Methoden moderner Röntgenphysik I + II: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik SS 2009

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Materials Science

7. 5.	Martin v. Zimmermann	correlated electron materials – structural properties
12. 5.	Hermann Franz	glasses I
14. 5.	Hermann Franz	glasses II
19. 5.	Martin v. Zimmermann	correlated electron materials – magnetic properties

correlated electron materials: overview

- phase transitions
- structural phase transition of $SrTiO_3$
- x-ray diffraction to investigate phase transitions
- structural aspects of transition metal oxides
- orbital and charge order in $La_{1-x}Ca_xMnO_3$
- resonant scattering to study orbital/charge order

- magnetic properties of transition metal oxides
- magnetic scattering
- resonant magnetic scattering

Phase transitions

examples:

- solid - liquid - gas
- structural phase transition ($SrTiO_3$)
- magnetic phase transition
- Mott-metal-insulator transition
- macroscopic quantum phenomena (superconductivity, suprafluidity)
- quantum phase transitions (at zero temperature, driven by pressure, magnetic field)

- glass transitions (amorphous solids, spin-glasses, quasi-crystals)
  (non-equilibrium states)

classification of phase transitions

Ehrenfest classification:

smoothness of the chemical potential **μ**

First order if the entropy $s = -\partial\mu/\partial T$ is discontinuous at the transition.

Problem: derivatives of **μ** can diverge as a transition is approached.

Modern classification:

Fist order transitions have non-zero latent heat.

Are also called discontinuous.

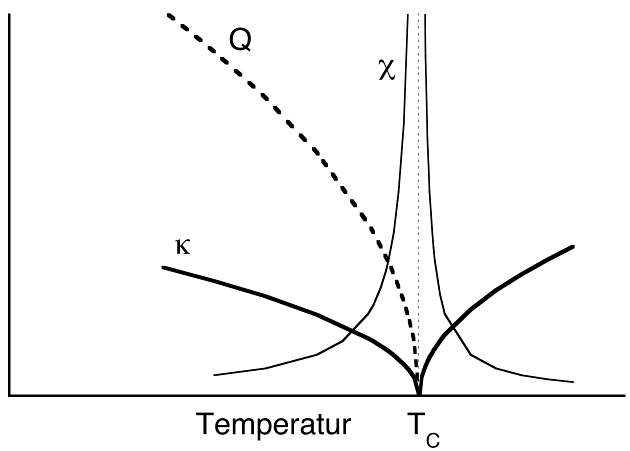
All other transitions are continuous phase transitions.

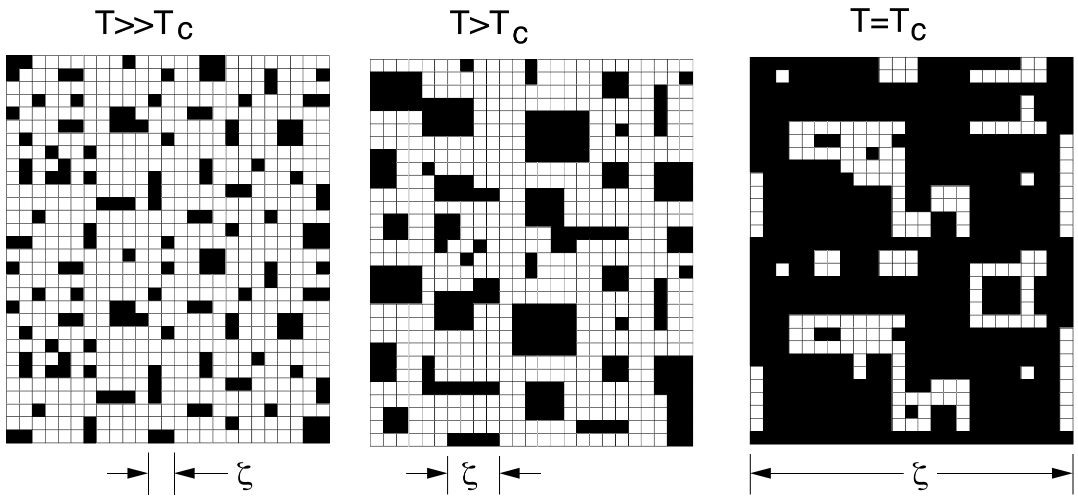
structural phase transition of $SrTiO_3$

- phase transition - breaking of symmetry
- stable structure at temperature T determined by minimum of the free energy $F = U - T \cdot S$
- Orderparameter Q

  Q=0 in the disordered phase

  Q=1 in the completely ordered phase
- Phase transition at temperature T_c
- For continuous phase transitions, ordered and disordered regions form at T_c with out energy cost - critical fluctuations





Landau theory

phenomenological description of phase transitions

$$F(Q,T) = 1/2aQ^2 \ + \ 1/3bQ^3 \ + \ 1/4cQ^4 \ + \ \ldots$$

$$\left.\frac{\partial F}{\partial Q}\right|_{Q_o} \ = \ 0 \ \ \text{und} \qquad \left.\frac{\partial^2 F}{\partial^2 Q}\right|_{Q_o} \ > \ 0$$

$$\text{a} > 0 \ : \qquad a \ = \ a'(T - T_c) \qquad \text{b=0}$$

$$F(Q,T) = 1/2a'(T - T_c)Q^2 \ + \ 1/4cQ^4$$

$$Q_o^2(T) \ = \begin{cases} 0 & \forall \quad T > T_c \\ \frac{a'}{c}(T_c - T) & \forall \quad T < T_c \end{cases}$$

$$\Longrightarrow \qquad Q_o(T) \ \sim \ (T_c - T)^\beta \ \ \text{mit} \ \ \beta \ = \ 0.5$$

β kritischer Exponent

Suszeptibility - korrelation function

$$\mathcal{F} = \left.\frac{\partial F}{\partial Q}\right|_T \qquad \chi(T) = \left.\frac{\partial Q}{\partial \mathcal{F}}\right|_{\mathcal{F}=0}$$

$$\chi(T) = \begin{cases} \frac{1}{a'(T-T_c)} & \forall \quad T > T_c \\ \frac{1}{2a'(T_c-T)} & \forall \quad T < T_c \end{cases}$$

$$\Longrightarrow \quad \chi(T) \sim |T_c - T|^{-\gamma} \quad \text{mit} \quad \gamma = 1$$

$$G(\vec{x},T) = < Q(\vec{x},T)Q(0,T) > - < Q(T) >^2 = k_B T \chi(\vec{x},T)$$

$$\chi(\vec{q},T) = \int d\vec{x} \, \exp(-i\vec{q}\vec{x}) \, \chi(\vec{x},T) \sim \int d\vec{x} \, \exp(-i\vec{q}\vec{x}) \, G(\vec{x})$$

$$\text{mit} \quad G(\vec{x},T) \sim \frac{e^{-|\vec{x}|/\zeta}}{|\vec{x}|} \quad \Longrightarrow \quad \chi(\vec{q},T) \sim \frac{1}{\kappa^2 + q^2} \, .$$

Landau theory and beyond

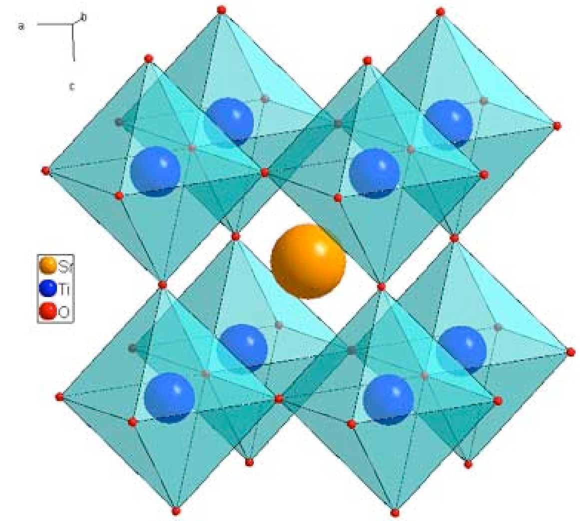
- Landau theory is independent of the dimension of the system and dimension of the orderparameter, fails to describe fluctuations around T_c, good approximation for $T \neq T_c$
- Landau-Ginzburg theory takes position dependent fields into account and describes behavior around T_c
- Renormalizing Group theory most complete theory to describe phase transitions. Results in proper values for critical exponents and could predict the scaling laws, the relation between different critical exponents.
- Predicts also the universality hypothesis, that the behavior at a phase transition is given only by the dimension of the system and the dimension of the orderparameter, but not the specific interactions.

example: structural phase transition in $SrTiO_3$

perovskite structure:

Pm3m (#221)

lattice parameter a_c



below 105 K:

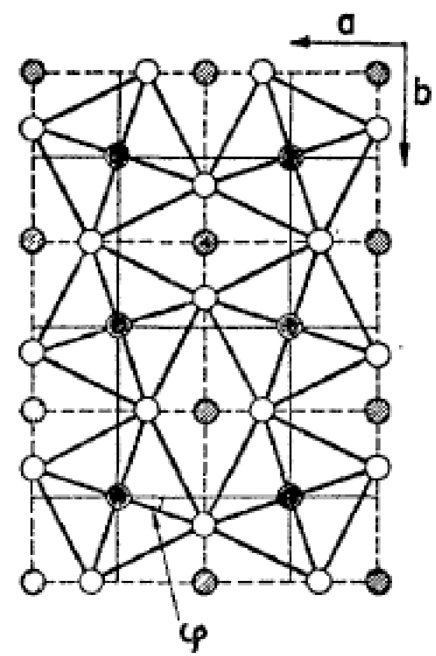
I4/mcm (#140)

$a_t = \sqrt{2}\, a_c\, ,\, c_t$

orderprameter: spontaneous strain

$\varphi^2 = c_t(T)/a_0(T) - 1$

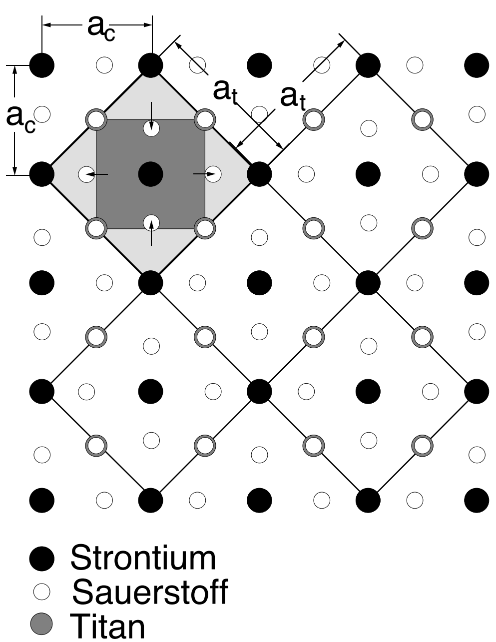
$a_0(T) = 2/3\, a(T) + 1/3\, c(T)$

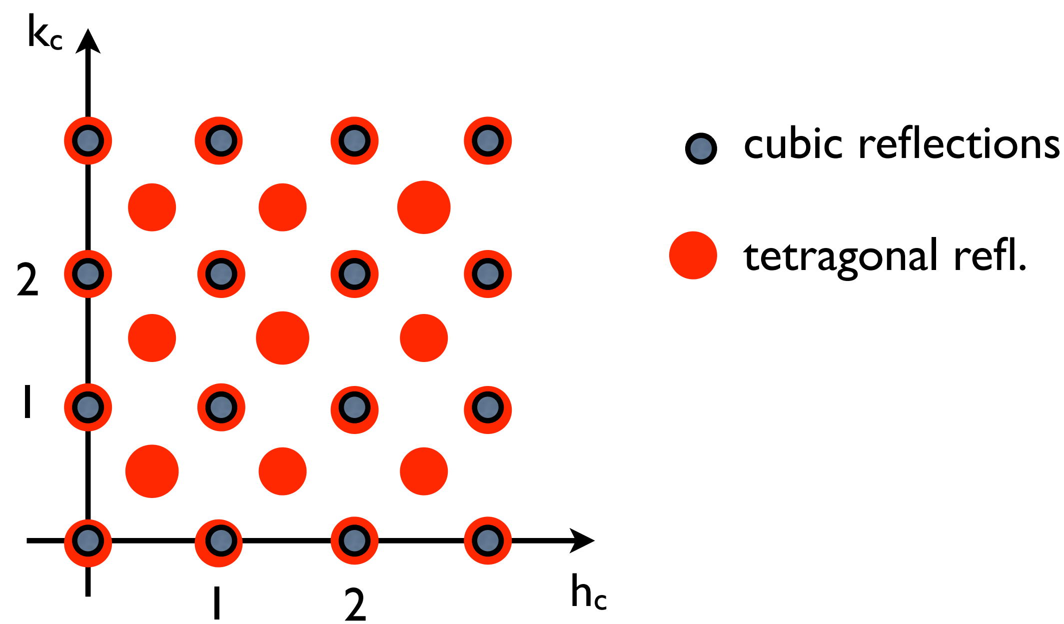


investigation of structural phase transitions by x-ray diffraction

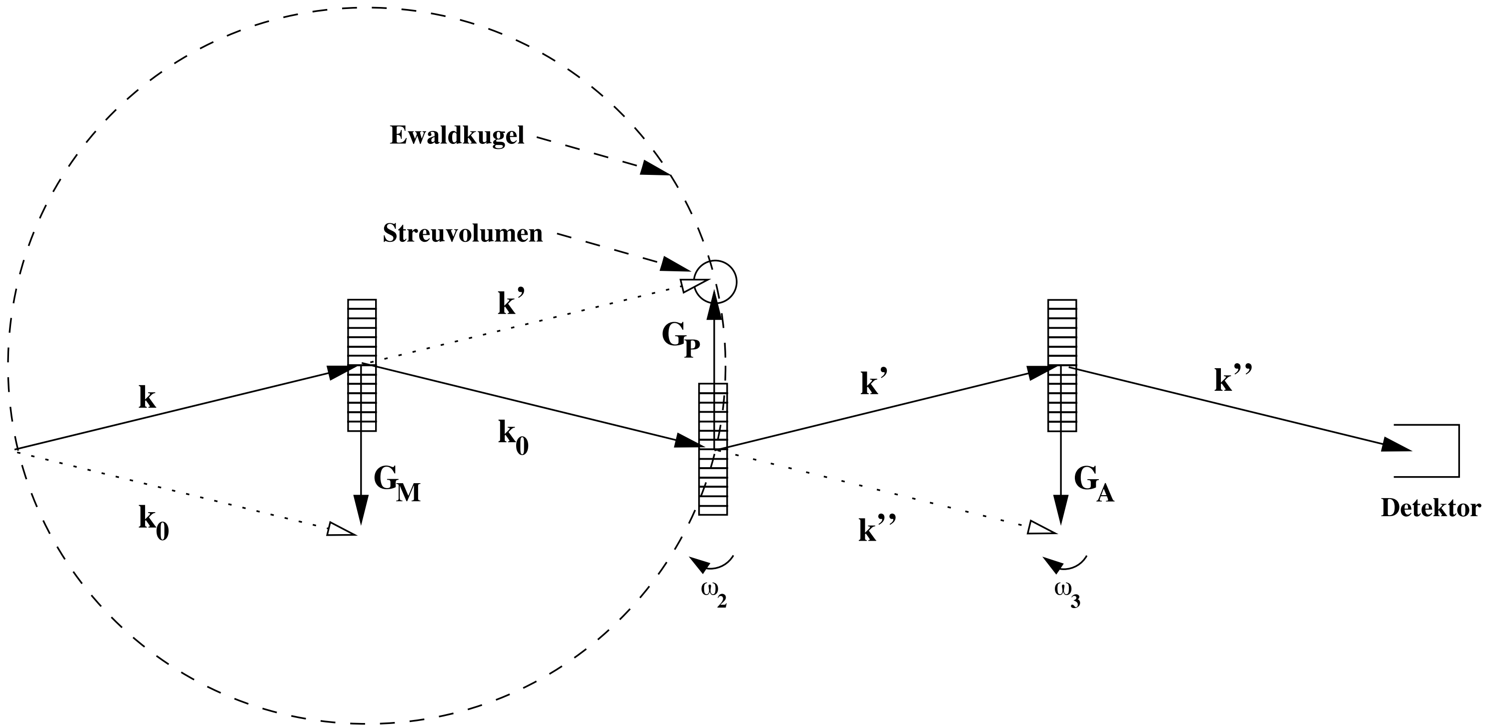
1st approach: determination of lattice parameters

2nd approach: determinations of intensity of high-temperature phase "forbidden" reflections

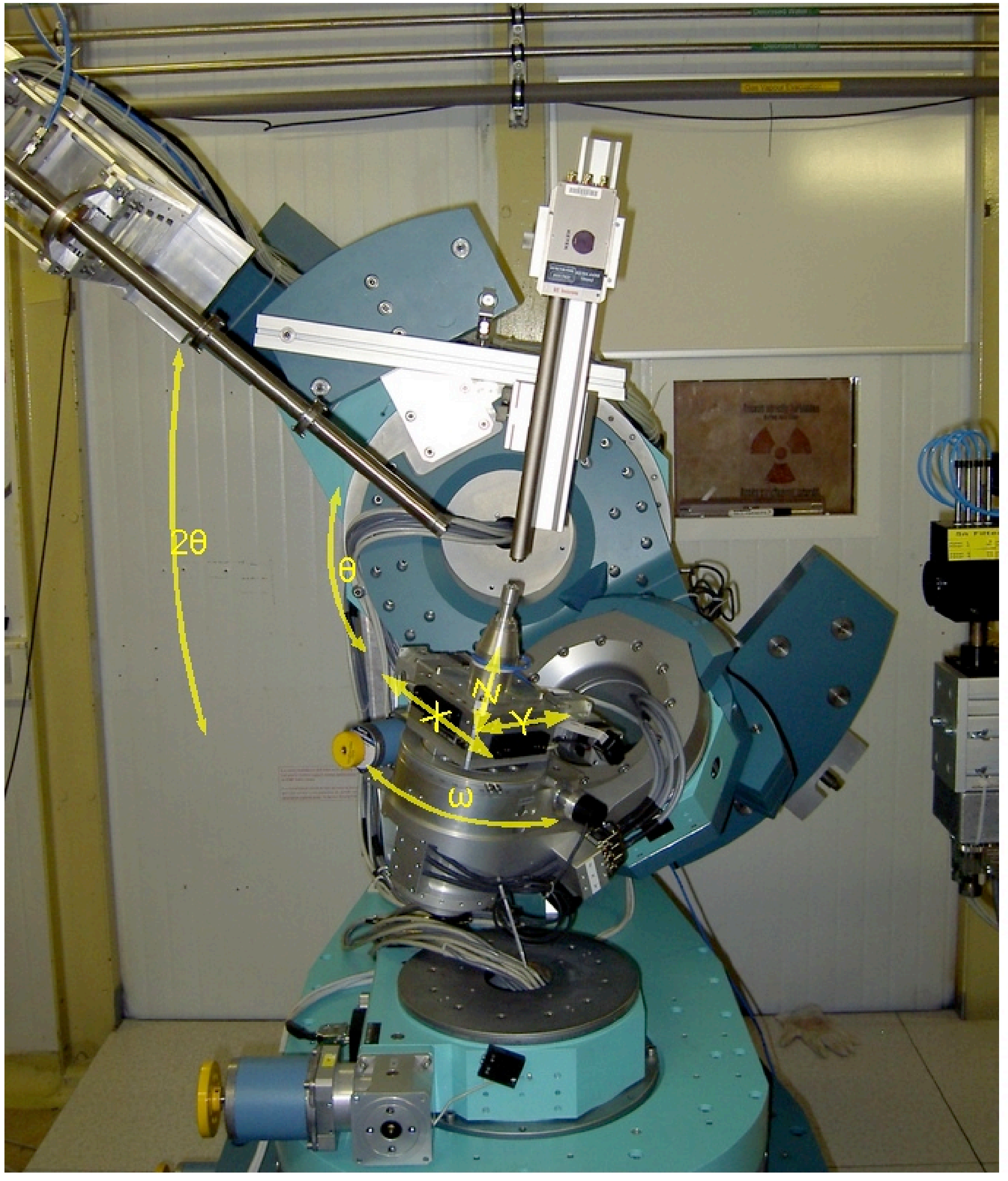




3-axis diffractometer



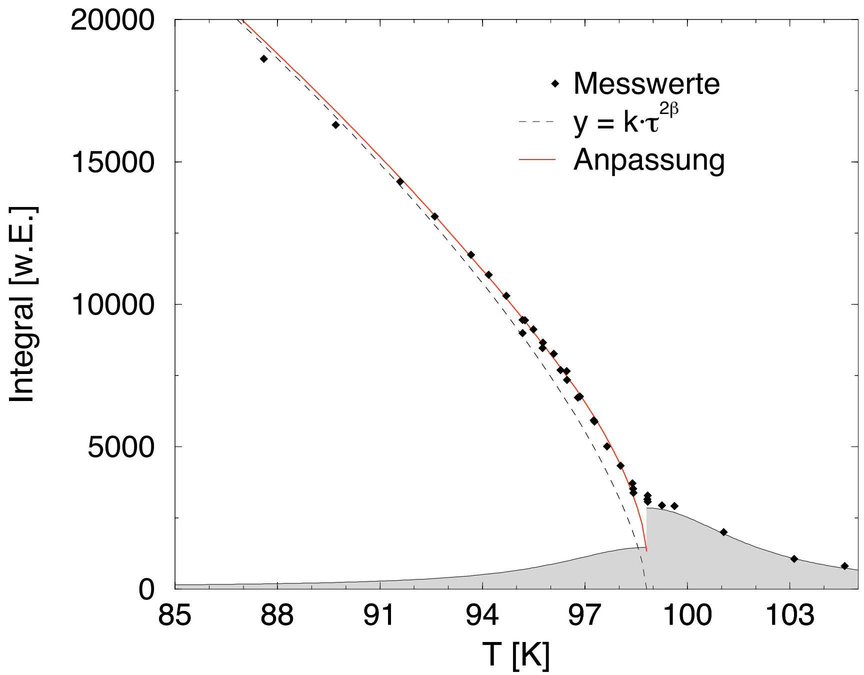
diffractometer

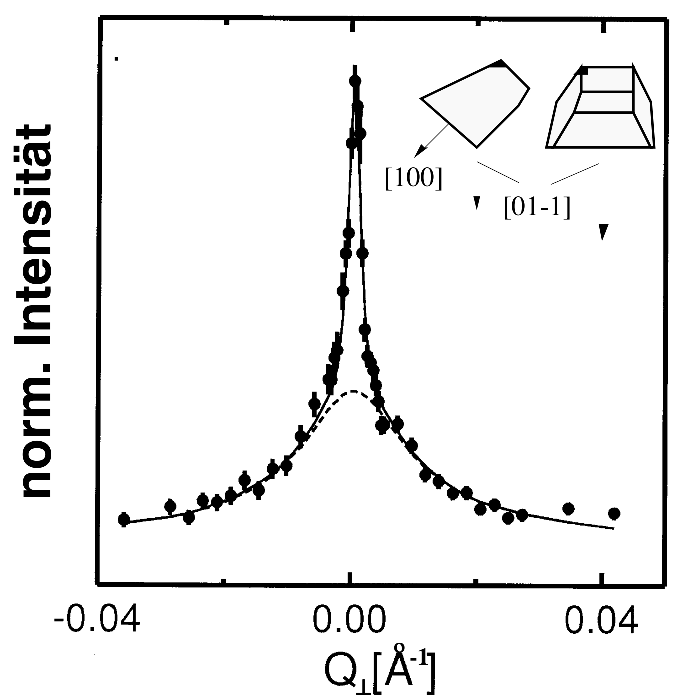


investigation of structural phase transitions by x-ray diffraction

$$I_{Bragg} \sim |F_{hkl}|^2 \sim Q_o^2 \sim (T_c - T)^{2\beta}$$

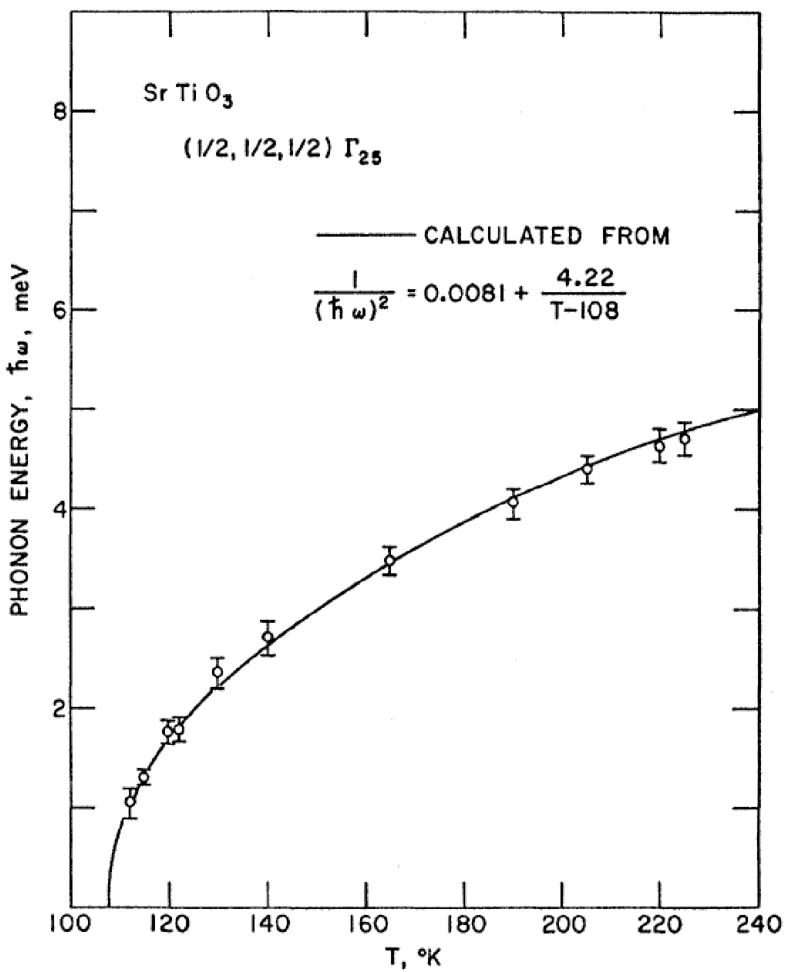
$$I_{Fl}(\vec{q}, T) \sim \chi(\vec{q}, T) \sim \frac{1}{\kappa^2 + q^2}$$





soft mode transition

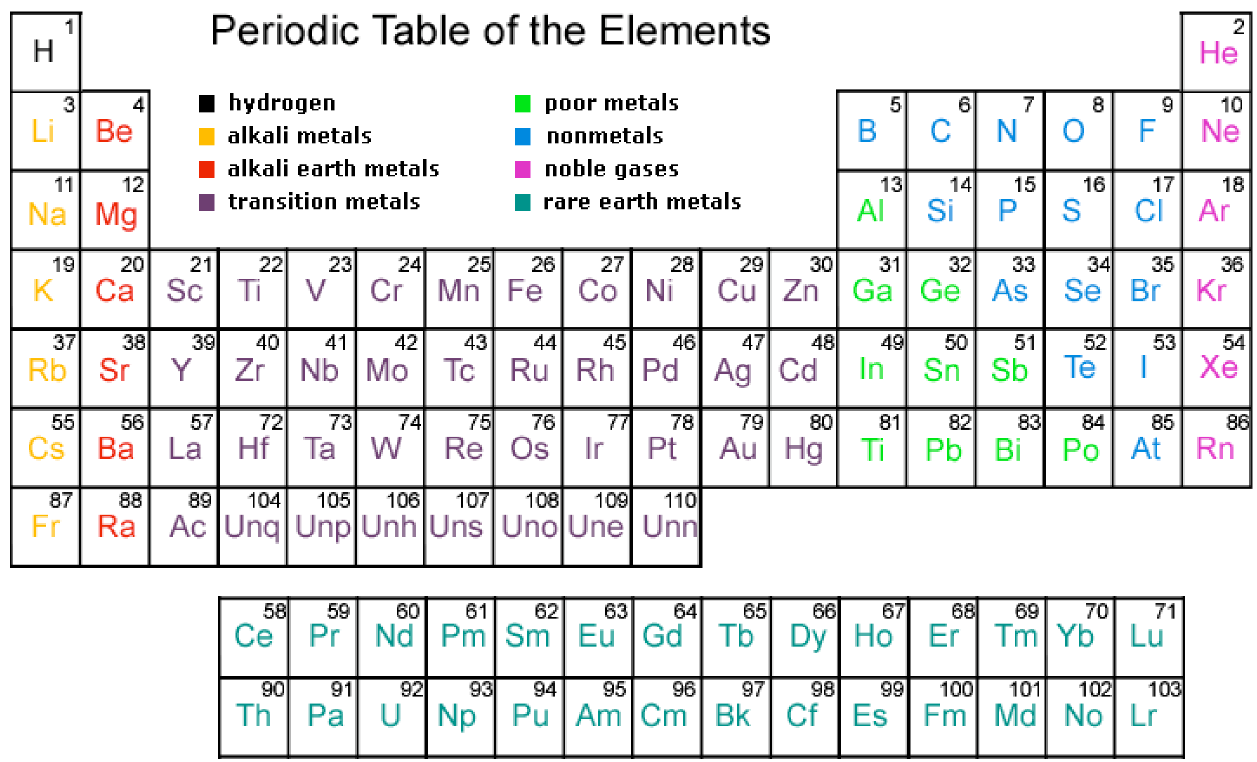
phonon energy:
inelastic neutron scattering



static lattice distortion:
x-ray diffraction

correlated electron materials: transition metal oxides

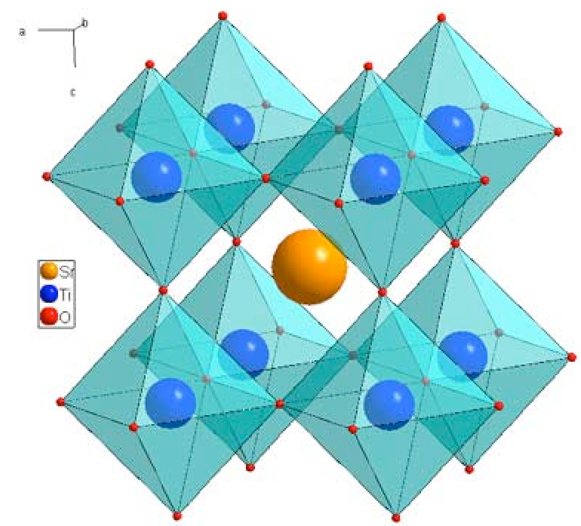
- physical properties determined by interplay of charge, orbital, spin and lattice degrees of freedom
- high Tc superconductivity
- colossal magnetoresistance
- multiferroic behavior



correlated electron materials: transition metal oxides

3d electronic Eigenstates: $R_n * Y_m^2(\Theta,\phi)$
quantum numbers:
  n=3 (radial)
  l =2 (angular momentum)
 m= -2 ... +2 magentic   5-fold degenerate

perovskite structure



in a cubic crystal field: e.g. $LaMnO_3$

$V(r) = \sum Z_i\, e^2/|\mathbf{r} - \mathbf{R}_i|$ Madelung Potential

in rectangular coordinates:
$V_4(\mathbf{r}) = 5/2\, V_{40}\, (x^4 + y^4 + z^4 - 3/5 r^4)$

cubic crystal field

Eigenstates in cubic crystal field:

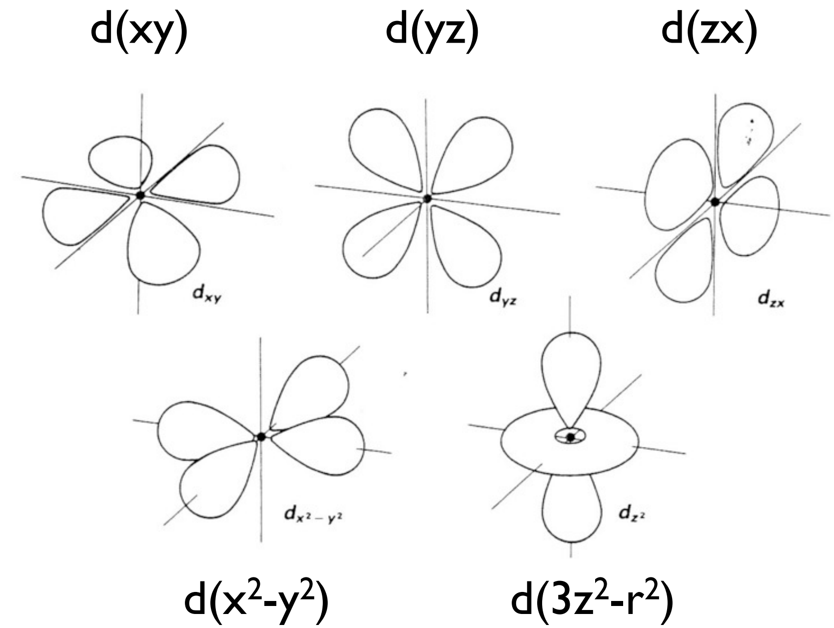
$d(x^2\text{-}y^2) \propto \sqrt{2\pi/5}\,(Y_2^2 + Y_2^{-2}) = 1/2\sqrt{3}\,(x^2 - y^2)/r^2$

$d(3z^2\text{-}r^2) \propto \sqrt{4\pi/5}\,Y_2^0 = 1/2\,(3z^2 - r^2)/r^2$

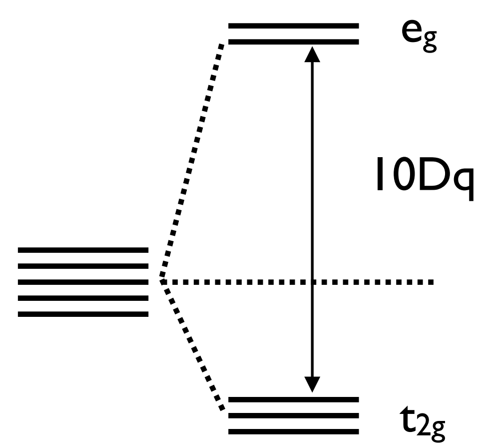
$d(xy) \propto 1/i\,\sqrt{2\pi/5}\,(Y_2^2 - Y_2^{-2}) = \sqrt{3}\,(xy)/r^2$

$d(yz) \propto \sqrt{2\pi/5}\,(Y_2^{-1} + Y_2^1) = \sqrt{3}\,(yz)/r^2$

$d(zx) \propto 1/i\,\sqrt{2\pi/5}\,(Y_2^{-1} - Y_2^1) = \sqrt{3}\,(zx)/r^2$



crystal field splitting:



Hund's rules

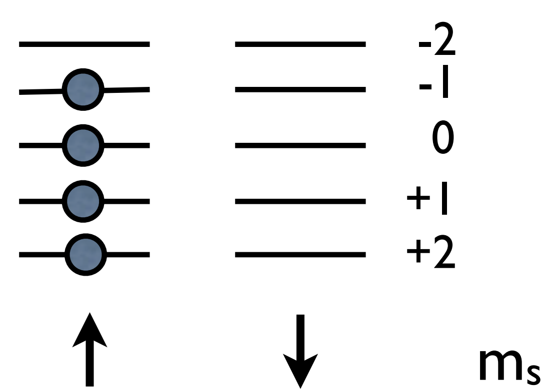
electrons occupy orbitals such that the gound state is characterized by:

1. the maximum value of the total spin S allowed by the exclusion principle

2. the maximum value of orbital angular momentum L consistent with S

3. Spin-orbit interaction:
   J = |L + S| for more that half filled shell
   J = |L - S| for less than half filled shell

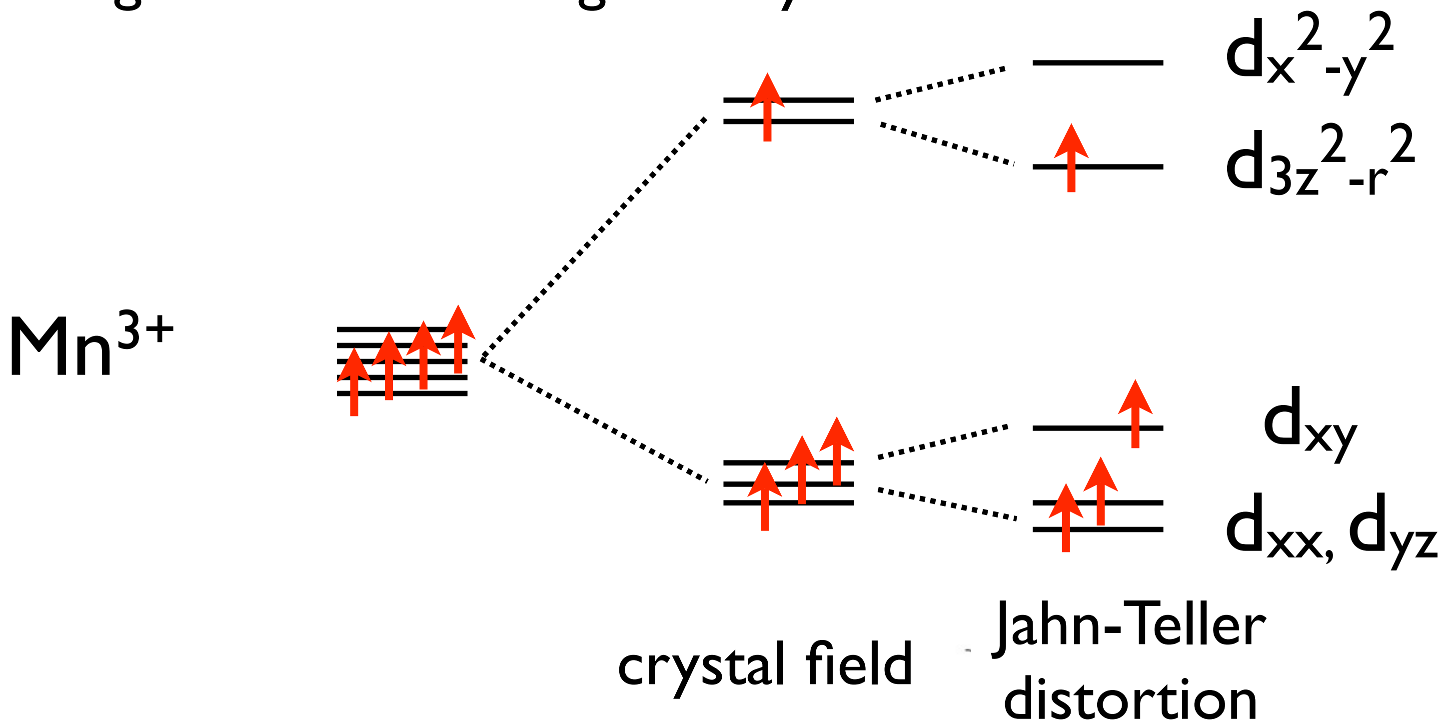
Mn3+: [Ar] $3d^4$

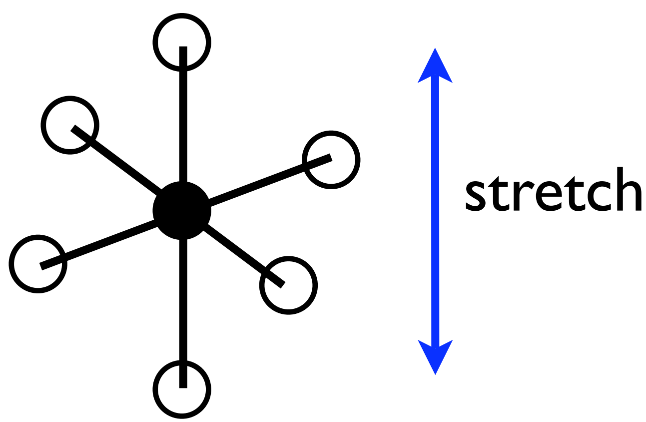


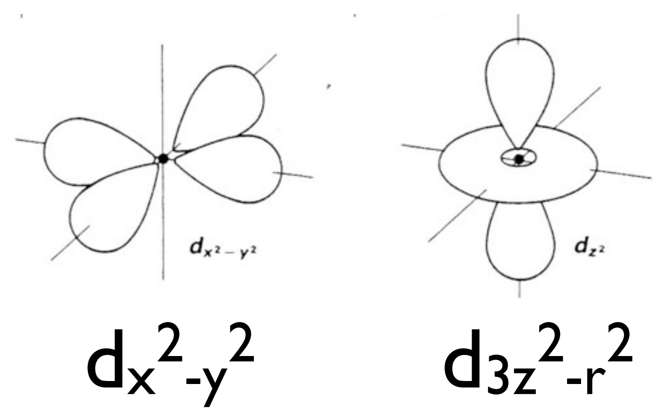
S=0 (4 x 1/2)
L=2 (2+1+0-1)
J =0 (|2-2|)

Jahn-Teller distortion

lifting of d-electron degeneracy

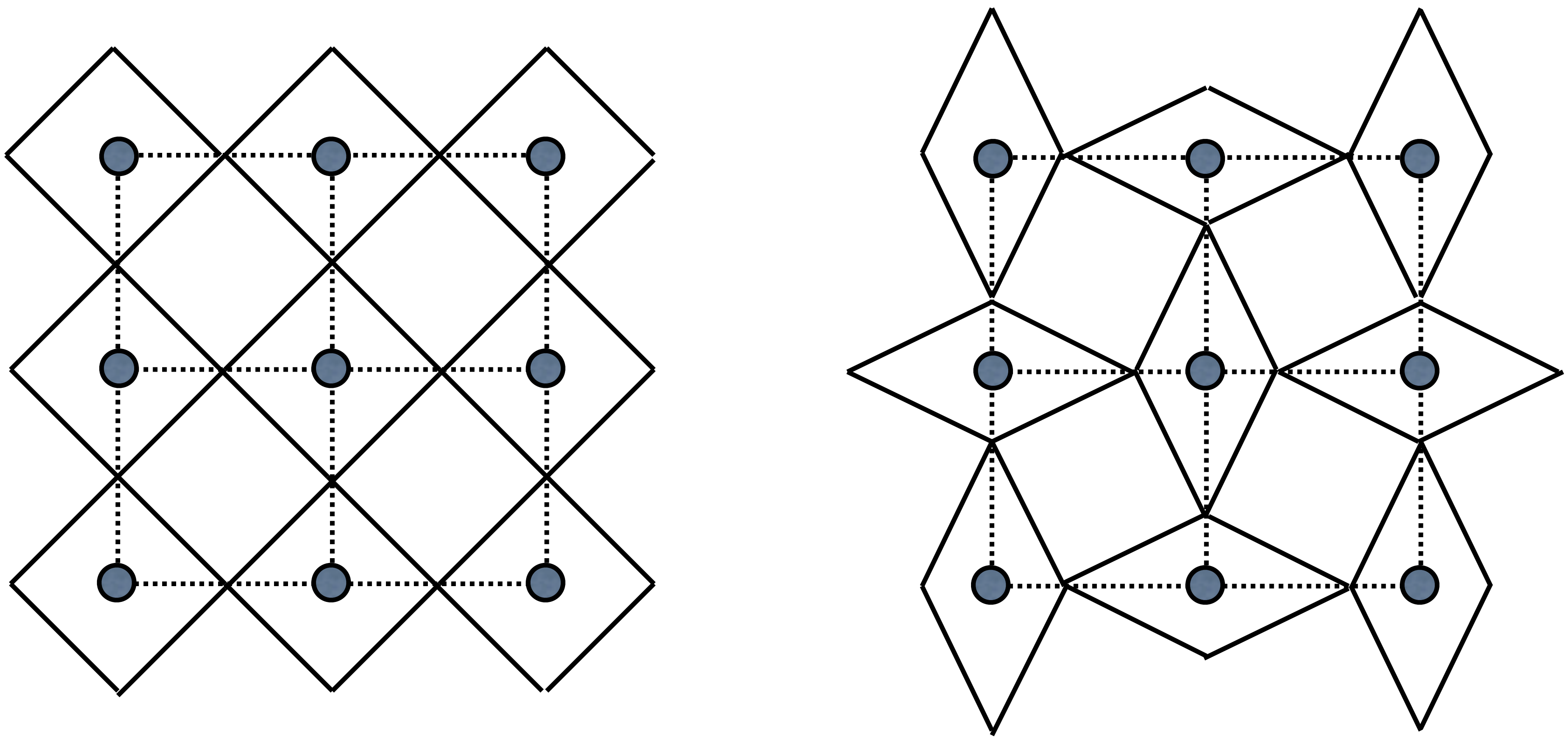






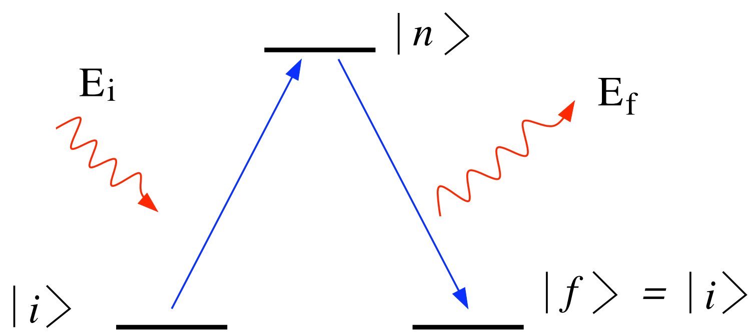
cooperative Jahn-Teller distortion - orbital order

e.g. $LaMnO_3$

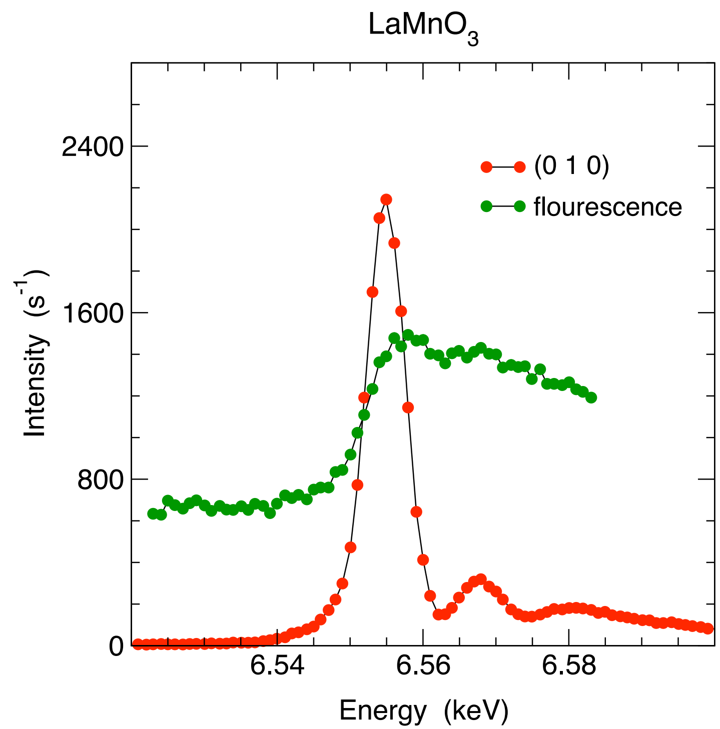


no change in lattice parameters

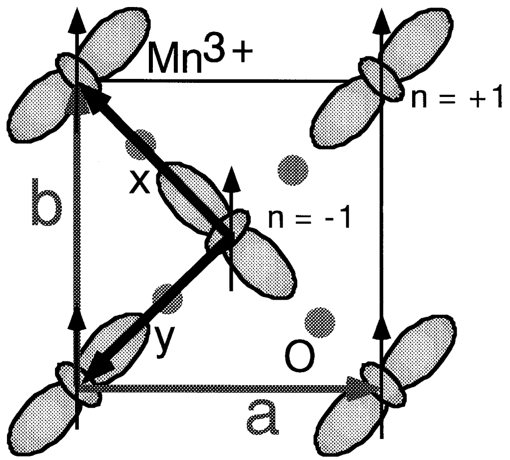
resonant x-ray scattering

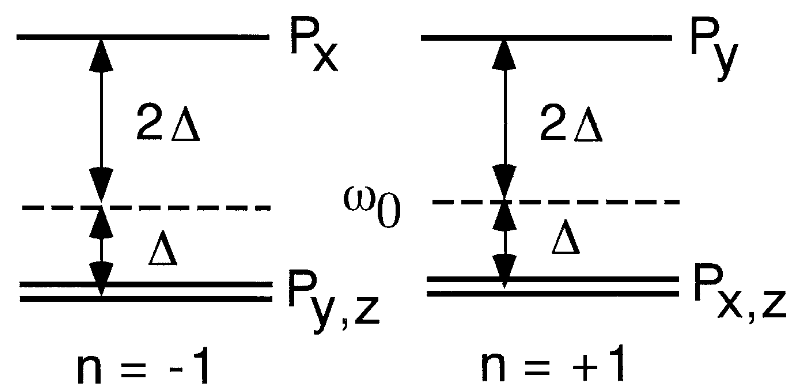


at Mn K-edge: $|i >= 1s$
$|n >= 4p$



resonant x-ray scattering





at the absorption edge the atom form factor depends on the incident and scattered polarization:

$$f = f0 + \Delta f(\omega)$$

$$\Delta f(\omega) = \mathbf{e}^t_f \cdot f'(\omega) \cdot \mathbf{e}_i$$

$$f' = (f'_{\alpha,\beta}) = r_0/m \sum_j \frac{\langle 1s \mid P_\beta \mid 4p_j \rangle \quad \langle 4p_j \mid P_\alpha \mid 1s \rangle}{E(4p_j) - E(1s) - h\omega - i\Gamma/2}$$

$$f_{||} = \frac{r_0}{m} \; \frac{|D|^2}{h(\omega-\omega_0)+2\Delta-i\Gamma/2}$$

$$f_\perp = \frac{r_0}{m} \; \frac{|D|^2}{h(\omega-\omega_0) - \Delta-i\Gamma/2}$$

with $\langle 1s \mid P_\alpha \mid 4p_j \rangle = D\,\delta_{\alpha j}$

(3 0 0) Intensity

$$I(\mathbf{Q}) = I_0 \cdot |F(\mathbf{Q})|^2 = I_0 \cdot |\sum_l o_l\, f_l\, e^{i\mathbf{Q}.\mathbf{b}_l}\, e^{-\mathbf{Q}^t.U_l.\mathbf{Q}}|^2$$

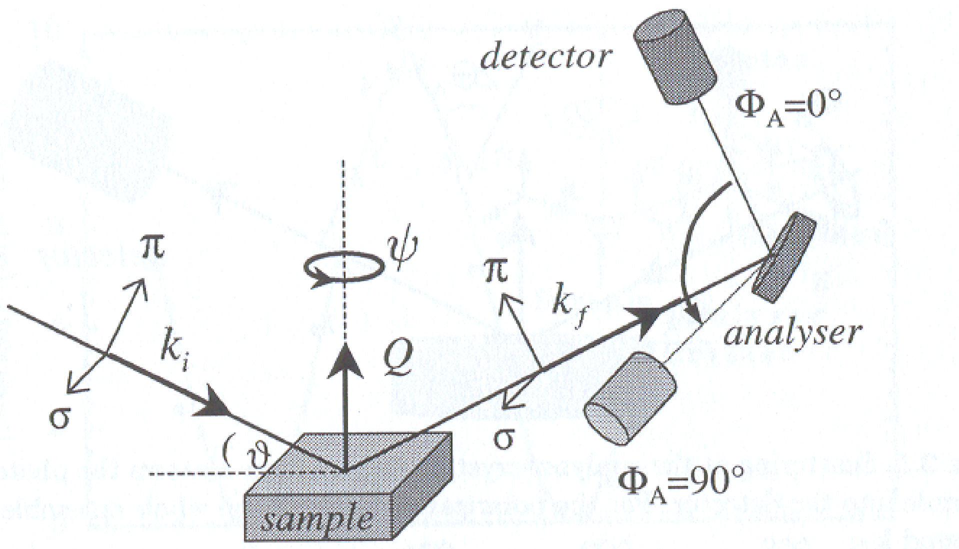
$$\begin{aligned} F(300) &= f_1(\omega, \mathbf{e}_i, \mathbf{e}_f) - f_2(\omega, \mathbf{e}_i, \mathbf{e}_f) \\ &= \mathbf{e}_f^t.[\hat{f}_1(\omega) - \hat{f}_2(\omega)].\mathbf{e}_i \\ &\doteq \mathbf{e}_f^t.\hat{F}(300).\mathbf{e}_i \quad , \end{aligned}$$

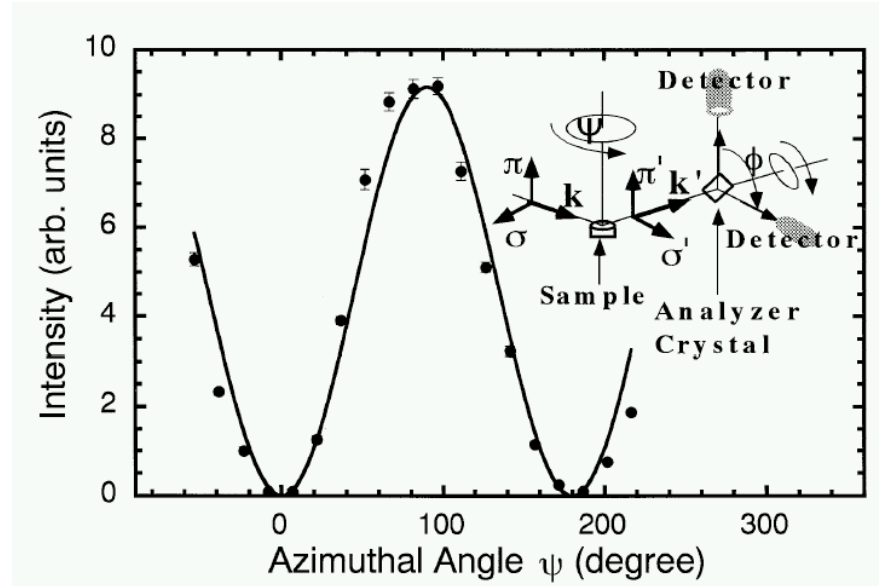
$$\hat{F}(300) = \hat{f}_1 - \hat{f}_2 = \begin{pmatrix} f_\perp - f_{||} & 0 & 0 \\ 0 & f_{||} - f_\perp & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

$$I = I_0 \cdot \left| \mathbf{e}_f.(U\,\hat{F}(300)\,U^t).\mathbf{e}_i \right|^2, \quad \text{where}$$

$$U\,\hat{F}(300)\,U^t = \begin{pmatrix} 0 & f_{||} - f_\perp & 0 \\ f_{||} - f_\perp & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

azimuthal dependence





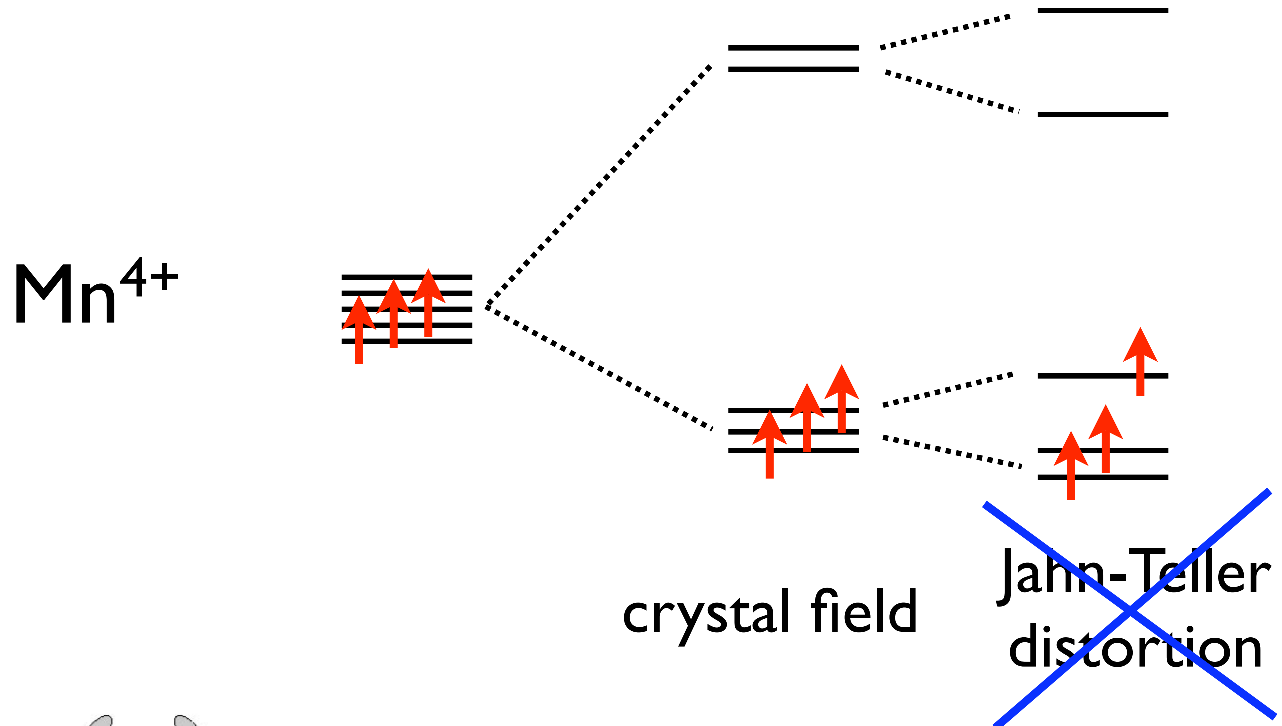
resonant scattering at transition metal L-edges

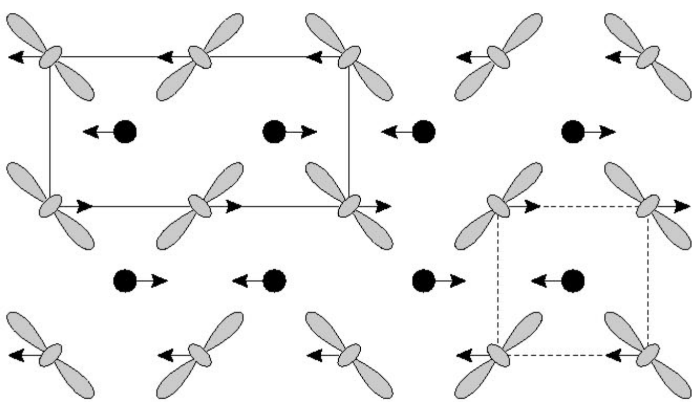
- direct sensitivity for d-electrons, thus orbital order is probed directly, not the Jahn-Teller distortion as for k-edge
- large resonant enhancement for magnetic order

- small momentum transfers achievable, (100) of $LaMnO_3$ out of reach
- surface sensitive
- ultra high vacuum conditions necessary

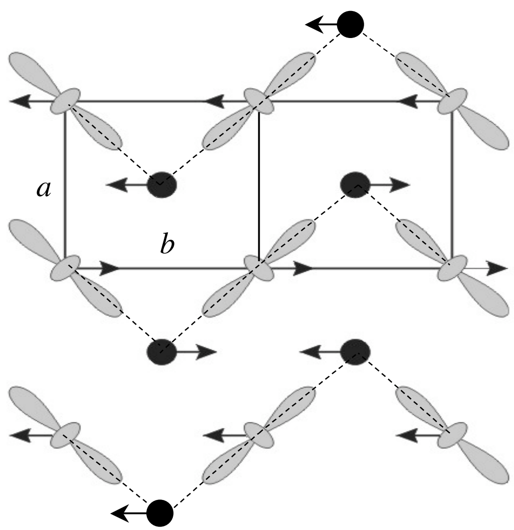
doping - charge order

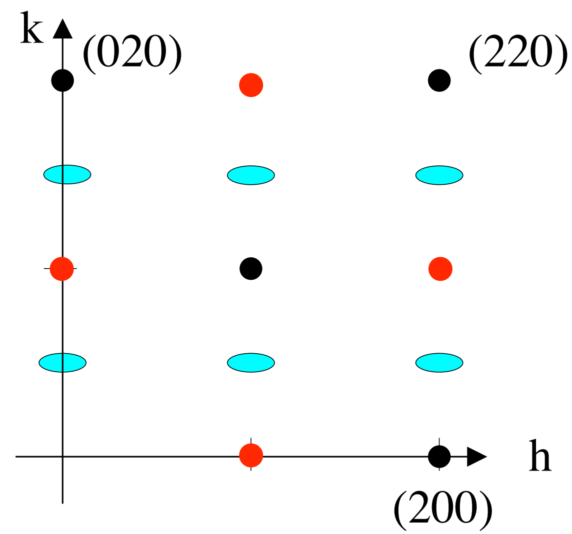
$La_{0.5}Ca_{0.5}MnO_3$

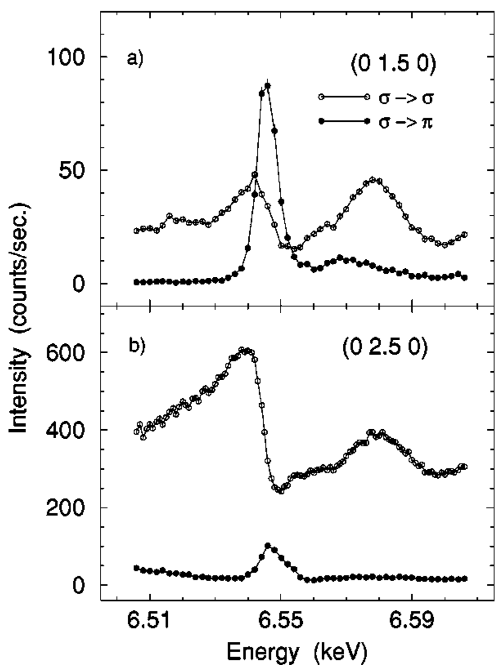


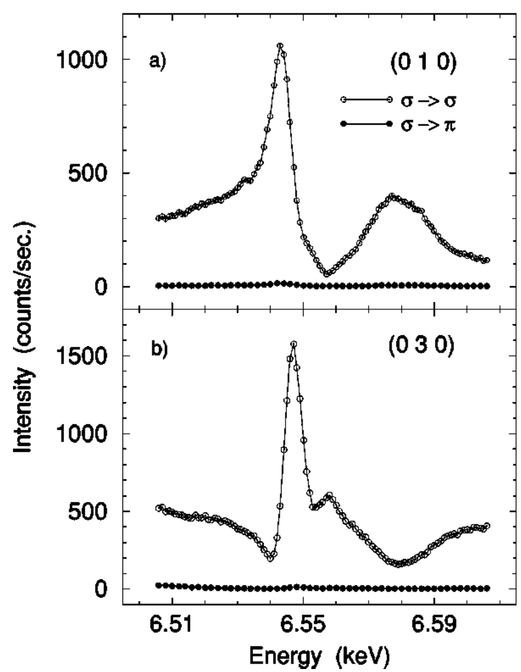


charge/orbital order resonant diffraction

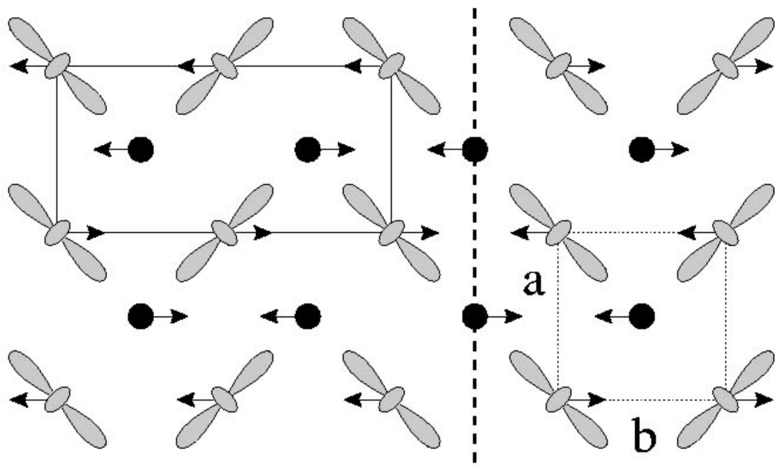


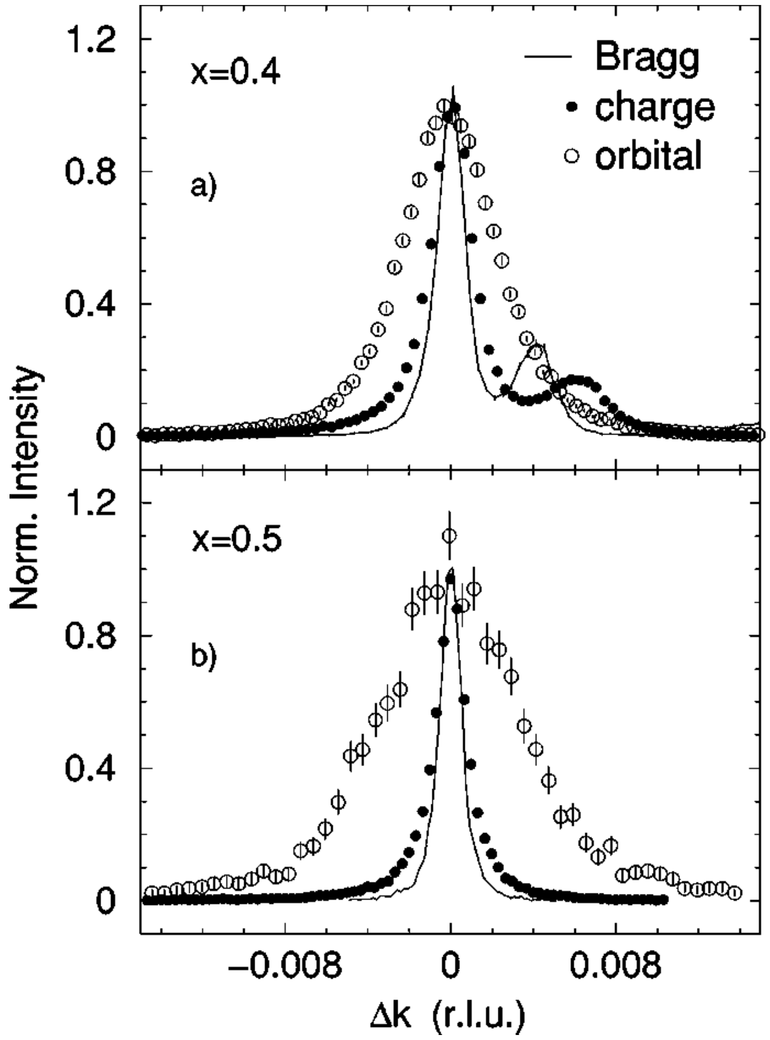






domains - correlation length





summary

solids state phase transitions
- order parameter
- power laws with critical exponents
- correlation length
- superlattice reflection

transition metal oxides
- symmetry of d-electrons in cubic crystal field
- Jahn-Teller effect
- resonant x-ray scattering

literature

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