Mechanism of the Verwey phase transition in magnetite Fe_3O_4

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Fe_3O_4

MAGNETITE (*gr. magnetis)*
the oldest known magnetic mineral (~1500 B.C.)

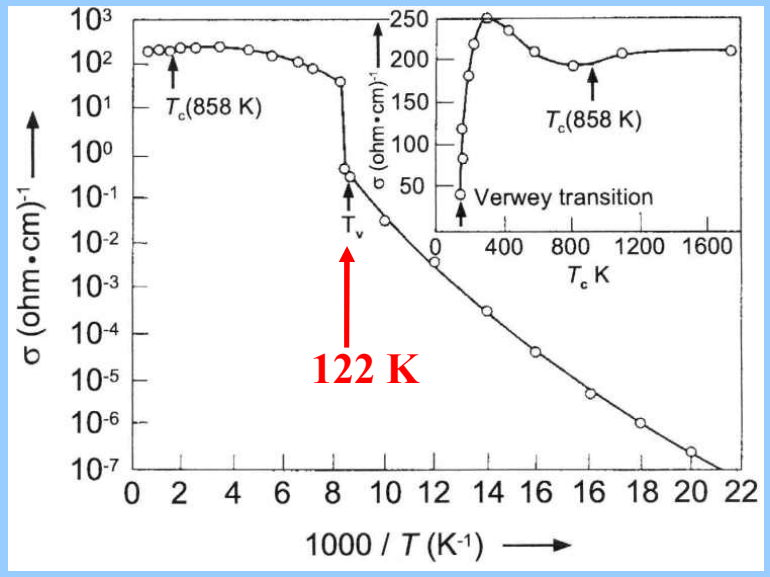
Verwey Transition, Nature 144, 327 (1939)

Insulator — Metal

0 — **T_V = 122 K** — **T_N = 860 K**

Electrical conductivity

Metal – Insulator transition at 122 K



Fe_3O_4

What is the origin of Verwey transition?

electron interactions:

- charge ordering (Verwey)
- magnetism (exchange)
- long-range Coulomb interactions
- local (Hubbard) interactions
- orbital correlations

lattice:

- structural transition
- electron-phonon coupling
- Jahn-Teller effect
- polaron formation

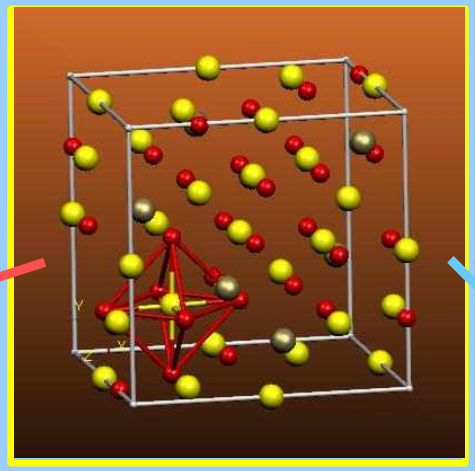
Two concepts of the Verwey Phase Transition

Fe_3O_4

T > 122K

Metal

Cubic, Fd-3m, Ferrimagnet



Fe^{3+} tetrahedral (spin-up)

$Fe^{2.5+}$ octahedral (spin-down)

O

Charge order of
Fe^{3+} and Fe^{2+} in octa

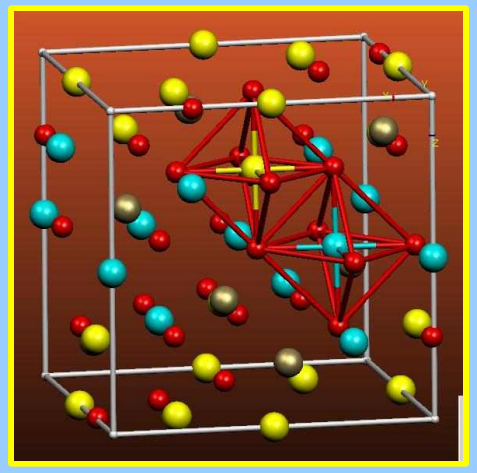
Monoclinic distortion

Fe^{3+} tetra

Fe^{3+} octa

Fe^{2+} octa

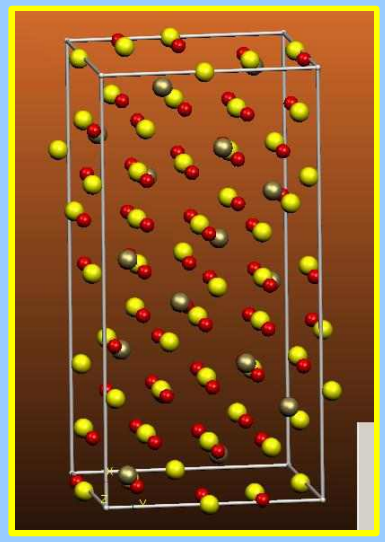
O



T < 122K

Metal–insulatr transition

Insulator



X-ray anomalous scattering
X-ray and neutron diffraction
Electronic band structure cal.
LDA+U

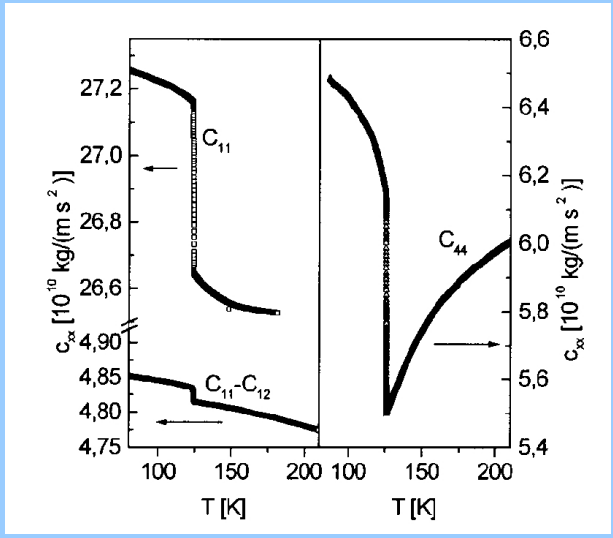
Diffraction methods
Diffuse scattering
Mossbauer, EXAFS

Fe_3O_4 Crystal distortions – diffuse scattering and c_{44} softening

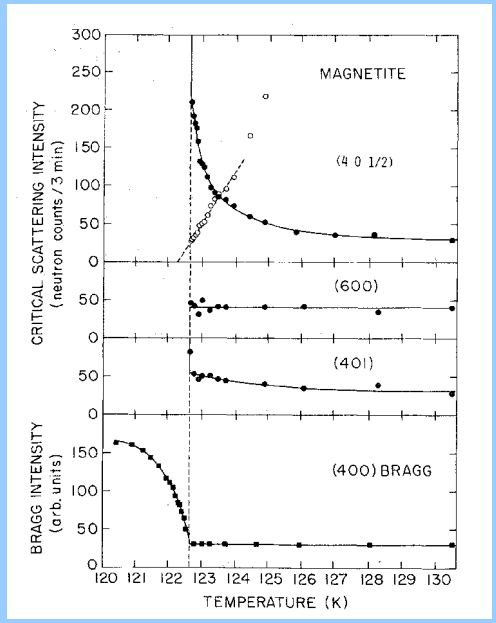
T.J. Moran and B. Luthi, Phys. Rev. **187**, 710 (1969)
H. Schwenk *et al.*, Eur. Phys. J. B **13**, 491 (2000)

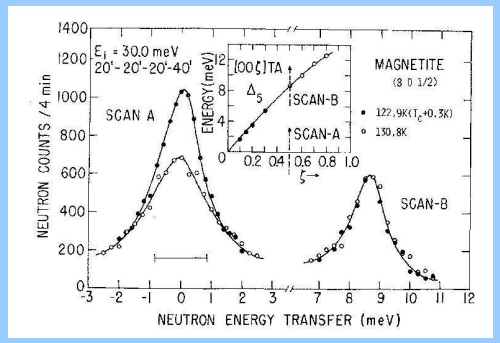
Y. Fujii *et al.*, PRB **11**, 2036 (1975)

k = (0,0,0) T_{2g}



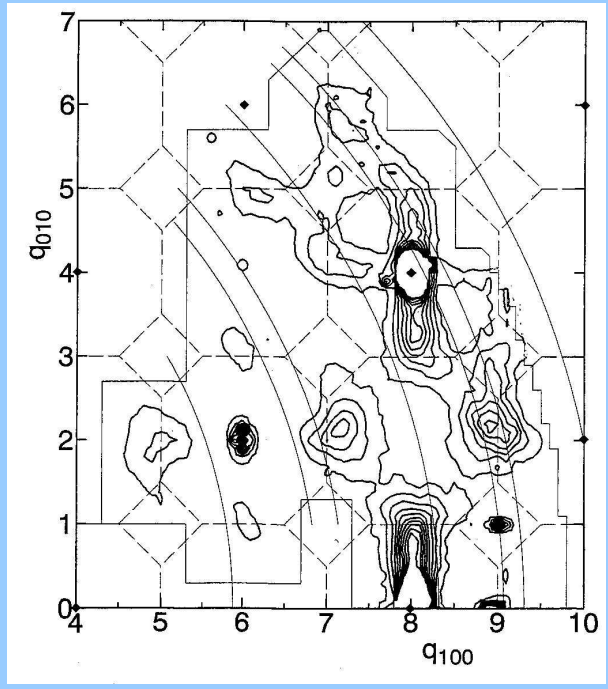
k = (0,0,1/2) Δ_5





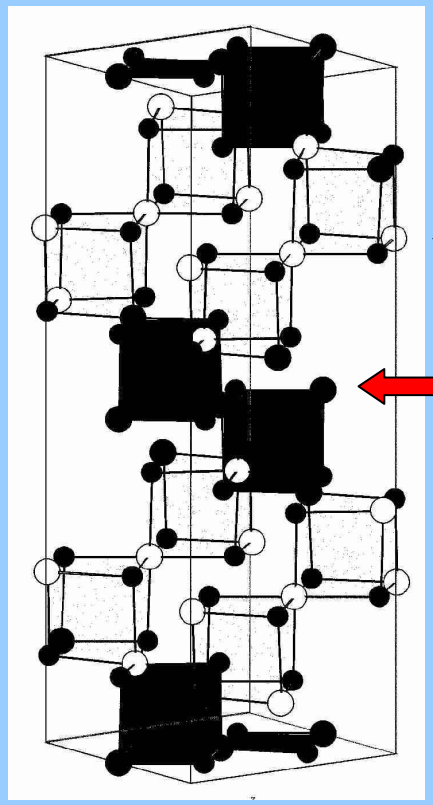
K. Siratori *et al.*, JPSJ **67**, 2818 (1998)

k = (0,0,1) X_5



Fe_3O_4 Charge ordering – neutron and X-ray diffraction

J.P. Wright, J.P. Attfield, and P.G. Radaelli, PRL **87**, 266401 (2001); PRB **66** 214422 (2002)



Fe(B4) +2.41

Fe(B2) +2.61

Fe(B1) +2.39

Fe(B3) +2.59

Orbital ordering – LDA+U

H.T. Jeng *et al.*, PRL **93**, 156403 (2004)
I. Leonov *et al.*, PRL **93**, 146404 (2004)

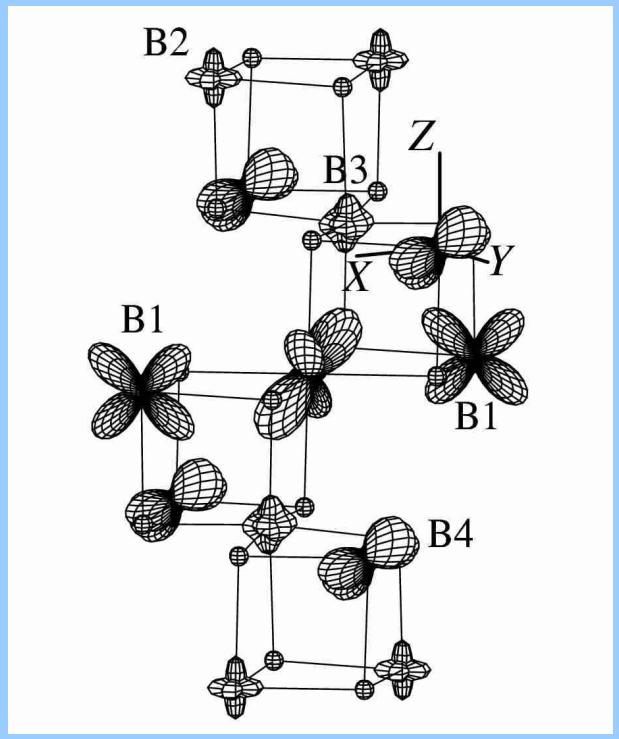


TABLE I. Total and *l*-projected charges, magnetic moments, and occupation of the most populated t_{2g} minority orbitals calculated for inequivalent Fe_B ions in the low-temperature $P2/c$ phase of Fe_3O_4 [28].

Fe_B ion	q	q_s	q_p	q_d	M (μ_B)	$t_{2g\downarrow}$ orbital	n
Fe_{B1}	6.04	0.17	0.19	5.69	3.50	$d_{xz} \mp d_{yz}$	0.76
Fe_{B2}	5.73	0.19	0.21	5.44	3.94		0.09
Fe_{B3}	5.91	0.19	0.21	5.51	3.81		0.09
Fe_{B4}	6.03	0.16	0.18	5.69	3.48	$d_{x^2-y^2}$	0.80

Fe_3O_4

Symmetry analysis of Verwey phase transition

Cubic **Fd-3m**, unit cell: a x a x a

Monoclinic **P2/c**, unit cell: $a/\sqrt{2}$ x $a/\sqrt{2}$ x $2a$

Searching irreducible representation (IR) of primary order parameter (OP)

Fd-3m => NO SINGLE IR => P2/c

Verwey phase transition does NOT have a (single) primary order parameter **!!!**

(Result of complex and sofisticated symmetry calculations.)

Symmetry reduction:

Fd-3m => Δ_5 => Pbcm (4)

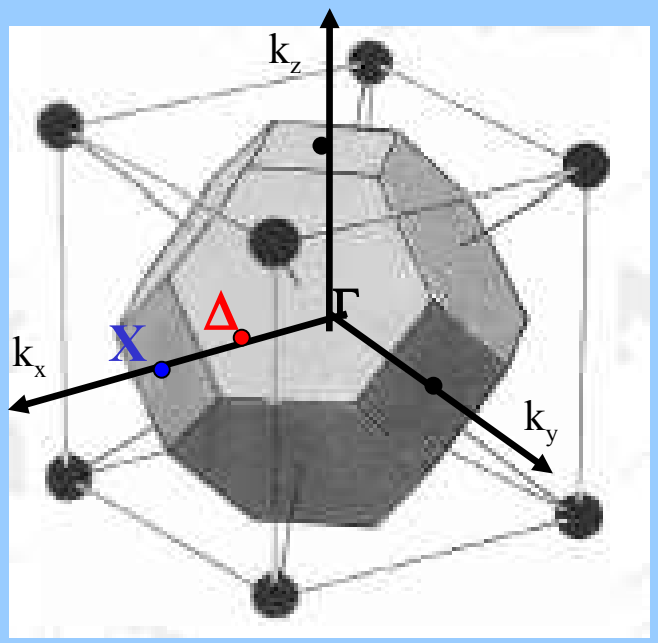
Fd-3m => X_3 => Pmna (2)

Common symmetry elements:

Pbcm (4) $\cap$ Pmna (2) = P2/c (4)

Verwey phase transition has TWO primary order parameters

Fd-3m => (Δ_5, X_3) => P2/c (4)



P.Piekarz, K.Parlinski, and A.M.Oles, Phys.Rev.Lett. **97**, 156402 (2006).

Fe_3O_4

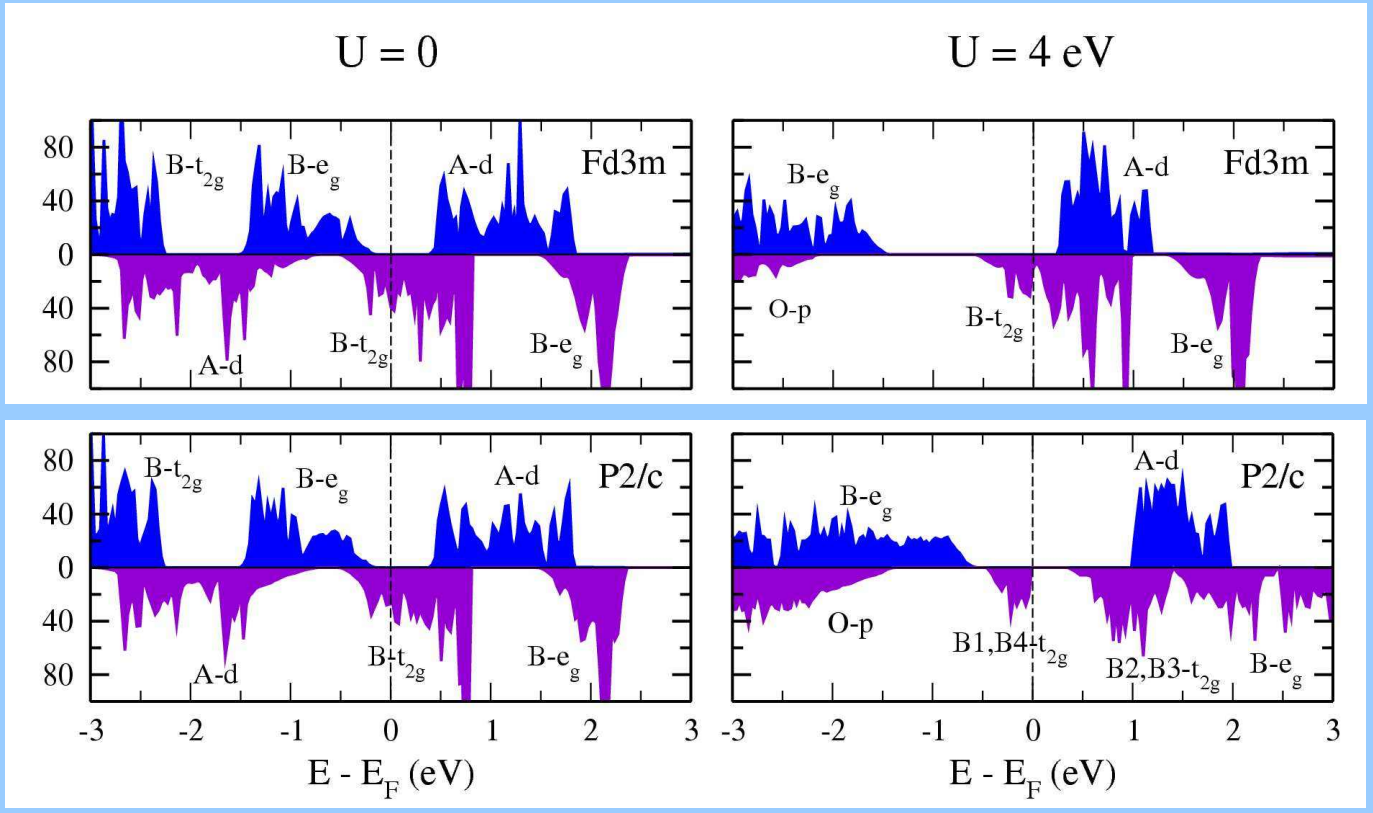
Primary and secondary order parameters

IR	Size	Subgroup	No	Dir
Γ_1^+ (A_{1g})	1	$Fd\bar{3}m$	227	(a)
Γ_3^+ (E_g)	1	$I4_1/amd$	141	$(b,0)$
Γ_4^+ (T_{1g})	1	$C2/m$	12	$(c,c,0)$
Γ_5^+ (T_{2g})	1	Imma	74	$(d,0,0)$
Γ_5^+ (T_{2g})	1	$C2/m$	12	$(d,e,-e)$
X_1	2	Pmma	51	$(f,0,0,0,0,0)$
X_3	2	Pmna	53	$(g,0,0,0,0,0)$
Δ_2	4	Pcca	54	$(0,0,0,0,h,-\frac{1}{\mu}h)$
Δ_4	4	Pcca	54	$(0,0,0,0,p,\mu p)$
Δ_5	4	Pbcm	57	$(0,0,0,0,0,0,0,0,q,-\mu q,-\mu q,-q)$

	IR's	Subgroups	No's
1.	X_3,Δ_5	Pmna ∩ Pbcm = P2/c	(53, 57) = 13
2.	X_3,Δ_2	Pmna ∩ Pcca = P2/c	(53, 54) = 13
3.	X_3,Δ_4	Pmna ∩ Pcca = P2/c	(53, 54) = 13
4.	X_3,Δ_5,Γ_5^+	Pmna ∩ Pbcm ∩ C2/m = P2/c	(53, 57, 12) = 13
5.	X_3,Δ_2,Γ_5^+	Pmna ∩ Pcca ∩ C2/m = P2/c	(53, 54, 12) = 13
6.	X_3,Δ_4,Γ_5^+	Pmna ∩ Pcca ∩ C2/m = P2/c	(53, 54, 12) = 13
7.	X_3,Δ_5,Δ_2	Pmna ∩ Pbcm ∩ Pcca = P2/c	(53, 57, 54) = 13
8.	X_3,Δ_5,Δ_4	Pmna ∩ Pbcm ∩ Pcca = P2/c	(53, 57, 54) = 13
9.	X_3,Δ_2,Δ_4	Pmna ∩ Pcca ∩ Pcca = P2/c	(53, 54, 54) = 13
10.	X_3,Δ_5,Δ_2,Γ_5^+	Pmna ∩ Pbcm ∩ Pcca ∩ C2/m = P2/c	(53, 57, 54, 12) = 13
11.	X_3,Δ_5,Δ_4,Γ_5^+	Pmna ∩ Pbcm ∩ Pcca ∩ C2/m = P2/c	(53, 57, 54, 12) = 13
12.	X_3,Δ_2,Δ_4,Γ_5^+	Pmna ∩ Pcca ∩ Pcca ∩ C2/m = P2/c	(53, 54, 54, 12) = 13
13.	X_3,Δ_5,Δ_2,Δ_4	Pmna ∩ Pbcm ∩ Pcca ∩ Pcca = P2/c	(53, 57, 54, 54) = 13
14.	X_3,Δ_5,Δ_2,Δ_4,Γ_5^+	Pmna ∩ Pbcm ∩ Pcca ∩ Pcca ∩ C2/m = P2/c	(53, 57, 54, 54, 12) = 13

Fe_3O_4 Electronic structure GGA+U

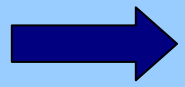
Supercell 56 atoms 24 Fe: $3d^6 4s^2$ 32 O: $2s^2 2p^2$
Projector Augmented Wave GGA+U: U = 4 eV J = 0.8 eV
k-point MP grids: 6x6x6 (Fd3m), 6x6x2 (P2/c), E_{cut}= 520 eV

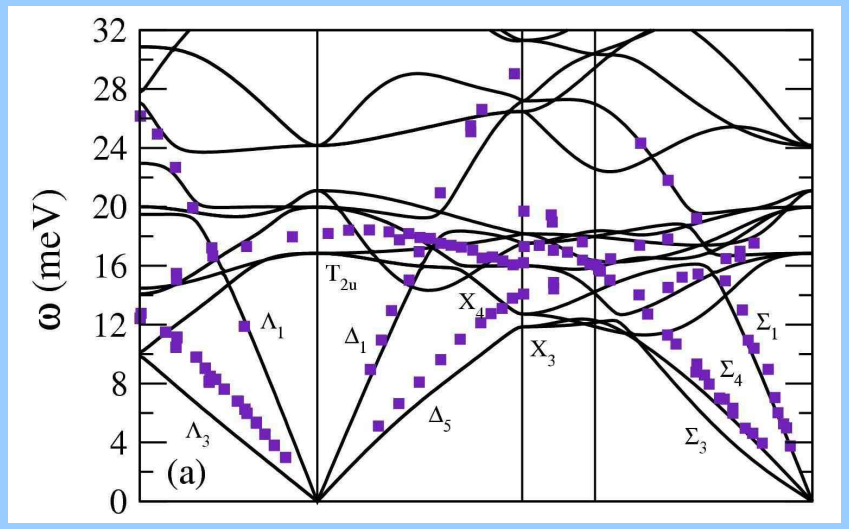


Fe_3O_4

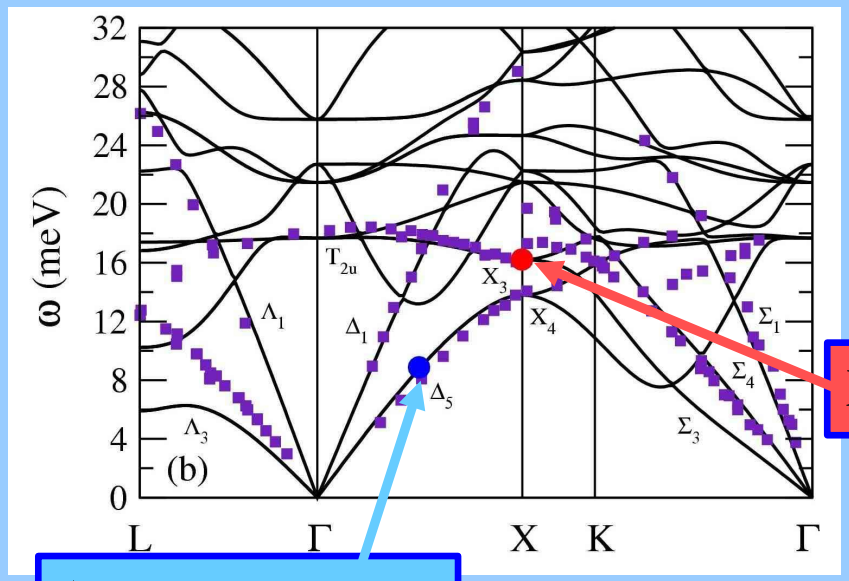
Phonon dispersion curves

PAW GGA:
U = J = 0





PAW GGA+U:
U = 4 eV J=0.8 eV



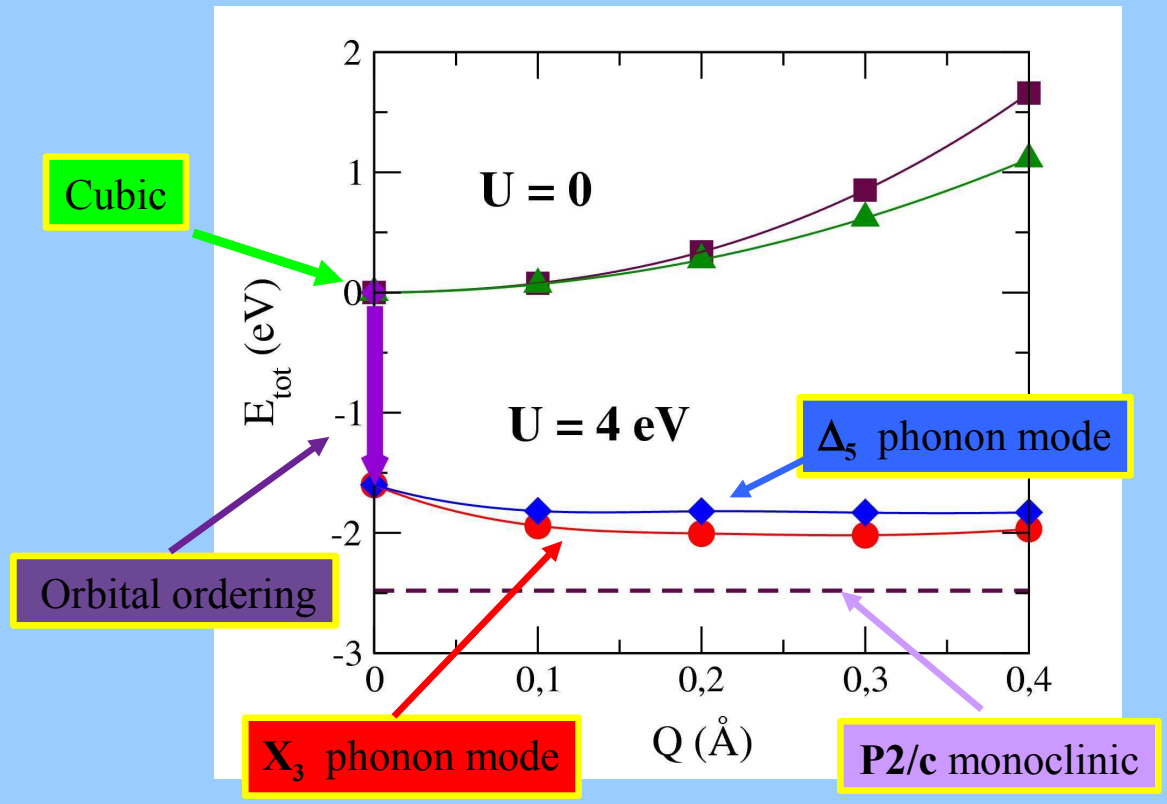
No soft phonon mode

X_3 phonon mode

Δ_5 phonon mode

Experimental points: E.J.Samuelsen and O.Steinsvoll, Phys.Status Sol. B61, 615 (1974).

Fe_3O_4 Ground state energy E_{tot} with phonon distorsions



Distorsions with symmetries of X_3 and Δ_5 **decrease** the ground state energy E_{tot}

Further decrease of E_{tot} is possible by fixing the X_3 and Δ_5 displacements, and permitting distorsions defined by the **secondary order parameters**:

$$A_{1g}\ \ E_g\ \ T_{1g}\ \ T_{2g}(C_{44})\ \ X_1\ \ \Delta_2\ \ \Delta_4$$

Electron-phonon coupling

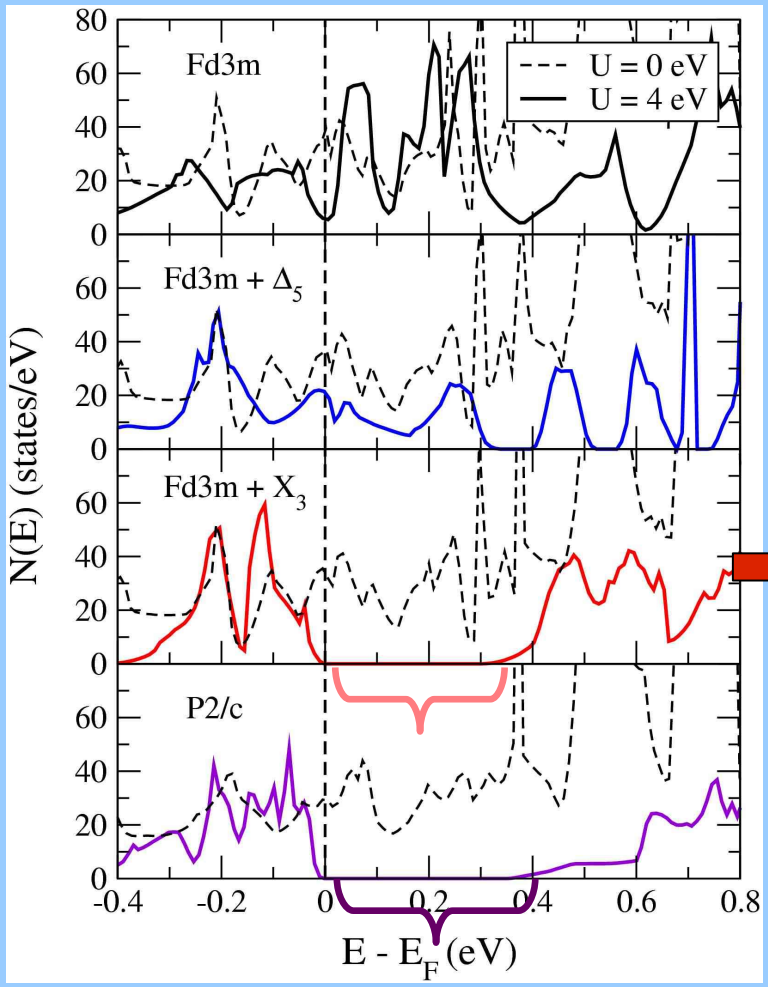
Fe_3O_4

Fd3m
no gap

Fd3m + Δ_5
no gap

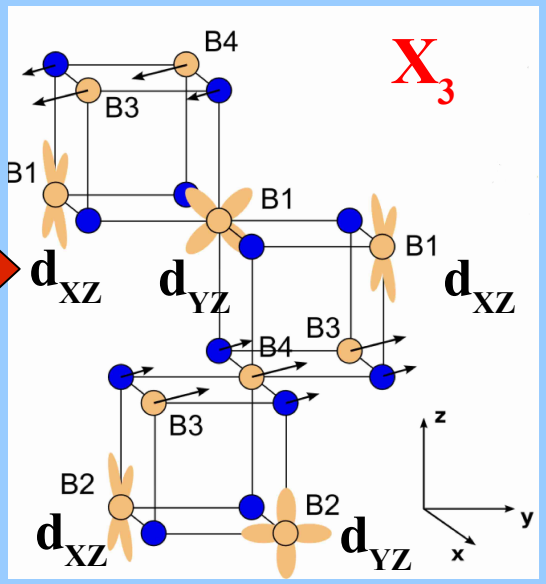
Fd3m + X_3
gap

P2/c
gap



GGA+U
U = 4 eV, J=0.8 eV

Orbital ordering

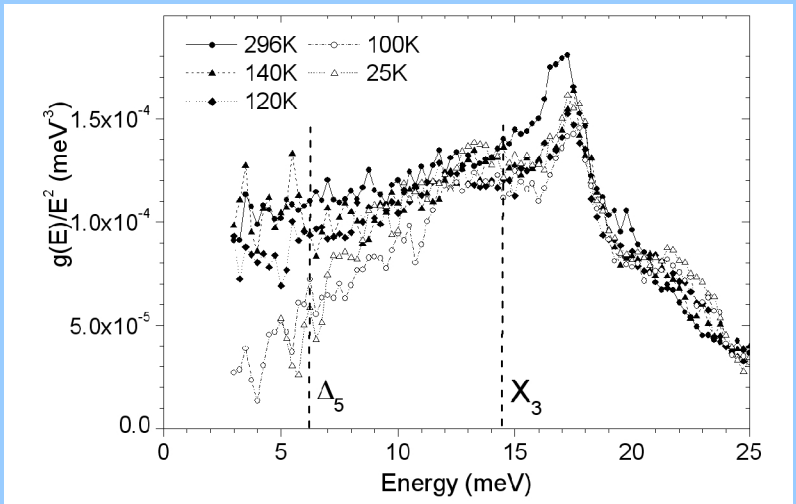


X_3 phonon mode in cubic crystal induces an electronic gap and orbital ordering

Fe_3O_4

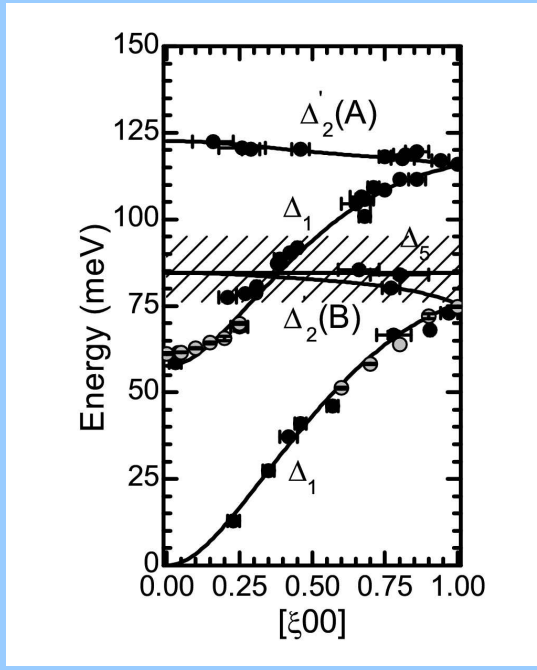
Nuclear inelastic scattering

B. Handke *et al.*, PRB **71**, 144301 (2005)
A. Kozłowski *et al.*, Acta Phys. Pol. A **111**, 537 (2007)



Spin-phonon coupling

R. McQueeney *et al.*, arXiv: 0707.2253



Future plans: IXS (ESRF)

M. Hoesch, M. Krisch, ...

Conclusions

(i) Two primary order parameters:

X_3 and Δ_5

(ii) Local electron interactions induce the charge-orbital ordering

The driving force: cooperation (synergy) of electron interactions with phonons