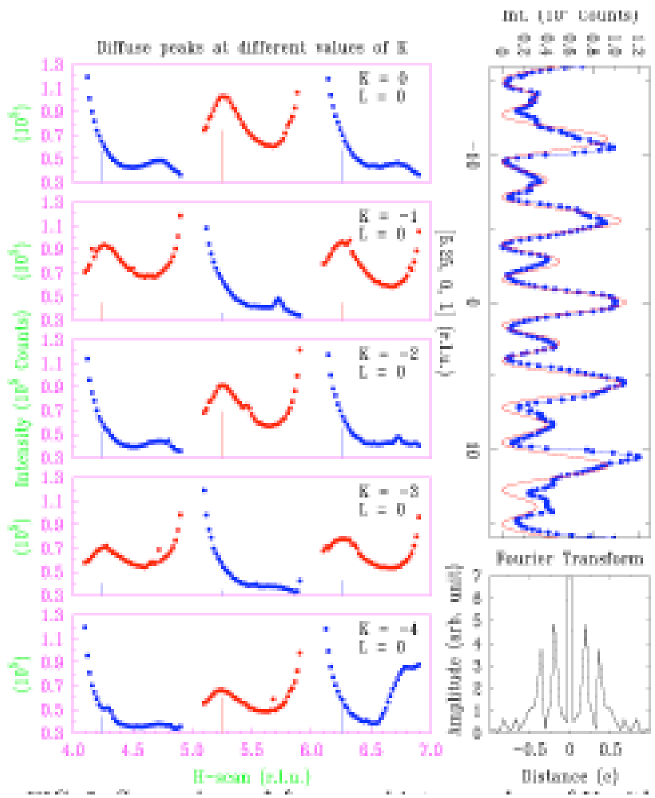


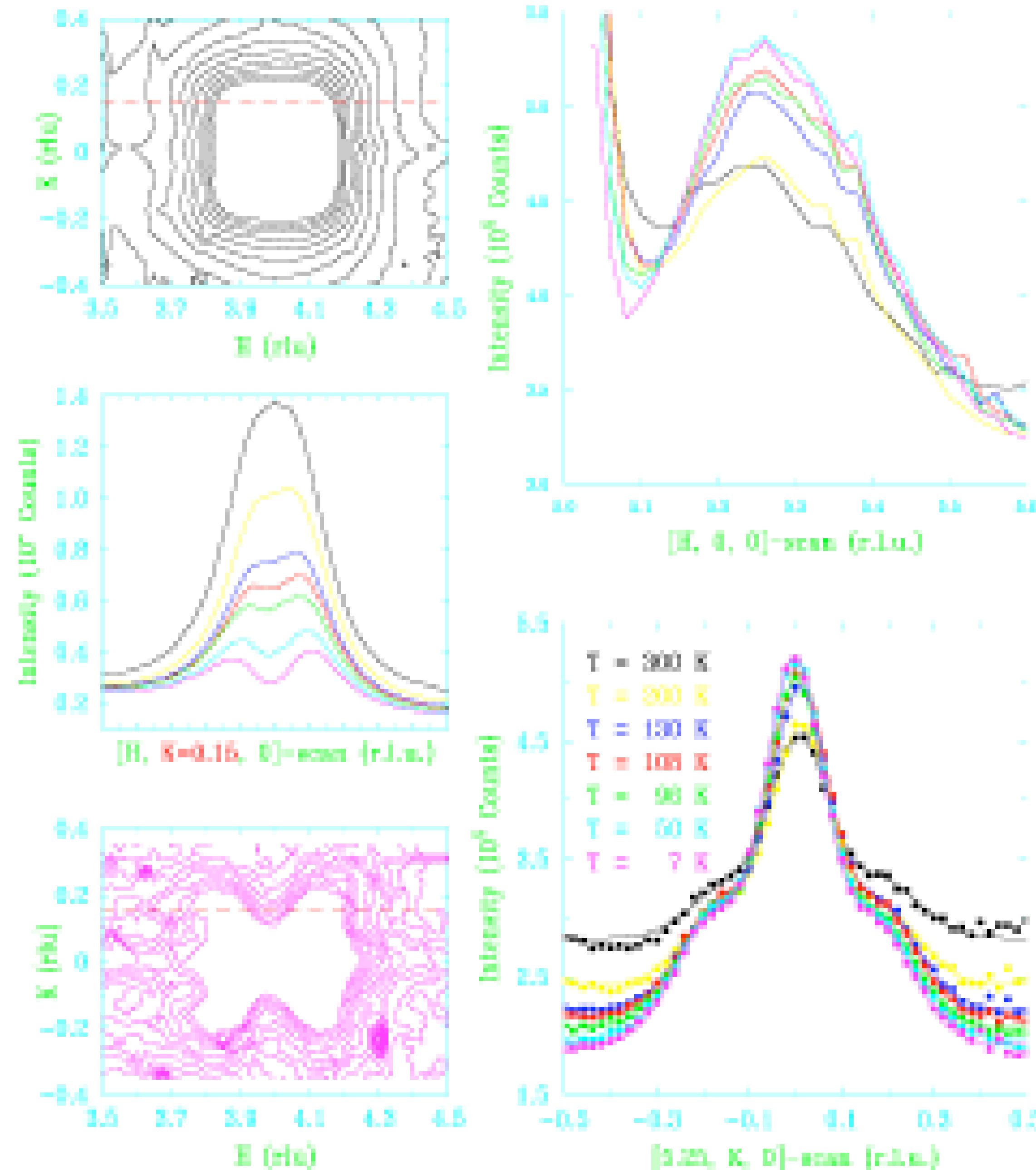
ybco.dat
1.0·10^4
5000
0.0




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)

YBa2Cu3O6.92 (Optimally doped Tc= 91.5K)




H (rlu)
K (rlu)
T = 300 K
T = 200 K
T = 130 K
T = 108 K
T = 90 K
T = 50 K
T = 7 K

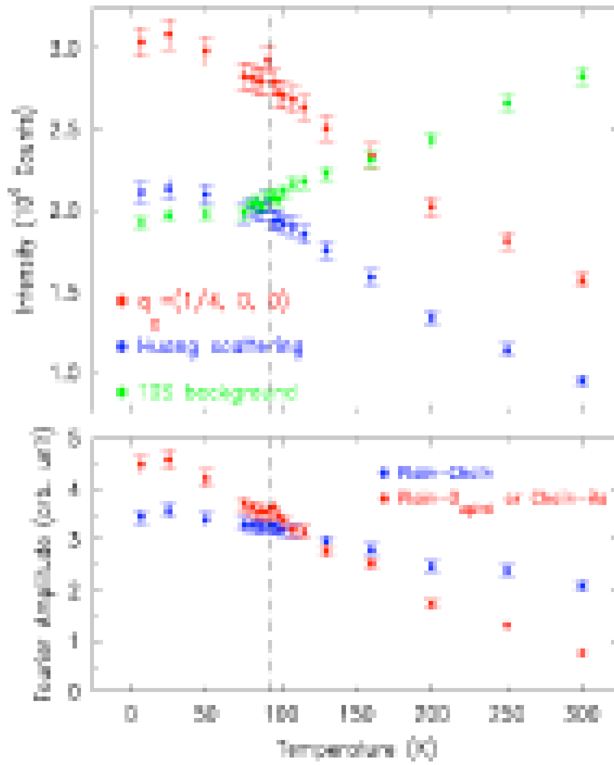


FIG. 4. Top panel: Temperature dependence of superstructure peak and Huang scattering. The average of the two Huang scattering peaks is displayed.

Conclusions

- For manganites in the PI phase Jahn-Teller polarons have been demonstrated to exist. Analysis of the Huang scattering reveals symmetry of distortion, related to d-orbital orientation.
- These polarons form a correlated but short-ranged ordered striped phase [q=(0.3, 0,1)]

*Both underdoped and optimally doped YBCO
show short range (fluctuating?) lattice modulations
along direction perpendicular to chains.
*For x=0.62, periodicity =5a; for x=0.92 periodicity=4a
*Correlations involve roughly 5 unit cells along a-axis
and only the Cu-O chain planes, the CuO2 planes
and the Barium layers.
*Correlations increase as T decreases and appear to
Saturate below Tc.