National Synchrotron Radiation Research Center

Spin, Charge, and Orbital Ordering of Transition Metal Oxides

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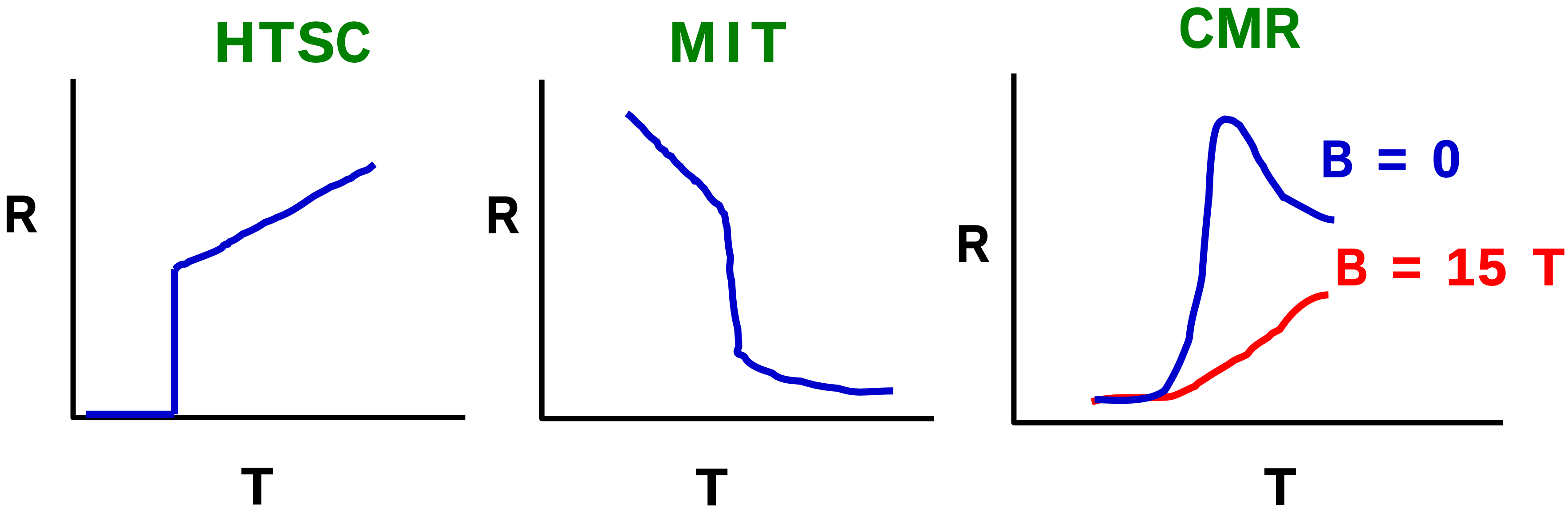
清華大學物理系演講 **Oct. 5, 2005**

Outline:

- Verwey transition and charge-orbital ordering of Fe_3O_4
- Multiferroics in $TbMn_2O_5$

  -- *coexistence and strong coupling of ferroelectricity and antiferromagnetism*

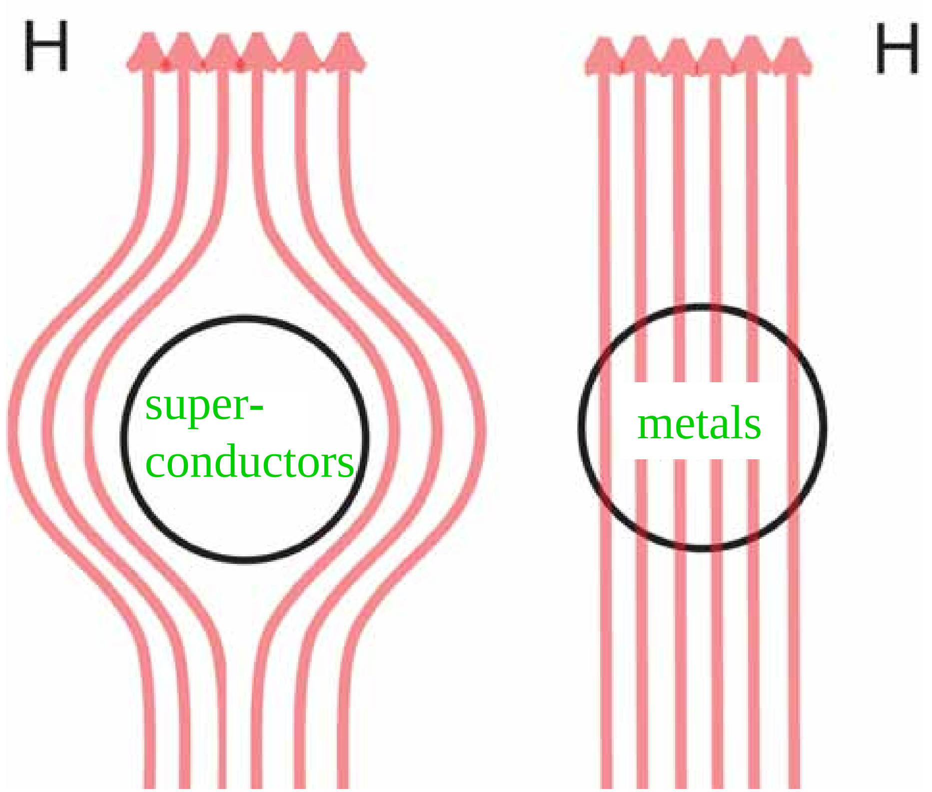
Phenomena of electron-correlated materials

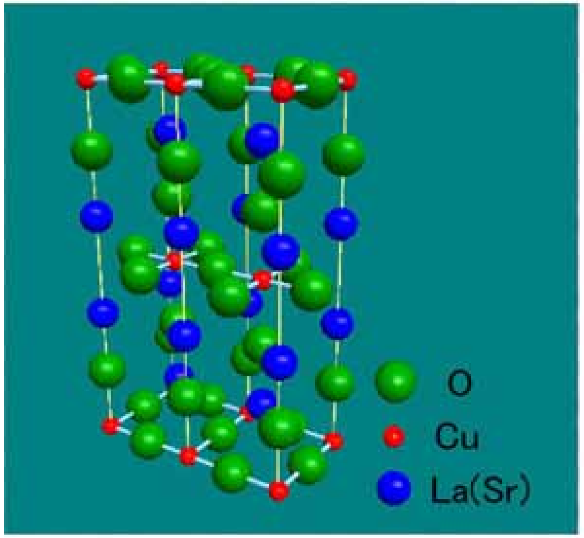


High **T**emperature **S**uper**C**onductivity

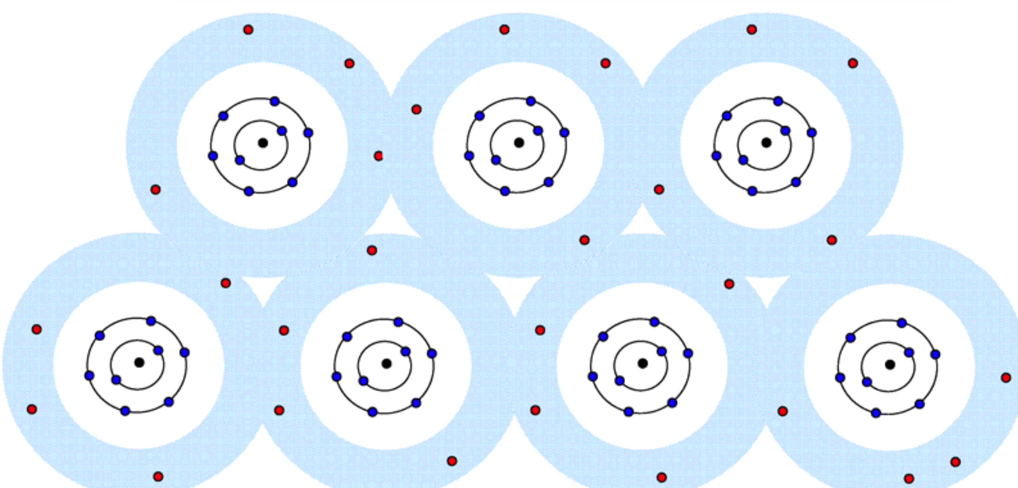
Metal-to-**I**nsulator **T**ransition

Colossal **M**agneto-**R**esistance


H
super-
conductors
metals
H

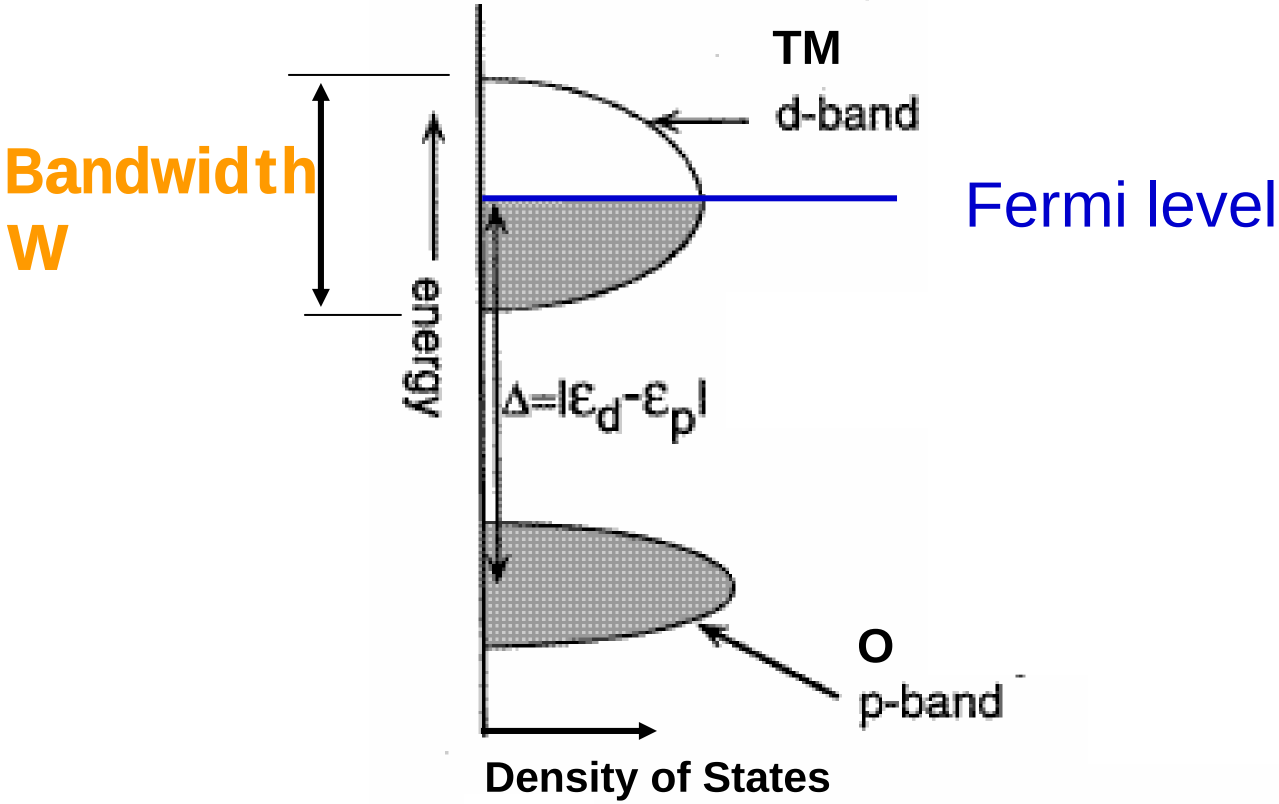


Physical properties of solids are primarily determined by valence electrons in a lattice.



Electronic structure of correlated materials:

- **bandwidth**
- **Coulomb interaction**
- **charge transfer energy**

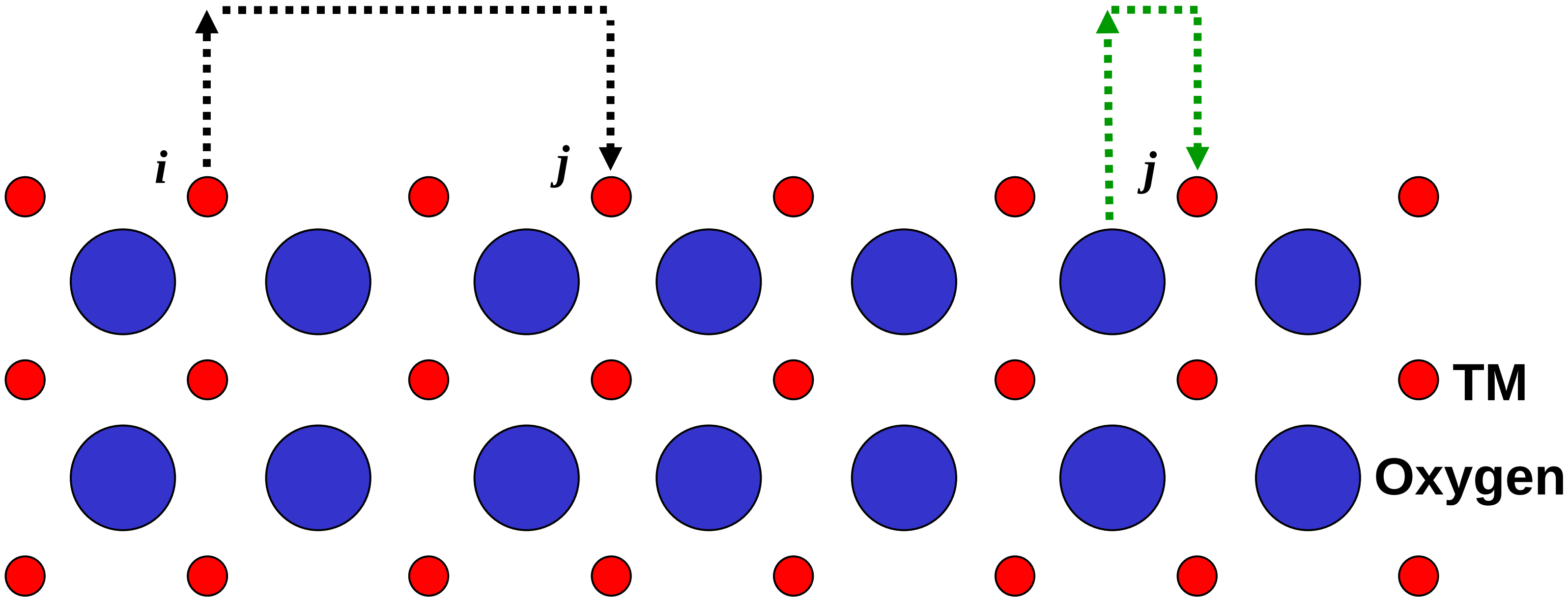


Metals, from the view point of band theory

Correlated-Electron Materials: U > W

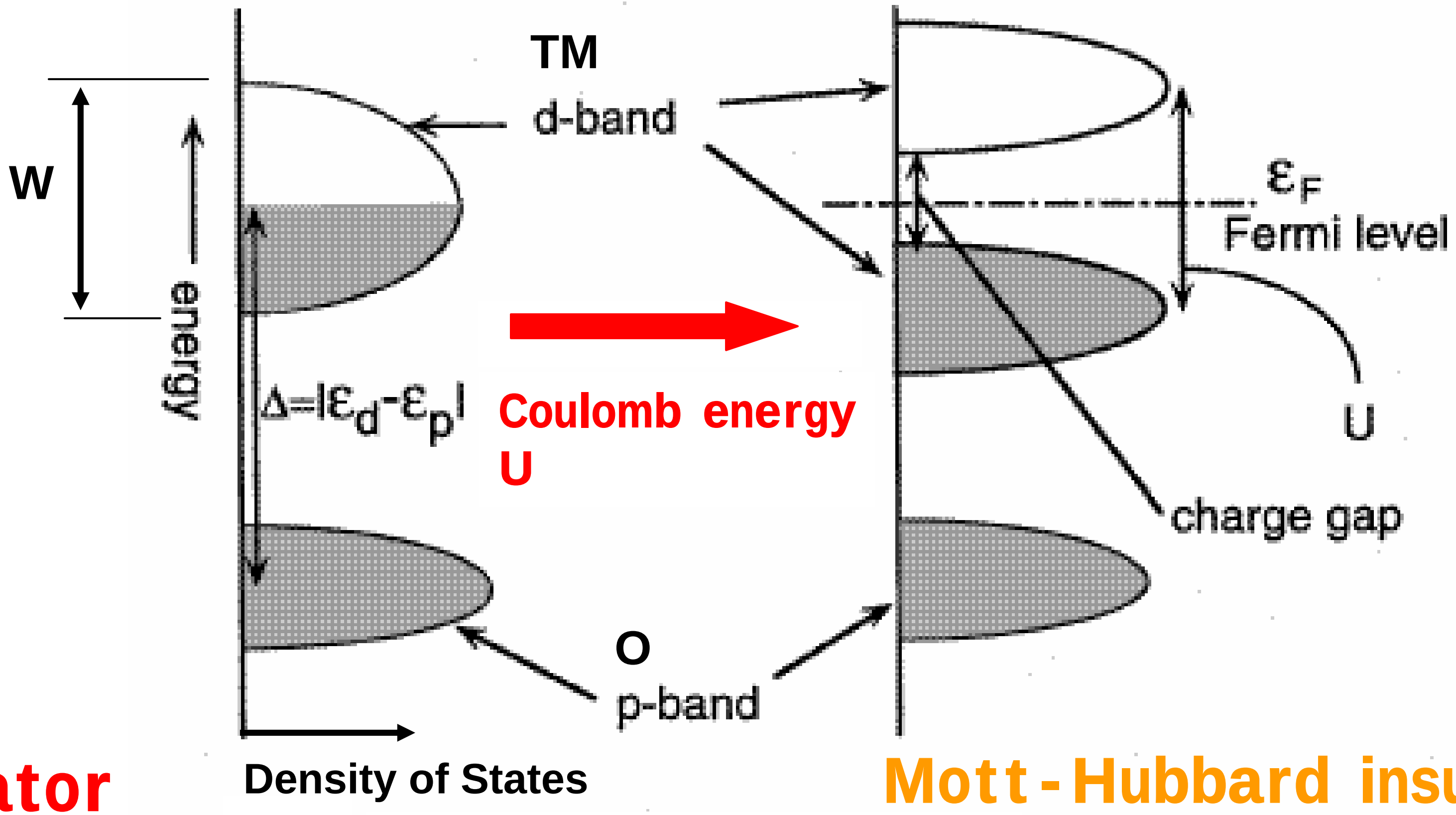
$d_i^n \, d_j^n \rightarrow d_i^{n-1} \, d_j^{n+1}$

$d_j^n \rightarrow d_j^{n+1} \, \underline{L}$



On-site Coulomb energy
U

Charge-transfer energy
Δ

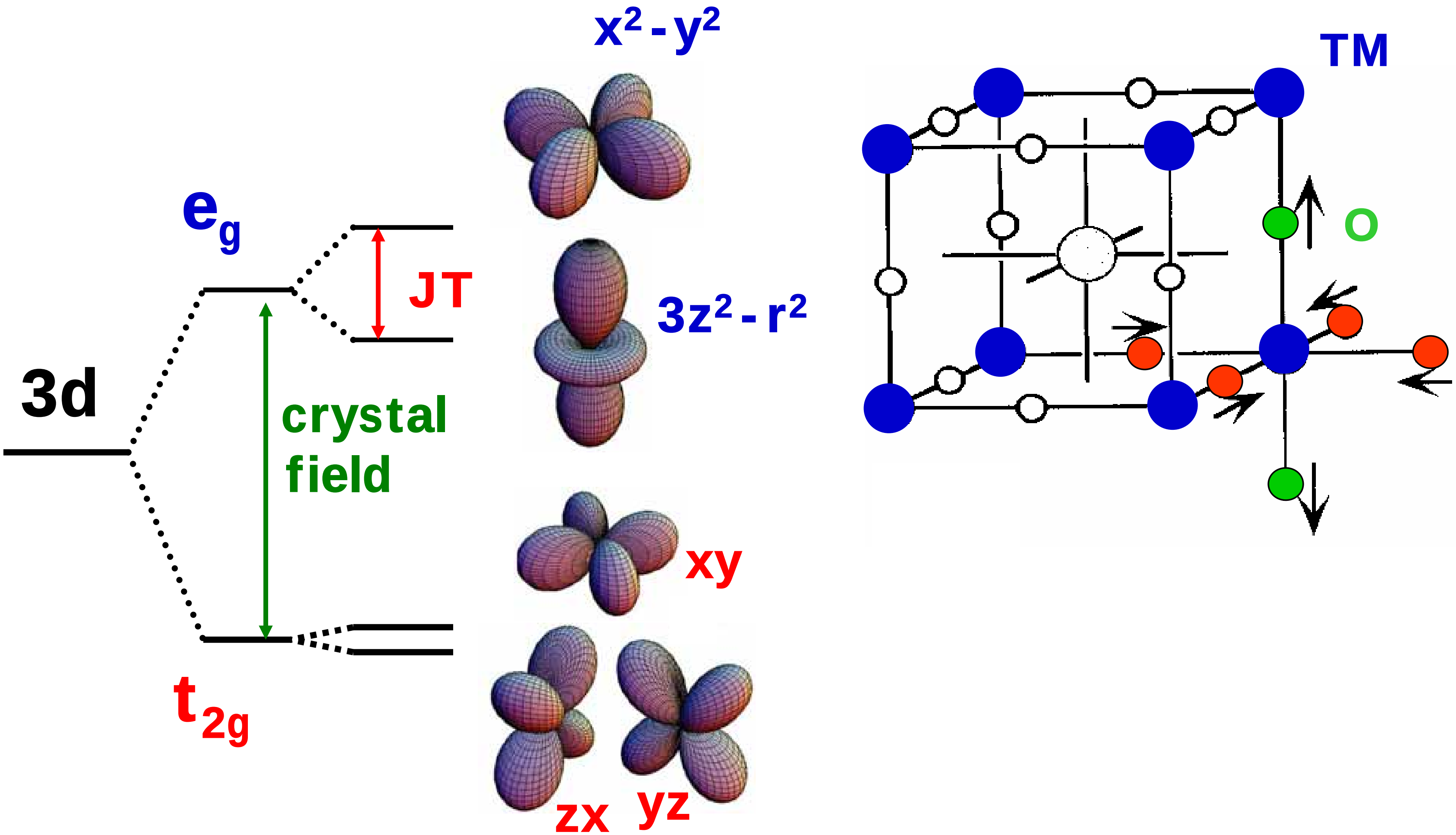


CoO: insulator

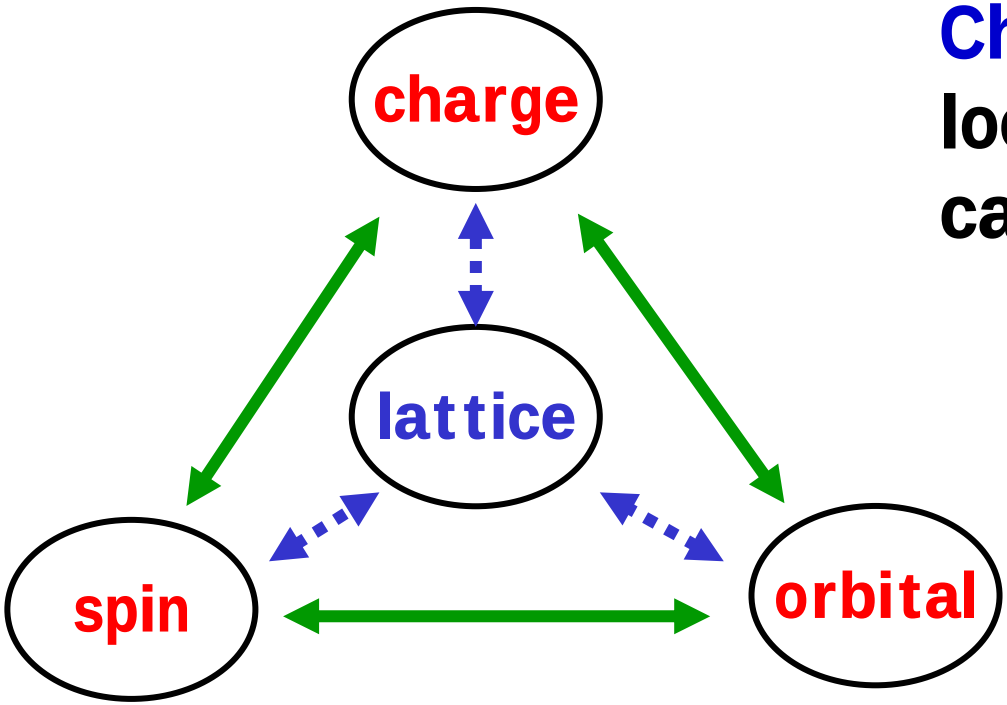
Mott-Hubbard insulator

Imada, Fujimori & Tokura
Rev. Mod. Phys. (1998)

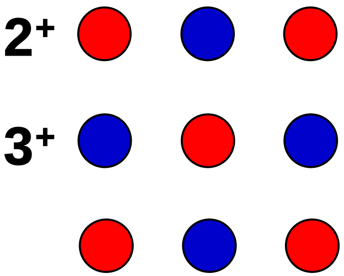
Band theory is insufficient to explain the physical properties of strongly correlated-electron systems.



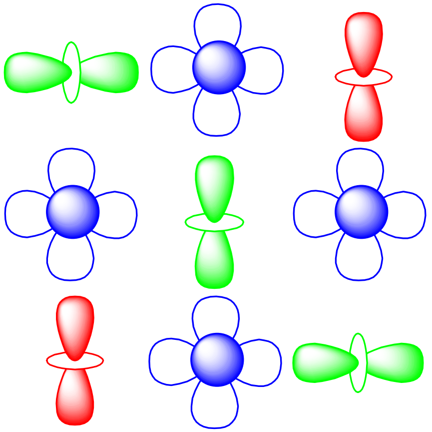
3d
eg
t2g
JT
crystal field
x2 - y2
3z2 - r2
xy
zx
yz
TM
O

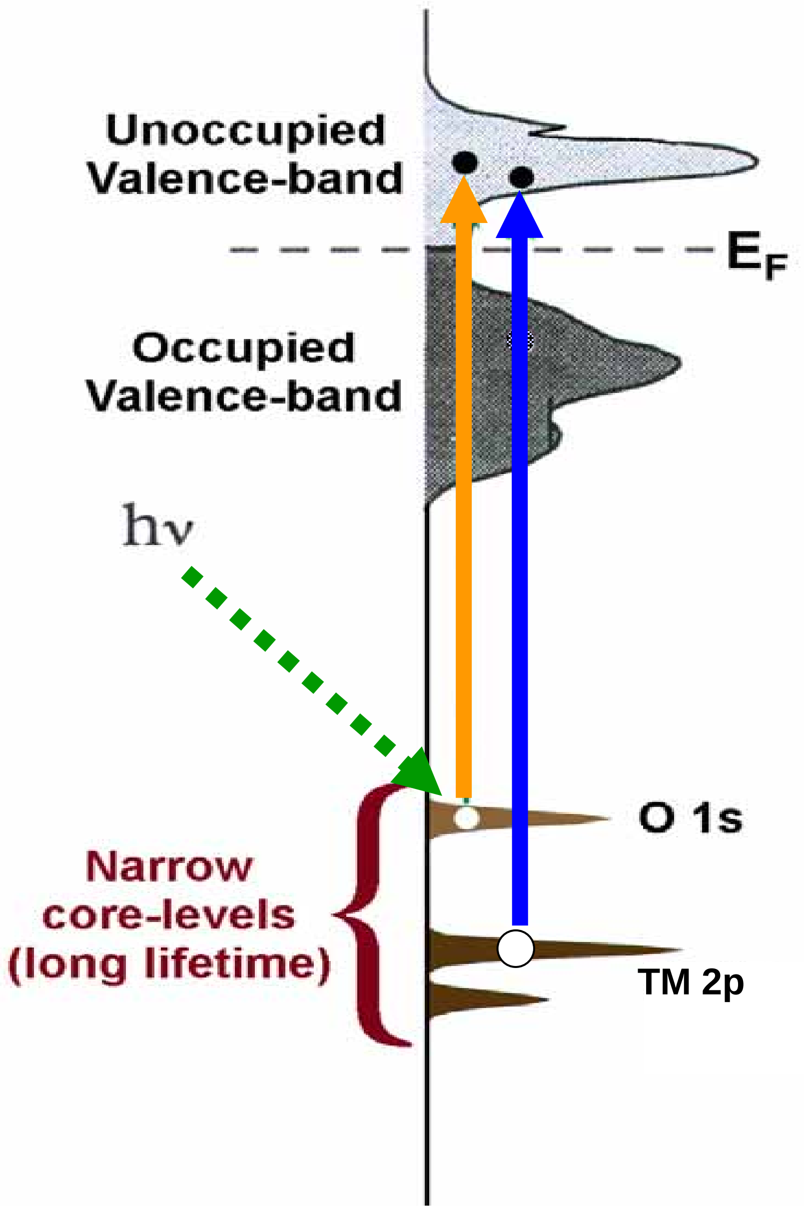


Charge ordering: spatial localization of the charge carriers on certain sites



Orbital ordering: periodic arrangement of specific electron orbitals



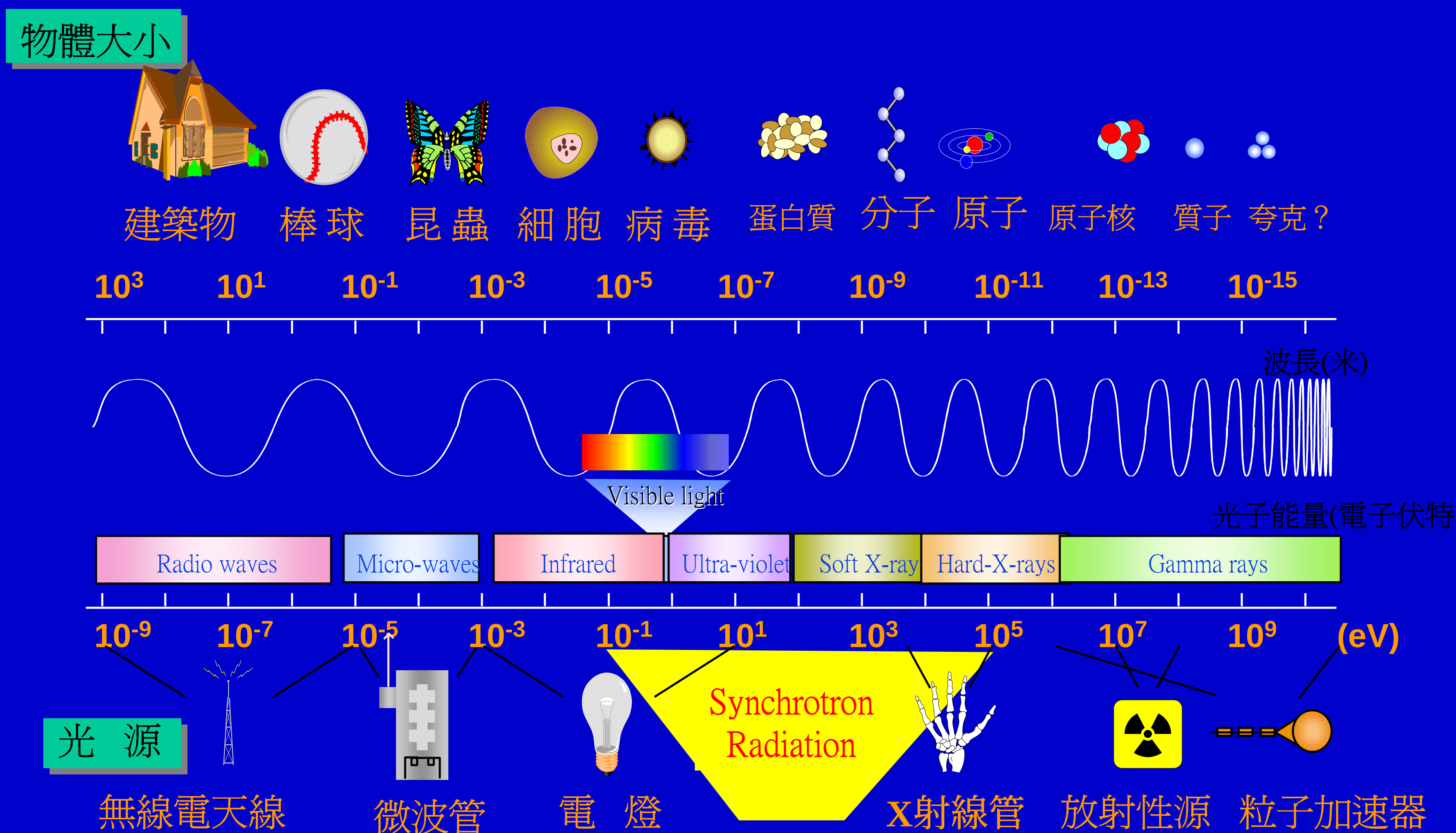


soft x-ray absorption & scattering

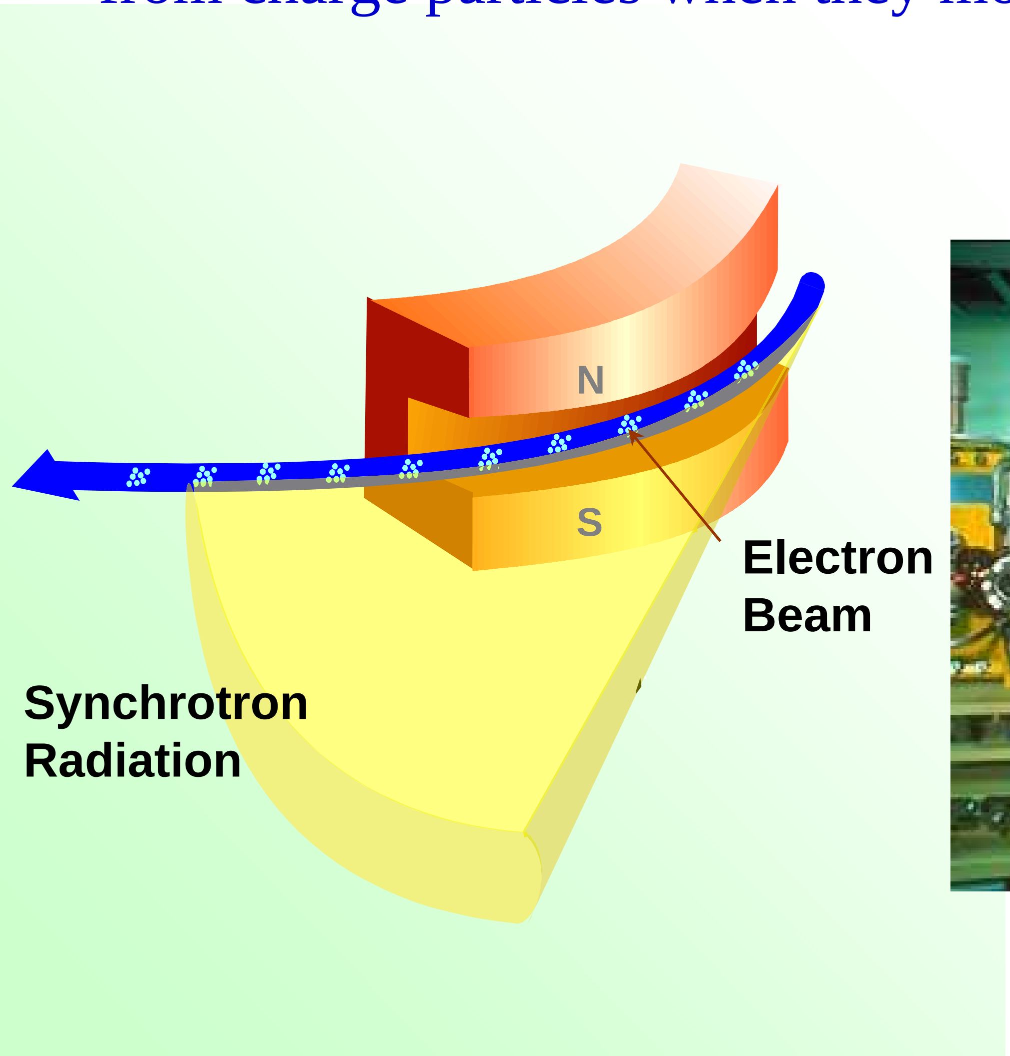
TM: 2p → 3d
O: 1s → 2p

direct, element-specific probing of electronic structure of TMO

The Electromagnetic Wave Spectrum

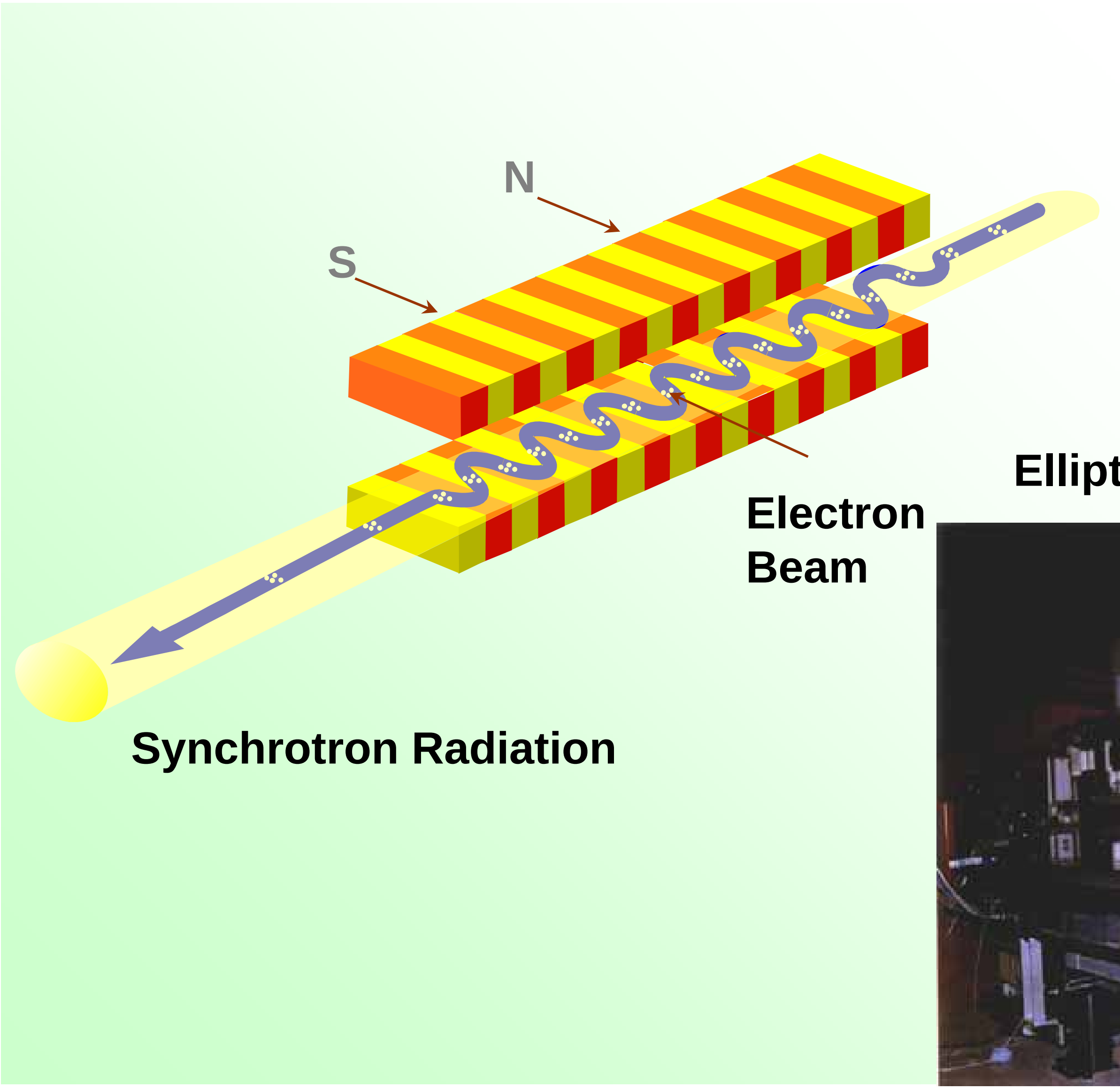


Synchrotron radiation is the electromagnetic waves emitted from charge particles when they move in a curved path.

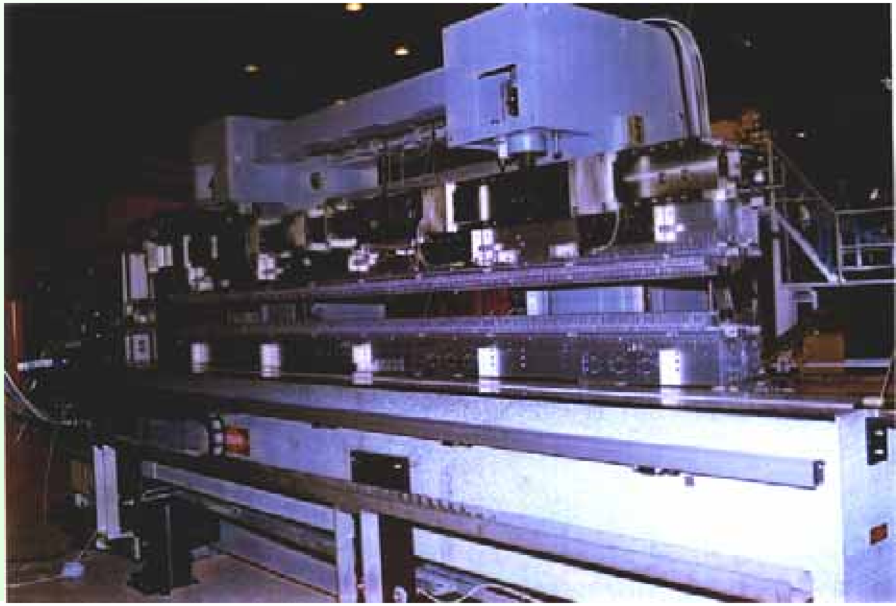


This light has been called "synchrotron radiation", since it was accidentally discovered in an electron synchrotron in 1947.

Insertion Device



Elliptically Polarized Undulator 5.6



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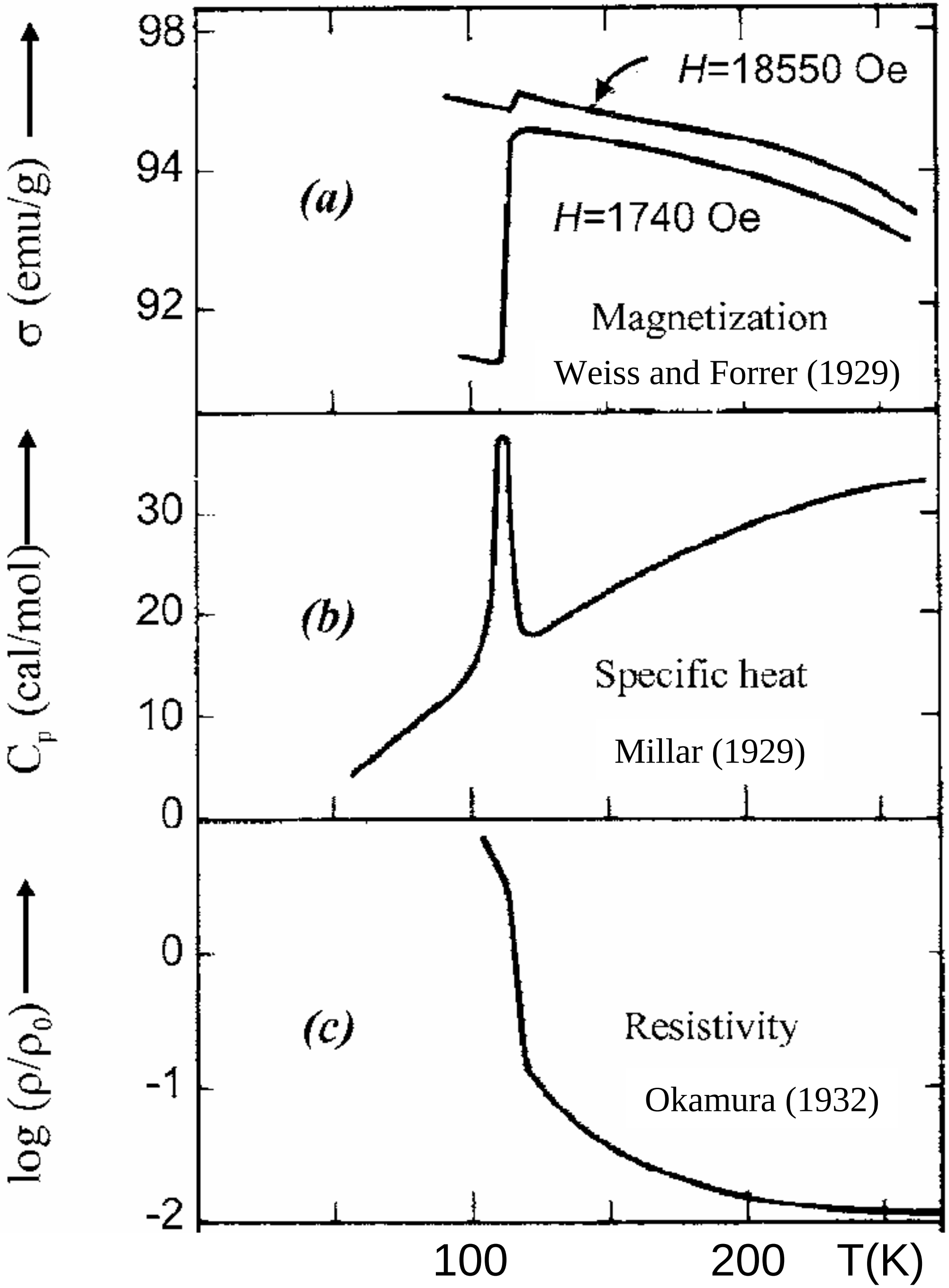
鄰近單位 9 高速電腦中心 10 交通大學

Research Highlights

- **Electronic structure of half-metal oxides**
  Huang et al., PRB (2003) ***Chen et al., PRB (2004)***
  Chang et al., PRB (2005)
- **Orbital ordering of manganites**
  Huang et al., PRL (2004)
- **Spin and orbital moments of magnetic oxides**
  Huang et al., PRB (2002) ***Huang et al., PRL (2004)***
- **Orbital symmetry and electron correlation of cobaltates**
  Wu et al., PRL (2005)

- **The Verwey transition**
- **Multiferroics in $TbMn_2O_5$**

Verwey transition and charge-orbital ordering of Fe_3O_4



macroscopic manifestation of the Verwey transition in Fe_3O_4

Recent Reviews

Imada, Fujimori, and Tokura
Rev. Mod. Phys. (1998)

Tsuda, Nasu, Fujimori, and Siratori
"Electronic Conduction in Oxides" (2000)

F. Walz, J. Phys: Condens. Matter (2002)

J. Garcia & G. Subias,
J. Phys: Condens. Matter (2004)

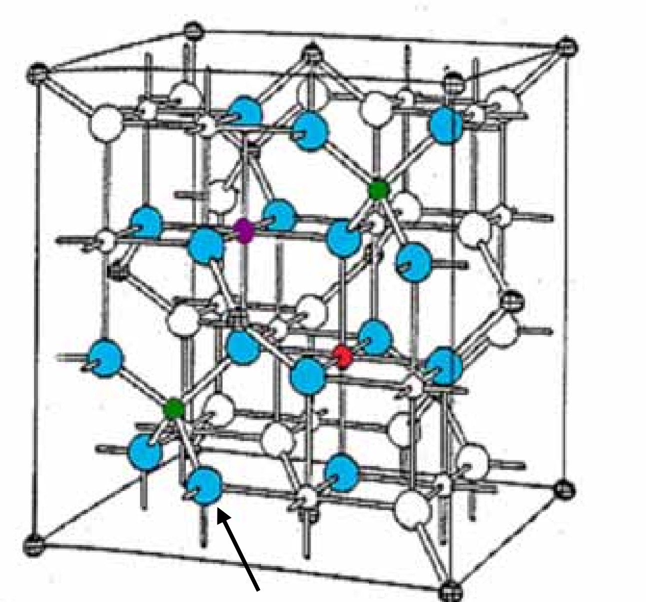
The Verwey transition of magnetite (Fe_3O_4)

➢ $T > T_V \sim 120$ K

Inverted spinel structure (cubic)

1/3: tetrahedral (A-site)) Fe^{3+}

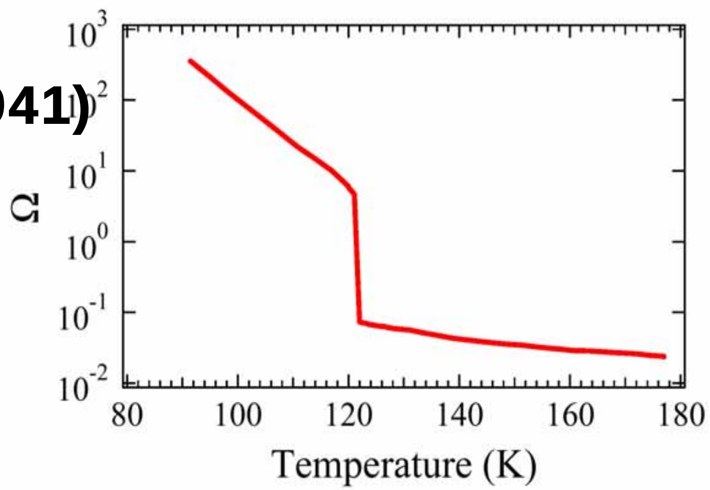
2/3: octahedral (B-site) Fe^{3+}, Fe^{2+}



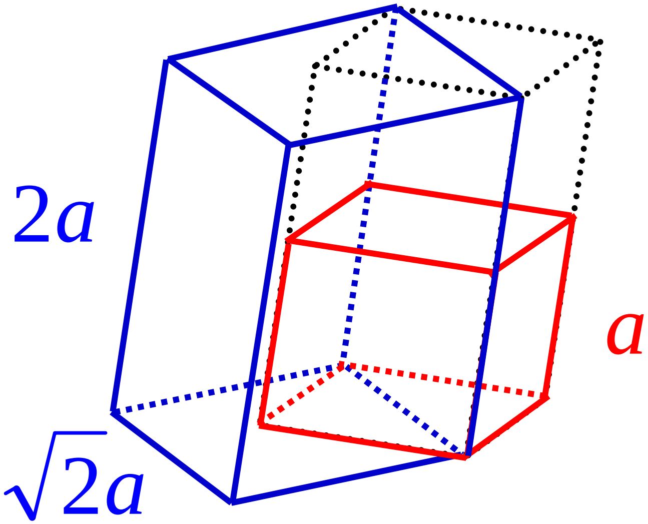
➢ A-site ↓, B-site ↑, $T_C \sim 860$K

➢ Verwey model:

charge order-disorder transition of B-site Fe (Verweyn & Haayman, 1941)



Fe_3O_4 is believed to be a classic example of charge ordering.



$T > T_V$

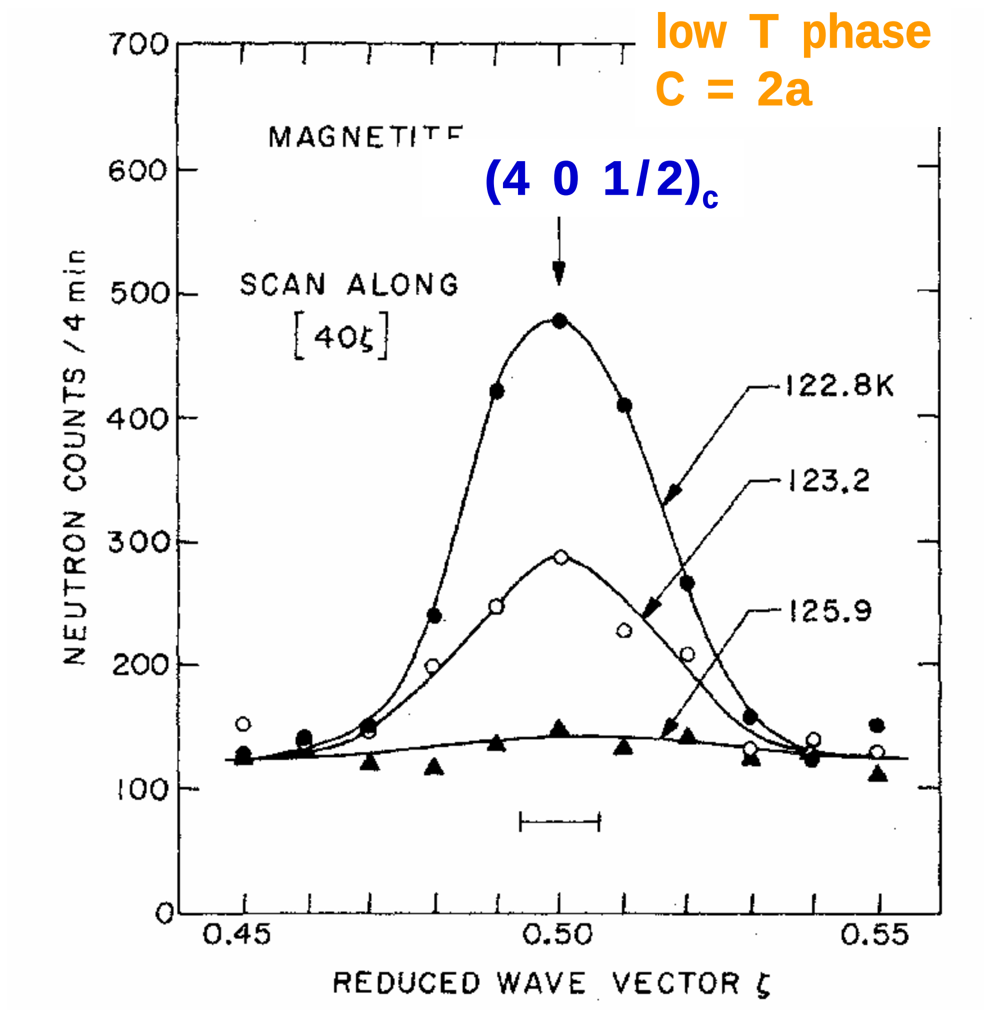
cubic, $a \times a \times a$ unit cell

$T < T_V$

monoclinic

$\sqrt{2}a \times \sqrt{2}a \times 2a$ supercell

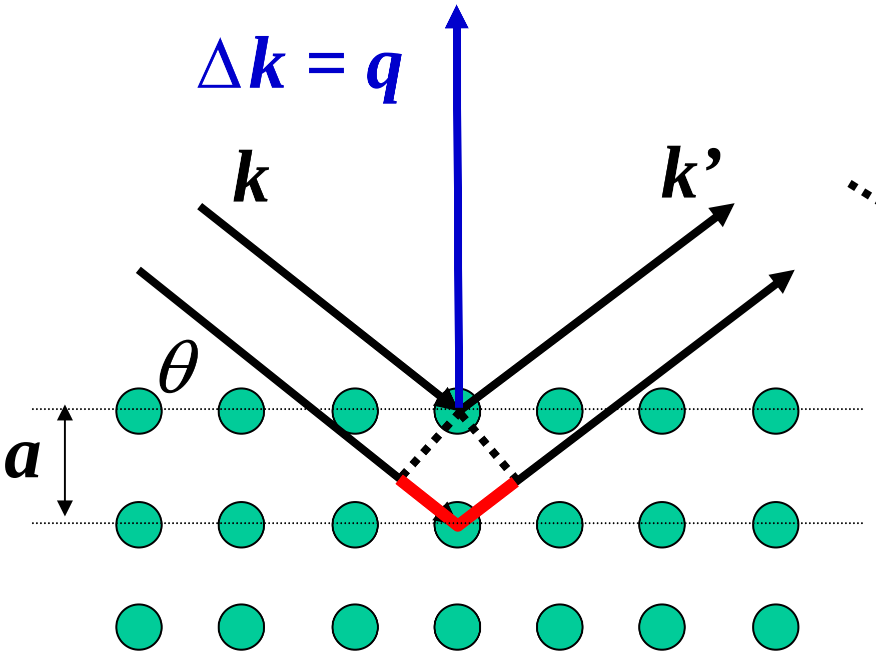
with space group *Cc*

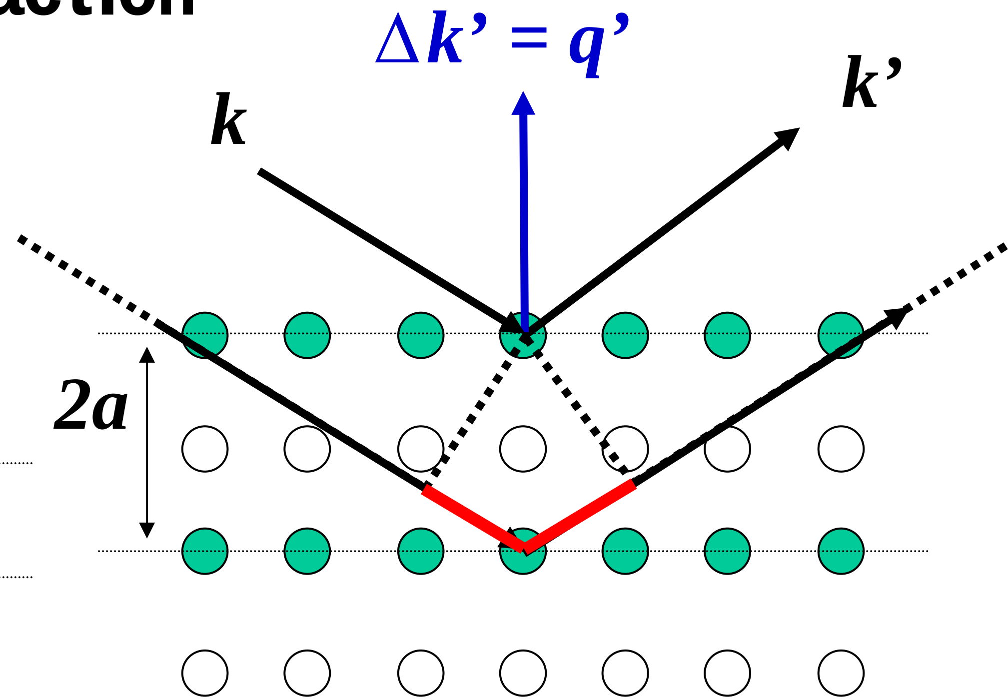


neutron scattering

Fujii et al. (1975)

Basic concept of diffraction





$$2a \sin\theta = \lambda = \frac{2\pi}{k}$$

$$2k \sin\theta = \frac{2\pi}{a}$$

$$2(2a) \sin\theta' = \lambda = \frac{2\pi}{k}$$

$$2k \sin\theta = \frac{1}{2}\frac{2\pi}{a}$$

momentum transfer $q = \dfrac{2\pi}{a}$

$$q' = \frac{1}{2}\frac{2\pi}{a}$$

lattice doubling → half-order diffraction

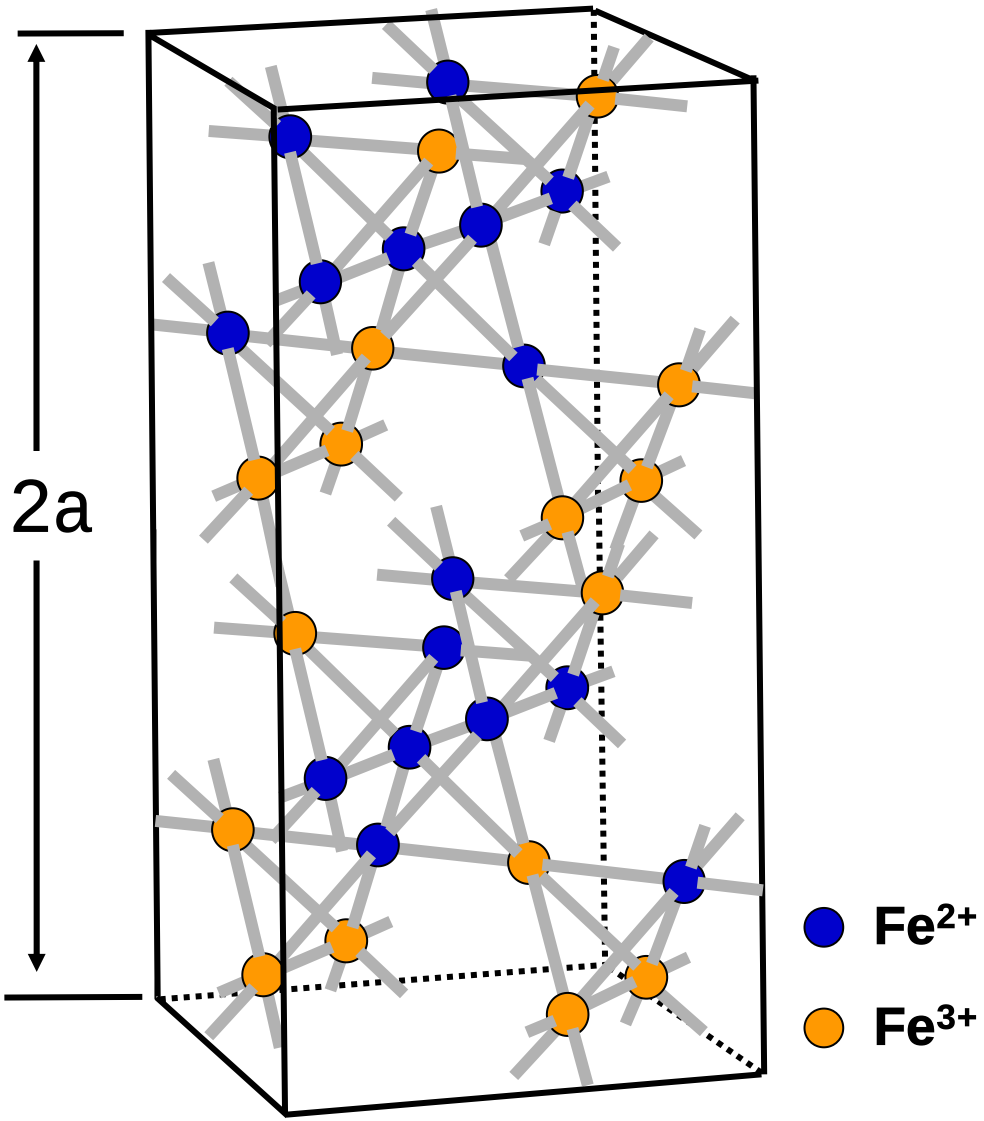
Does Fe_3O_4 exhibit charge ordering?

Neutron diffuse scattering
[Siratori *et al.*, J. Phys. Soc. Jpn. (1998)]
The atomic displacements are not of localized character, but spread over at least several unit cells, indicating the itinerant character of the 3d electrons.

NMR results [Novak et al., PRB (2000)]
The states of Fe ions on the *B* sublattice are mixed so strongly that the notion of 2+ and 3+ valency may lose its meaning.

X-ray scattering [Garcia et al., PRL (2000)]
The octahedral Fe atoms are electronically equivalent in a time scale lower than 10^{-16} sec.

Refinement of x-ray and neutron diffraction



Wright, Attfield, and Radaelli, PRL (2001), PRB (2002)

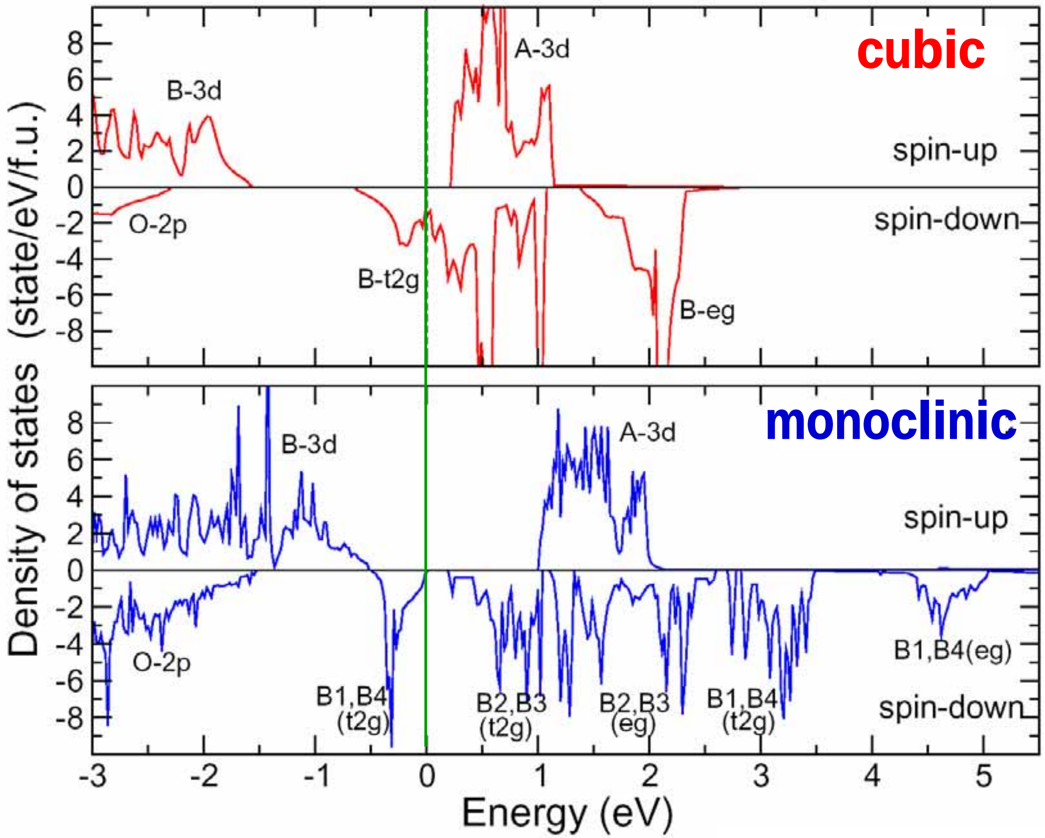
Charge ordering was deduced from the Fe-O distance.

4 independent B sites of Fe used; B1, B2, B3, B4

(B1 and B4 have 2.4 valence, B2 and B3 have 2.6 valence)

suggest:

1. **$(0\ 0\ 1)_c$ and $(0\ 0\ 1/2)_c$ charge modulation along the c-axis**
2. **Breakdown of Anderson's criterion**



LDA+U calculations

Jeng, Guo, and Huang, PRL (2004)

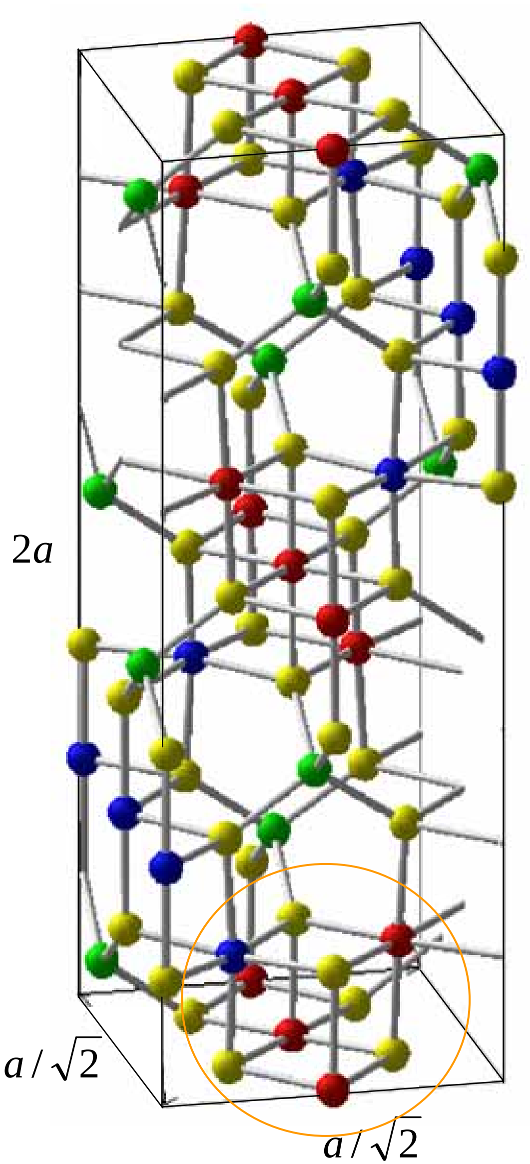
- **gap ~ 0.2 eV**
- **charge ordering of B-Fe**

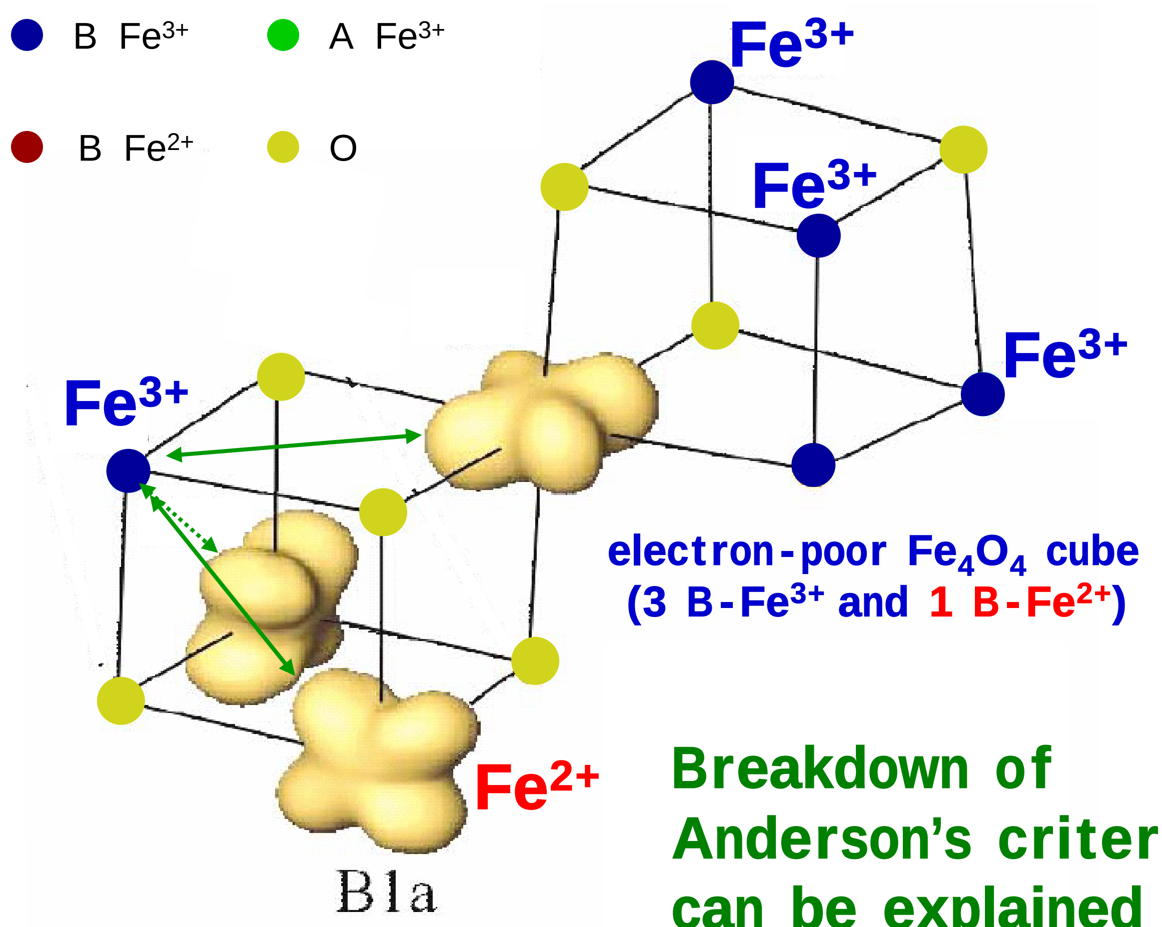
	Wright et al. valence charge	LDA+U valence charge	
Fe B1	**5.6**	**5.57**	Fe^{2+}
Fe B4	**5.6**	**5.58**	
Fe B2	**5.4**	**5.41**	
Fe B3	**5.4**	**5.48**	Fe^{3+}

cf: Leonov et al., PRL (2004)

LDA+U calculations: charge-orbital ordering

Jeng, Guo, and Huang, PRL (2004)

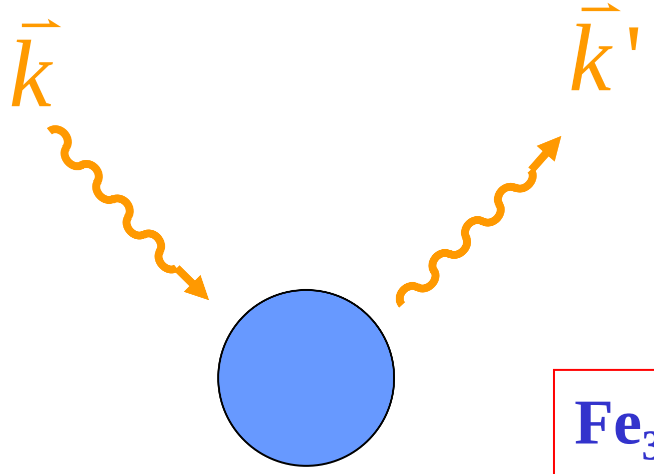




electron-rich Fe_4O_4 cube
(3 B-Fe^{2+} and 1 B-Fe^{3+})

Breakdown of Anderson's criterion can be explained by the existence of orbital ordering.

X-ray scattering



$$\vec{q} = \vec{k}' - \vec{k}$$

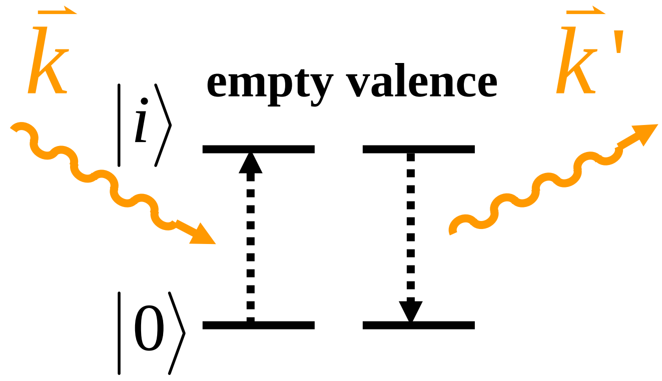
$n_i(r)$: **electron density**

$$f = 4\pi \int n_i(r) \frac{\sin(\vec{q}\cdot\vec{r})}{|\vec{q}\cdot\vec{r}|} r^2 dr$$

Fe_3O_4: charge disproportionation $\Delta Q = 0.2\ e$

$\Delta Q/Q_{total} \sim 1/550$

Resonant X-ray scattering

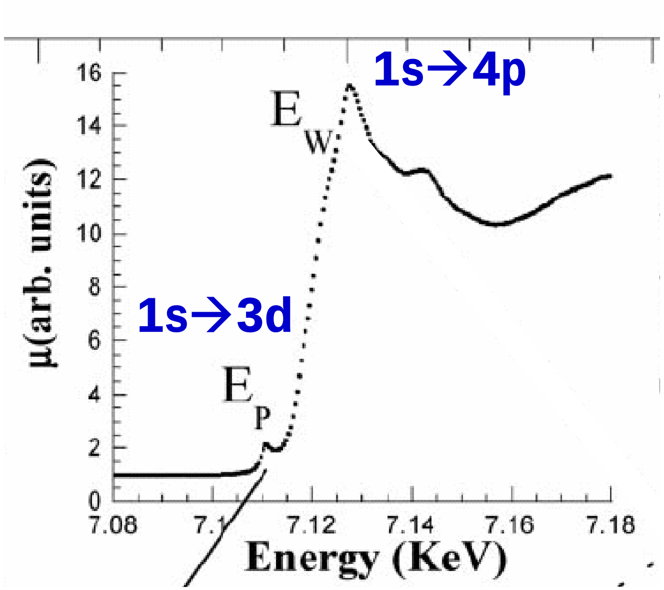


$$\Delta f \sim \sum_i \frac{\langle 0|\vec{\varepsilon}\cdot\vec{r}e^{i\vec{k}\cdot\vec{r}}|i\rangle\langle i|\vec{\varepsilon}'\cdot\vec{r}e^{i\vec{k}'\cdot\vec{r}}|0\rangle}{\hbar\omega - (E_i - E_0 - i\Gamma)}$$

to extract the valence disproportionation
and to learn about the spatial distribution of $|i\rangle$

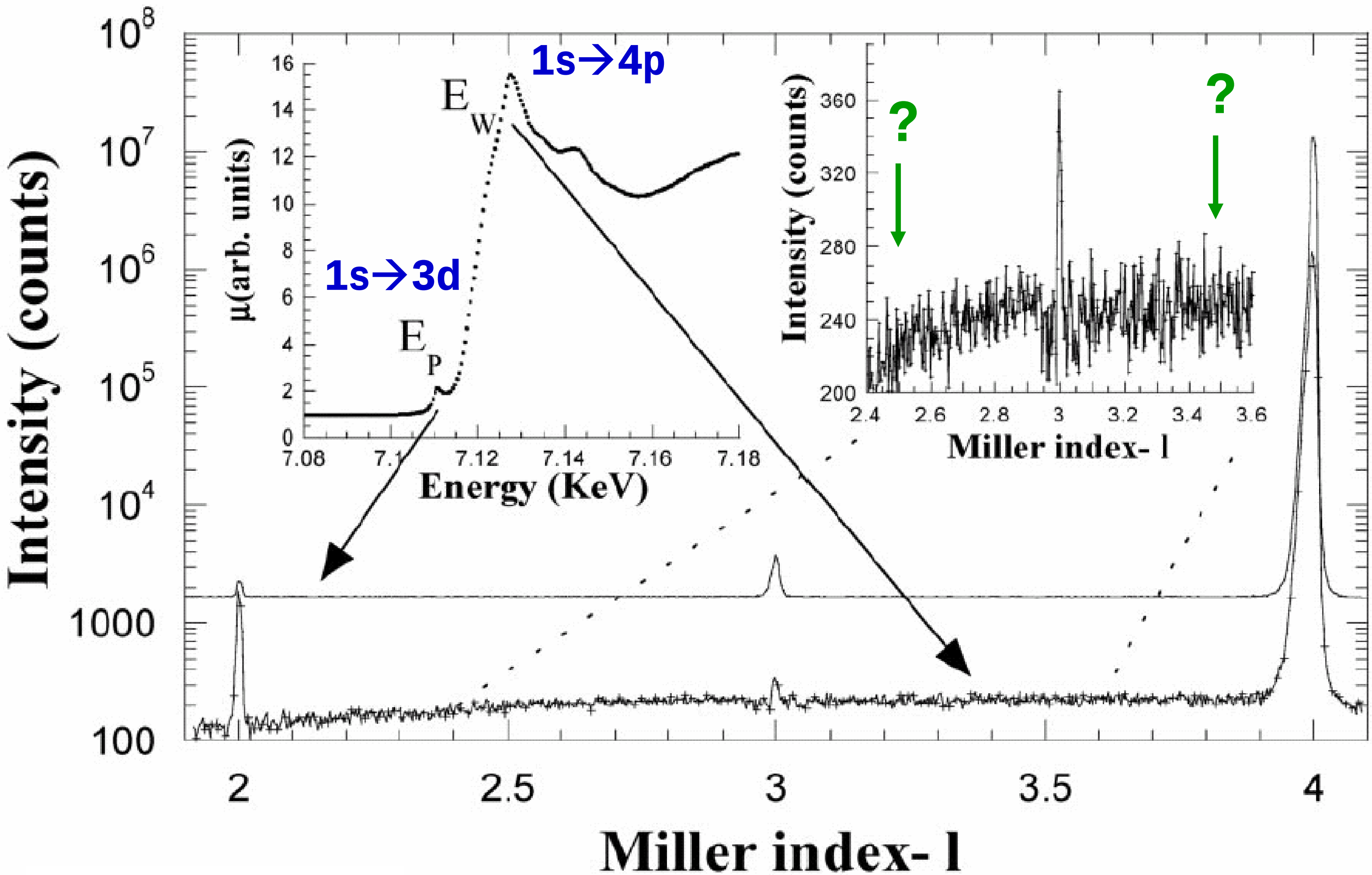
Resonant X-ray scattering

Subias et al., PRL (2004)



Resonant X-ray scattering

Subias et al., PRL (2004)



$(0\ 0\ l+1/2)_c$?

Fe K-edge resonant X-ray scattering failed to observe any charge ordering.

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Magnetite, a Model System for Mixed-Valence Oxides, Does Not Show Charge Ordering

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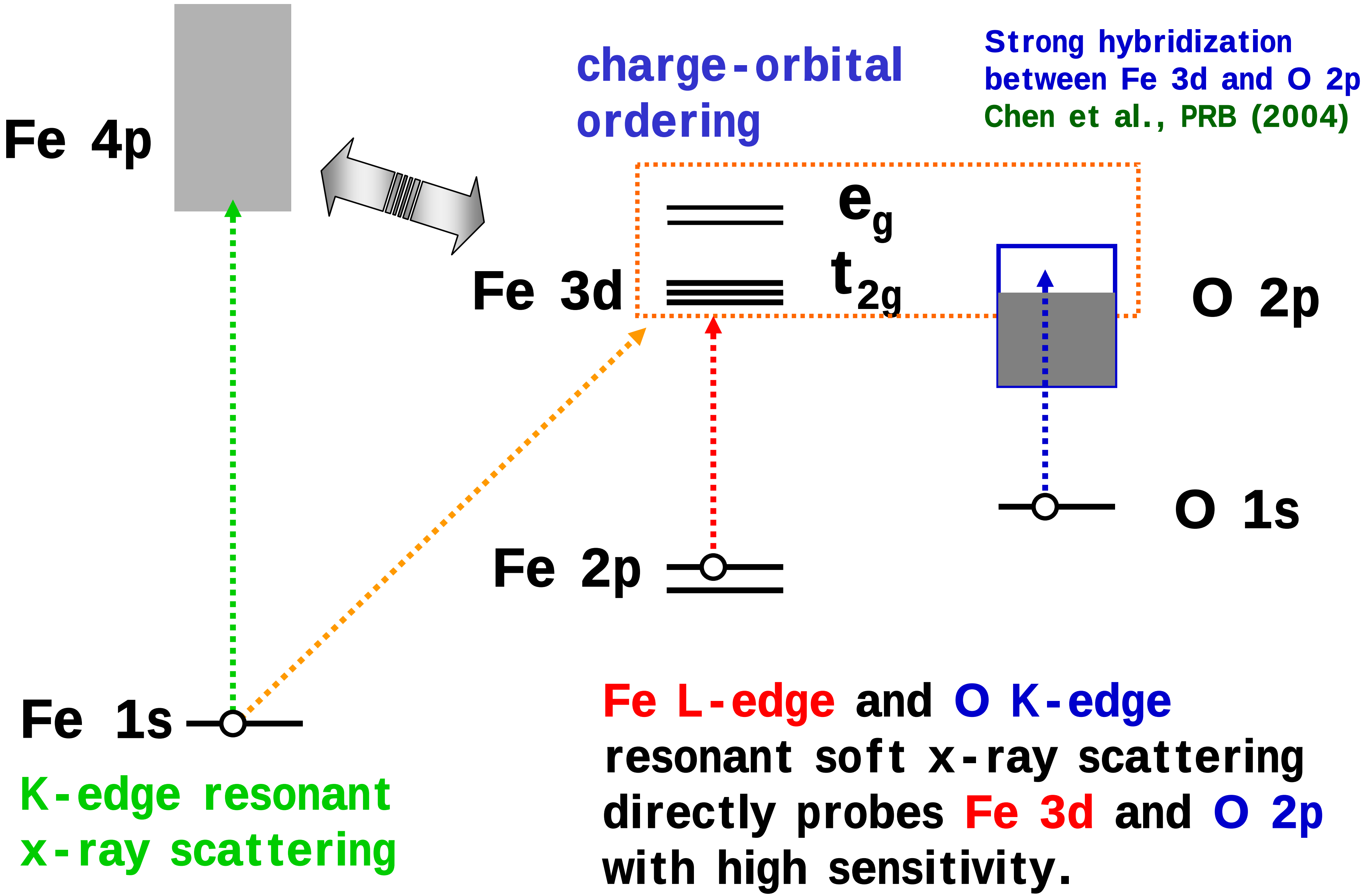
(Received 7 April 2004; published 7 October 2004)

We have investigated the charge ordering (CO) in magnetite below the Verwey transition. A new set of half-integer and mixed-integer superlattice reflections of the low-temperature phase have been studied by x-ray resonant scattering. None of these reflections show features characteristic of CO. We demonstrate the absence of CO along the c axis with the periodicity of either the cubic lattice $\mathbf{q} = (001)$ or the doubled cubic lattice $\mathbf{q} = (001/2)$. This result suggests that the Verwey transition is caused by strong electron-phonon interaction instead of an electronic ordering on the octahedral Fe atoms.

The existence of charge ordering in Fe_3O_4 remains controversial.

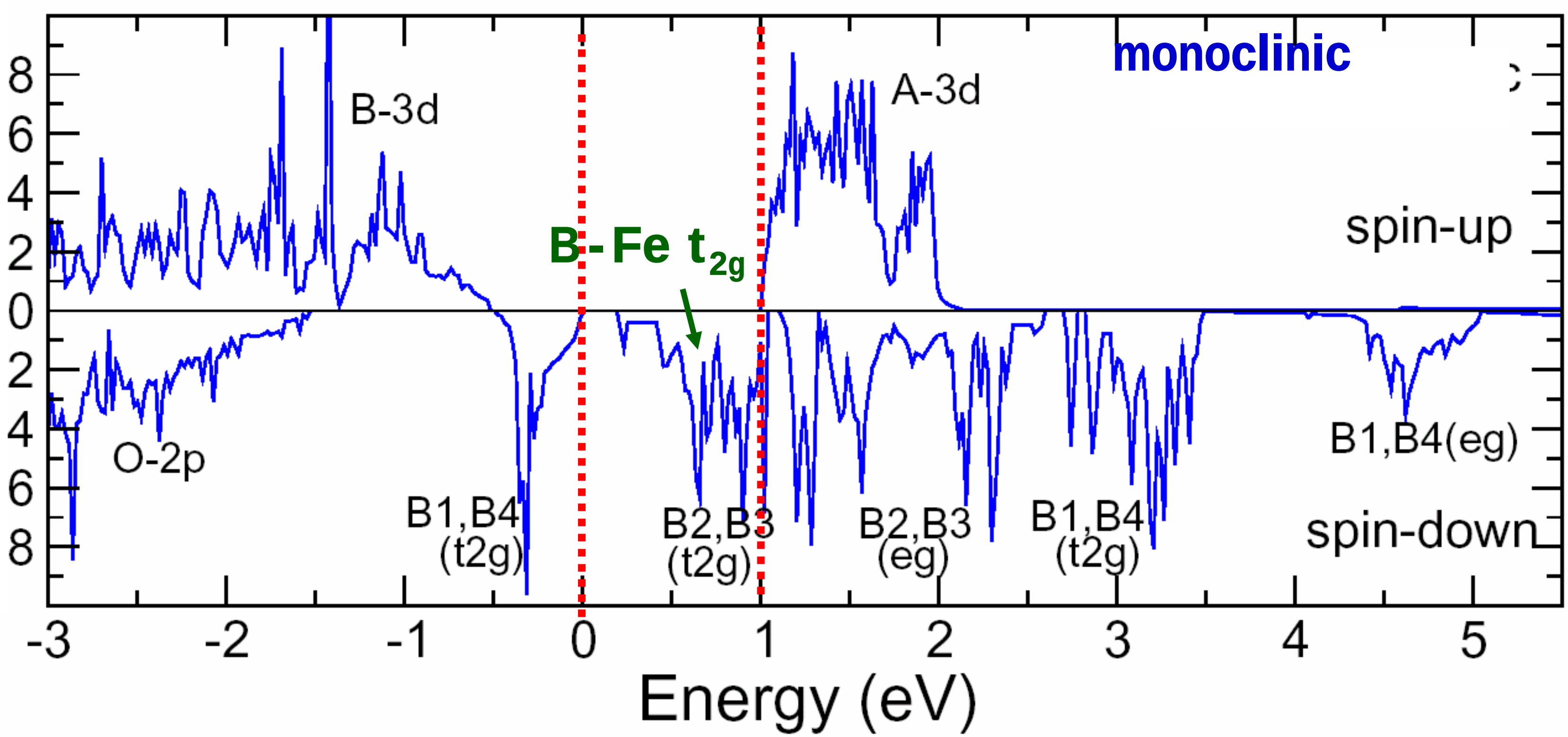
No freezing of the soft phonon mode has been observed. [Samuelsem, & Steinsvoll (1974)]

Mechanism of the Verwey transition?



Fe 4p
charge-orbital ordering
Strong hybridization between Fe 3d and O 2p
Chen et al., PRB (2004)
e_g
t_{2g}
Fe 3d
O 2p
O 1s
Fe 2p
Fe 1s
K-edge resonant x-ray scattering
Fe L-edge and O K-edge resonant soft x-ray scattering directly probes Fe 3d and O 2p with high sensitivity.

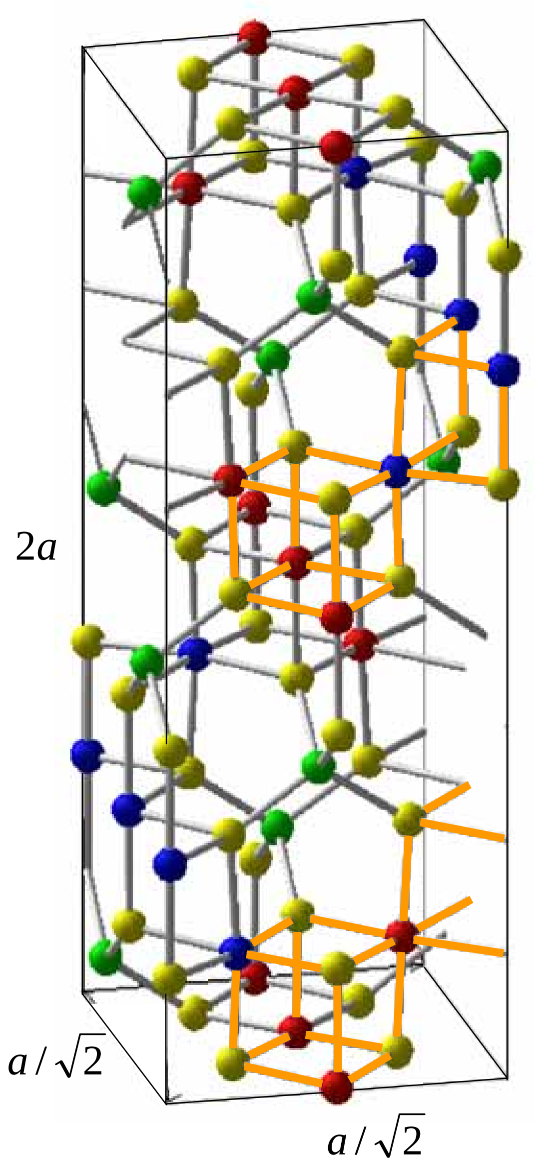
DOS from LDA+U calculations

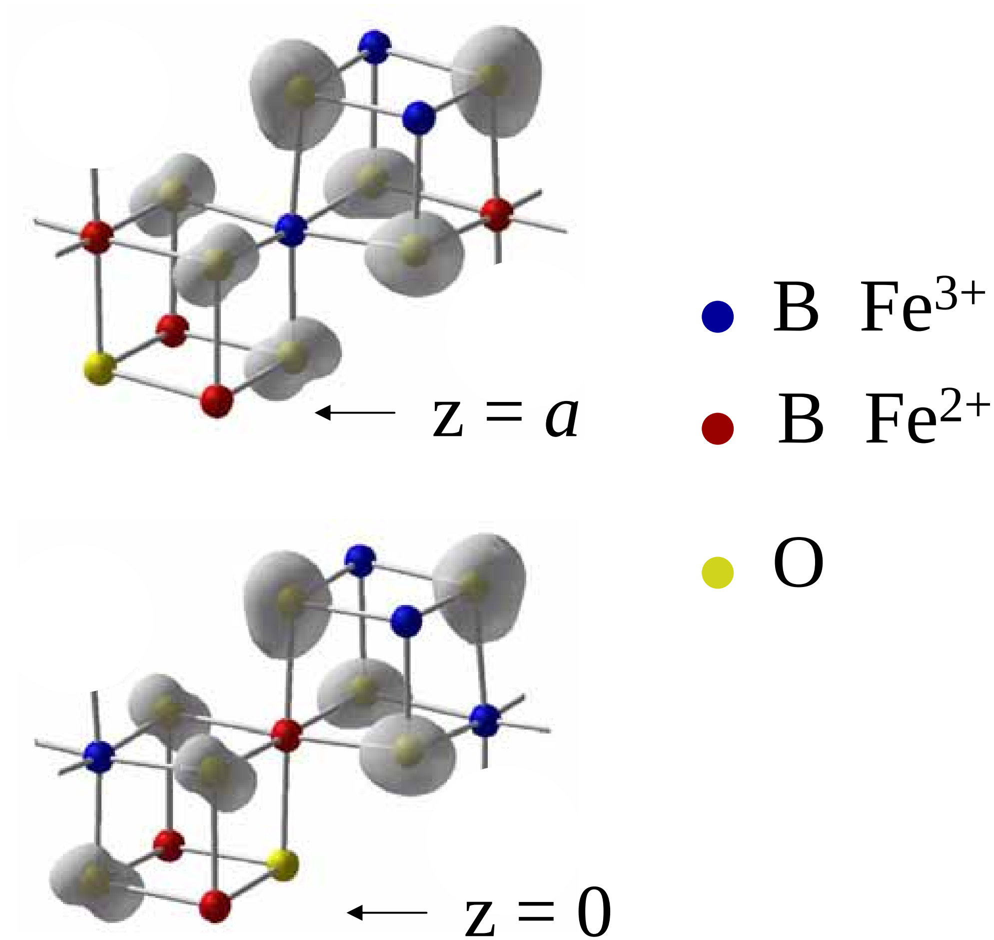


States between E_F and 1 eV above + 2a periodicity

→ $(0\ 0\ ½)_c$ resonant diffraction

Iso-surface of O 2p in Fe_3O_4 integrated between E_F and 1 eV above





monoclinic P2/c structure

LDA+U calculations: H.T. Jeng

Summary

- The Verwey transition is a transition of charge-orbital ordering.

- Experimental discovery of orbital-ordering mechanism for the Verwey transition, resolving the long-lasting debate.

Outline:

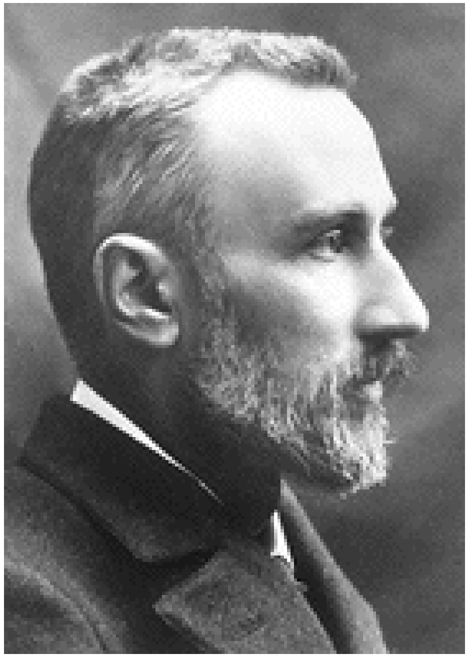
- Verwey transition and charge-orbital ordering of Fe_3O_4
- **Multiferroics in $TbMn_2O_5$**

  -- coexistence and strong coupling of ferroelectricity and antiferromagnetism

The magnetoelectric effect:

the induction of magnetization by an electric field; induction of polarization by a magnetic field.

- first presumed to exist by Pierre Curie in 1894



$$\nabla \times \vec{H} = \frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial}{\partial t}(\vec{E} + 4\pi\vec{P})$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

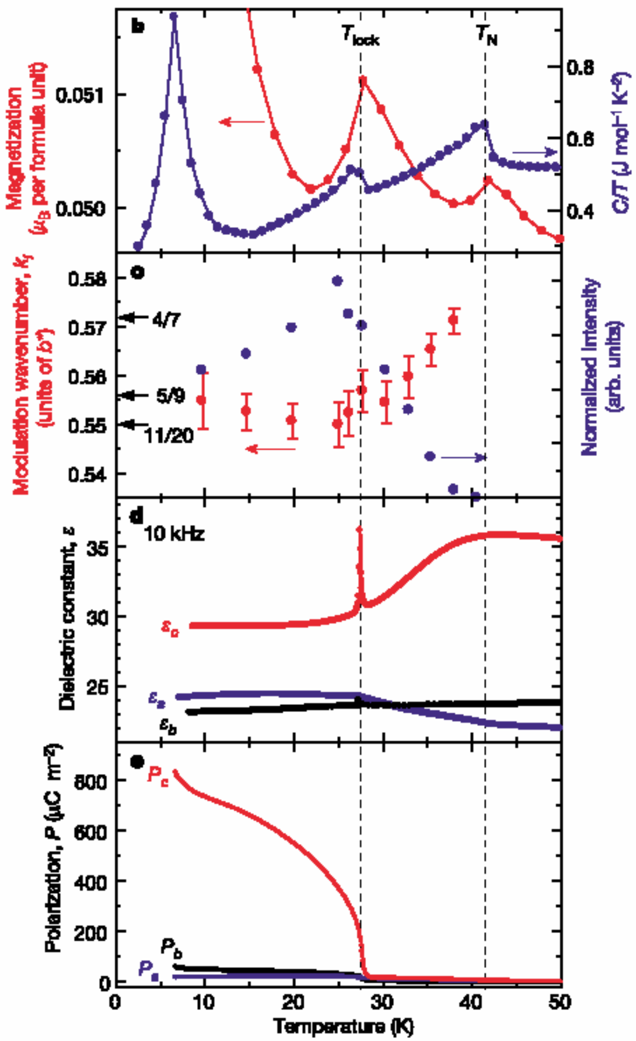
$$\nabla \cdot \vec{B} = 0$$

$$\nabla \cdot \vec{E} = 4\pi\rho$$

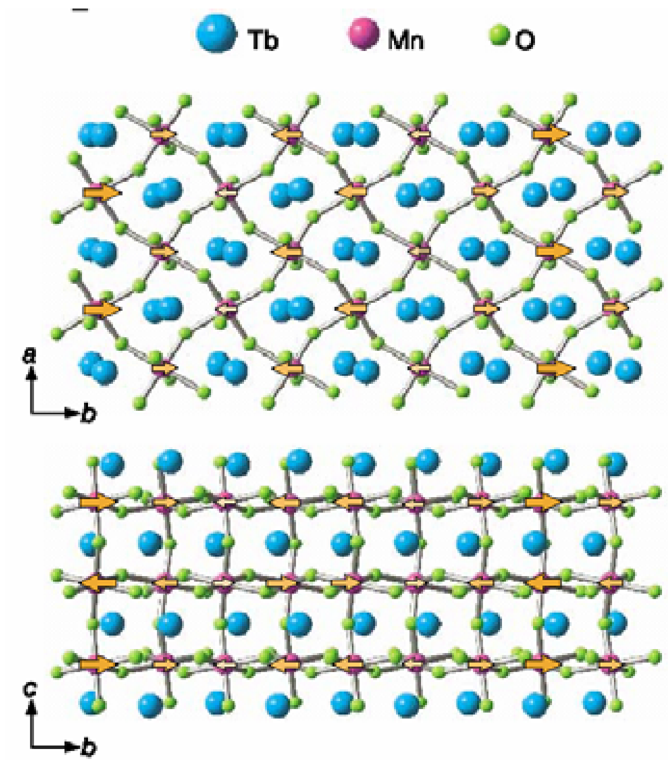
Magnetic control of ferroelectric polarization

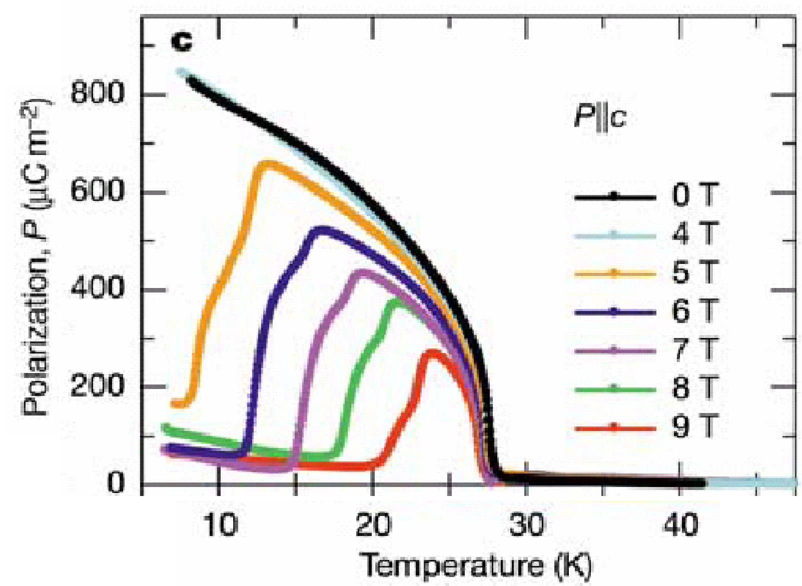
Nature, 426, 55 (2003)

T. Kimura[1]*, T. Goto[1], H. Shintani[1], K. Ishizaka[1], T. Arima[2] & Y. Tokura[1]



$TbMnO_3$



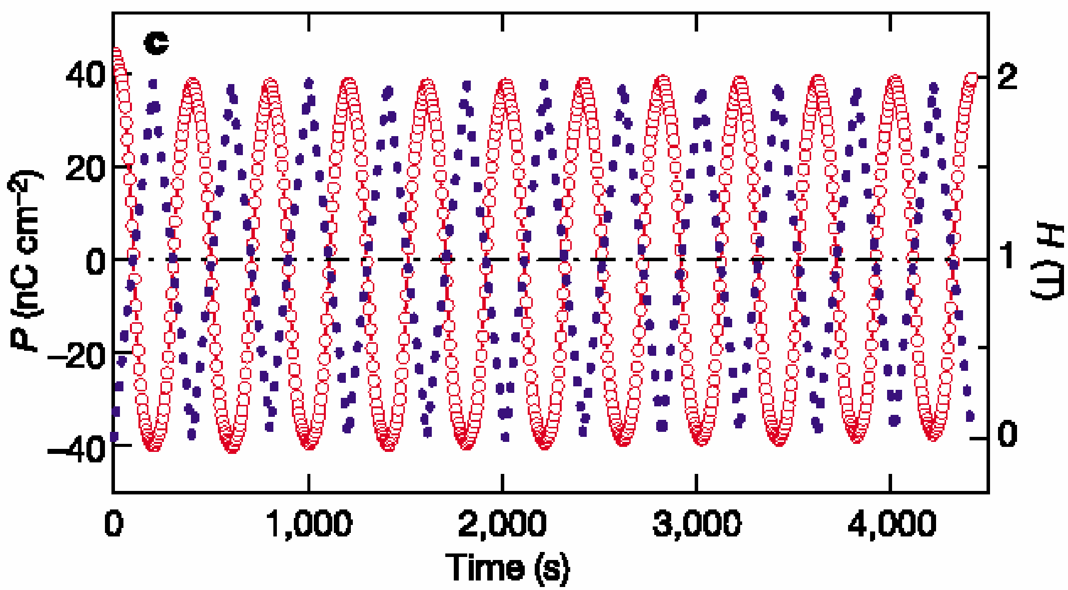


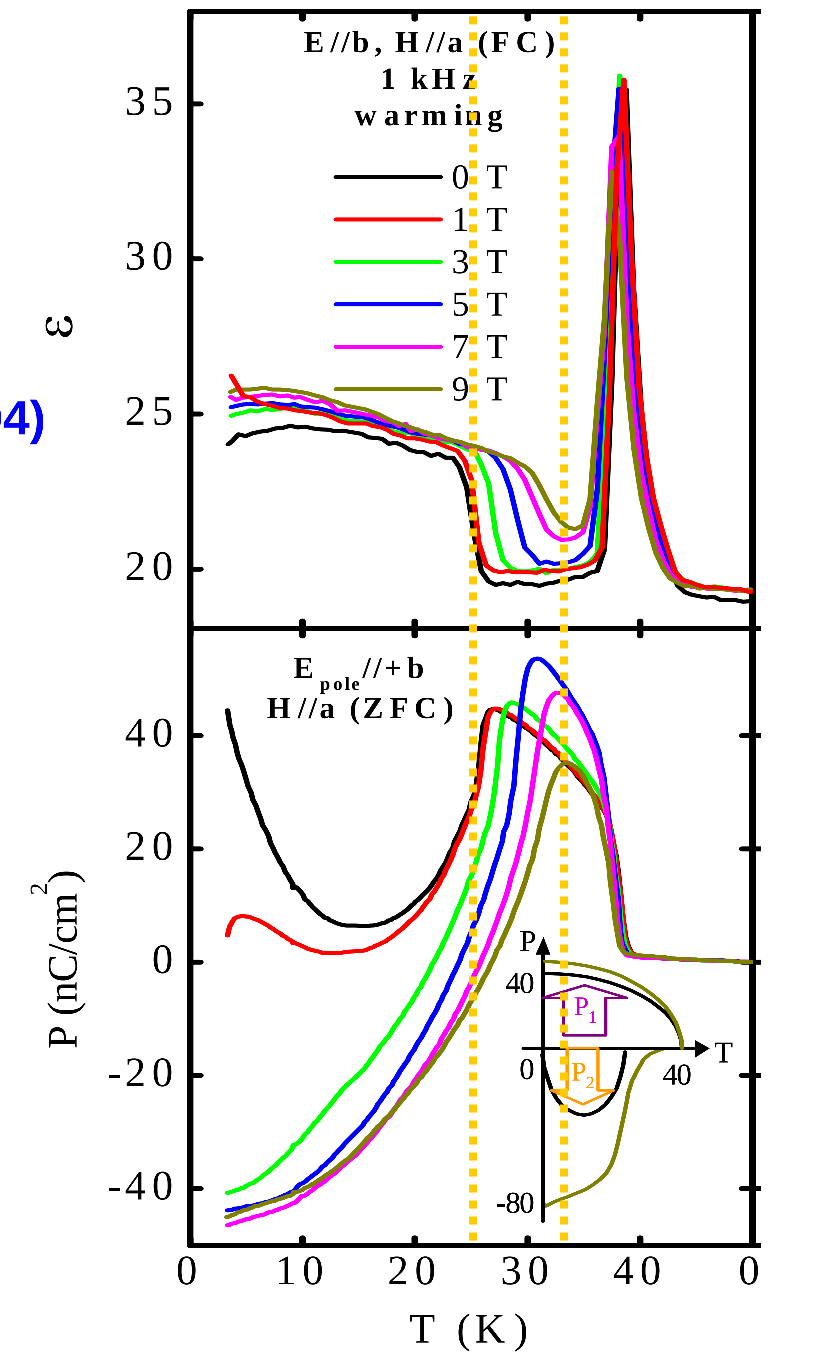
Electric polarization reversal and memory in a multiferroic material induced by magnetic fields

N. Hur, S. Park, P. A. Sharma, J. S. Ahn*, S. Guha & S-W. Cheong

$TbMn_2O_5$ Nature, 429, 392 (2004)

- **3 transitions on cooling.**
- **Magnetic field induces a sign reversal of the electric polarization.**

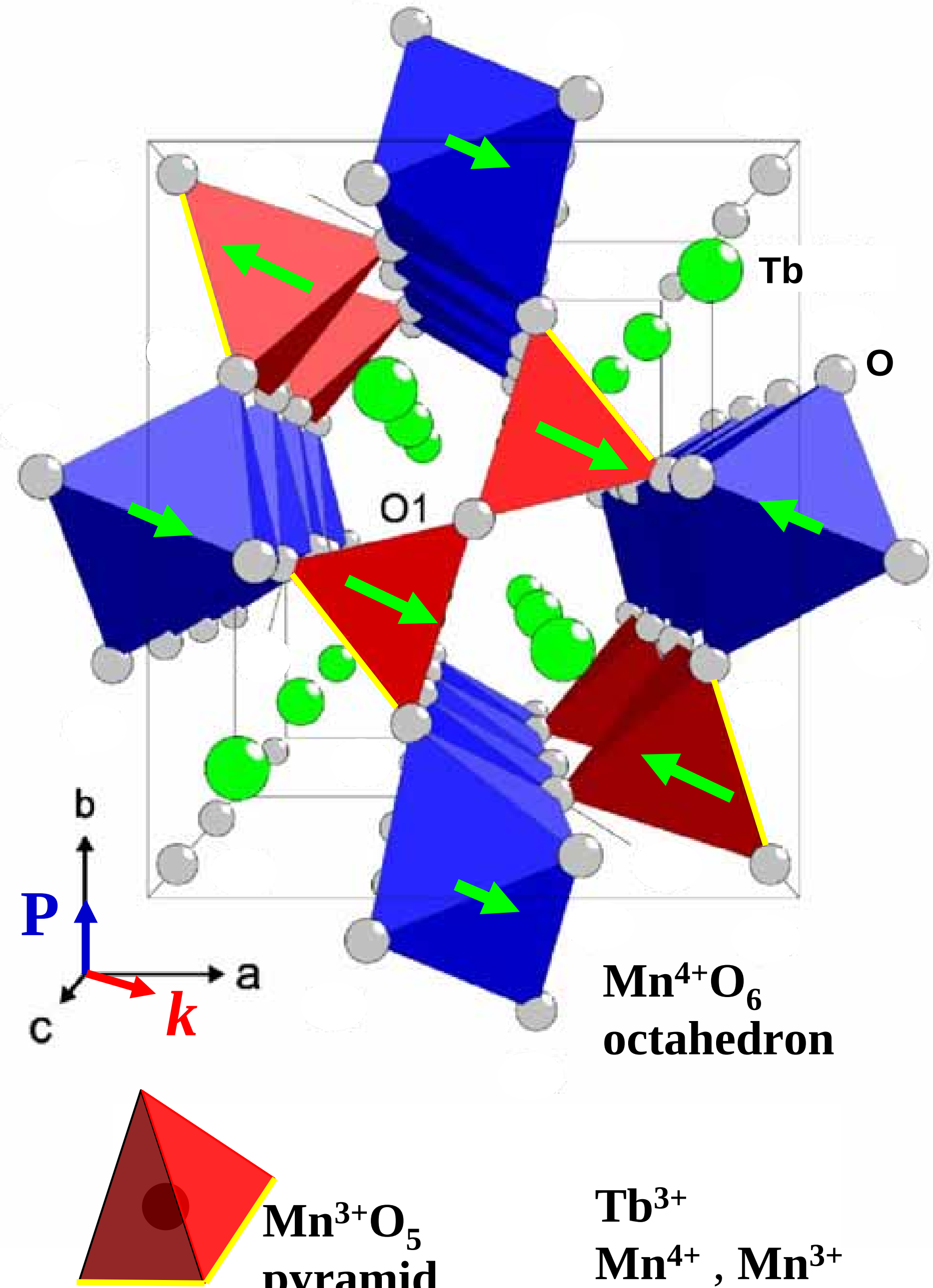




Recently discovery in the coexistence and strong coupling of antiferromagnetism and ferroelectricity in frustrated spin systems such $RMnO_3$ and RMn_2O_5 (R=Tb, Ho , …)

revived interest in "multiferroic" systems

The mechanism has not been yet clarified, although magnetic competing interactions are believed to be the key ingredient.



$TbMn_2O_5$

- orthorhombic structure (a 🕒 b 🕒 c, $\alpha = \beta = \gamma = 90^\circ$)

•AFM insulator (T_N=42 K)

AFM square lattice with asymmetrical next-nearest-neighbor interactions, i.e. geometrically frustrated

•Magnetization in the ab plane,

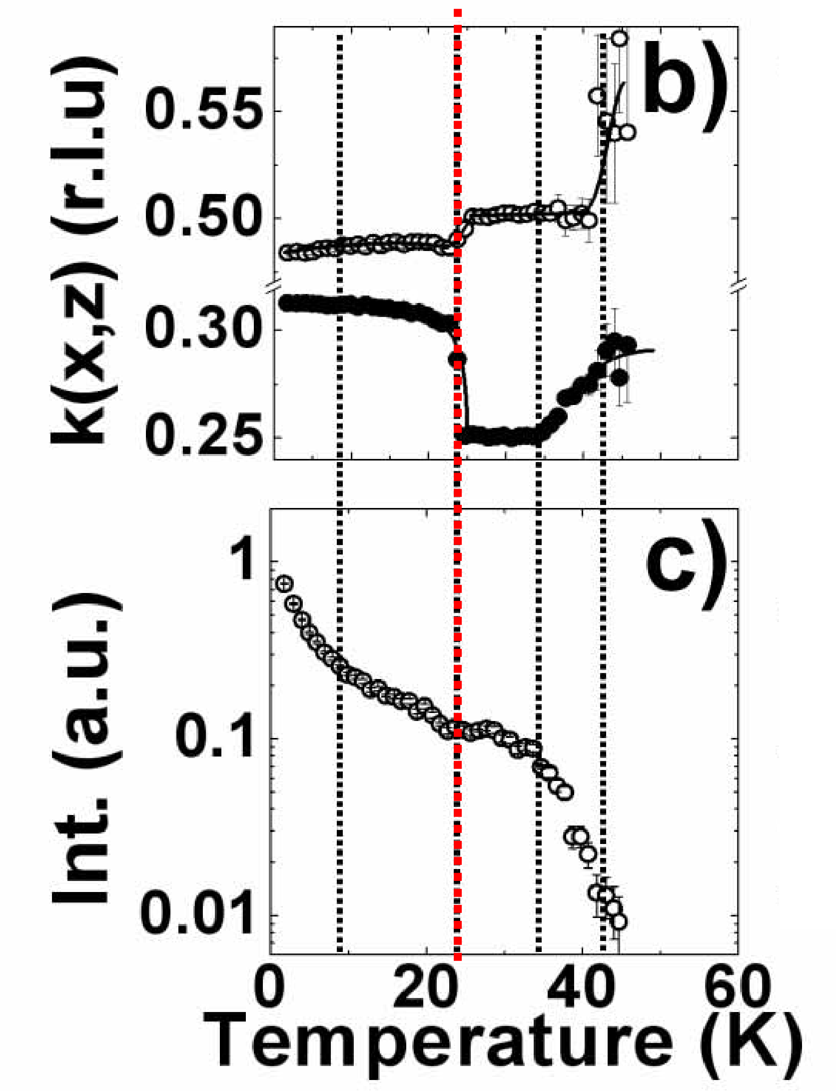
•Tb ferromagnetic below 10 K

•Spontaneous polarization **P** // **b**

•AFM modulation vector ***k*** ⊥ **P**

Neutron diffraction: complex spin structure

L.C. Chapon et al, PRL 94 , 177402 (2004)



3 AFM phases with different propagation vectors in the ac plane.

$k = (k_x\ 0\ k_z)$

propagation vectors k
in units of (2π/a 0 2π/c):

33 K < T 42 K

k ~ (1/2 0 0.30) **incommensurate**

24 K < T <33 K

k=(1/2,0,1/4), commensurate

T < 24 K,

k ~ (0.48,0,0.3), incommensurate

Summary

- **Resonant soft x-ray scattering of $TbMn_2O_5$**

  Two incommensurate orderings at T < 24:

  AFM ordering, consistent with neutron diffractions.

  A new type of ordering,

  --- charge-orbital ordering ?.

- **The AFM ordering is closely related to the dielectric response.**

Collaborators

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Resistivity measurements (Fe_3O_4):
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$TbMn_2O_5$: S. W. Cheong (Rutgers Univ.)

歡迎有興趣的研究生
加入我們的研究團隊!

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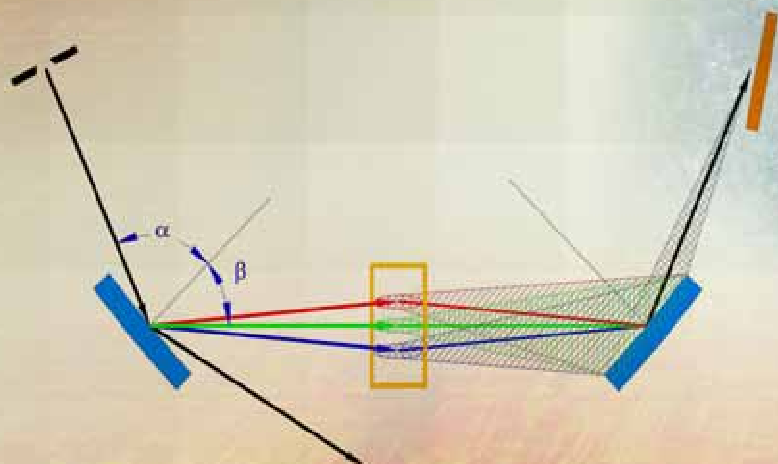
Fourth Workshop on Physics of Metal Oxides（第四屆氧化物物理研討會）



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Thank you !