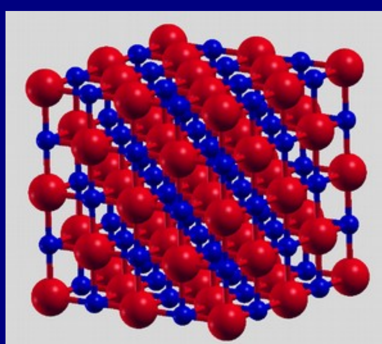
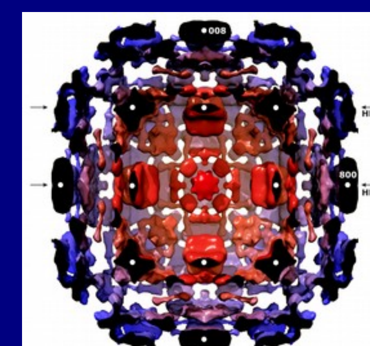
The Henryk Niewodniczański
Institute of Nuclear Physics
Polish Academy of Sciences

Ab initio studies of lattice dynamics in strongly correlated systems





Przemysław Piekarz

Department of Computational Materials Science
Institute of Nuclear Physics, Kraków

Collaboration

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Overview

- ***Ab initio* methods**

1) Hartree-Fock
2) DFT (self-interaction)
3) Hybrid potentials
4) LDA+U
5) Direct method

- **Examples**

1) Iron oxides
2) Rare-earths: EuO, Nd

- **Conclusions**

Ab initio methods

$$H\psi = E\psi$$

Ab initio methods

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Hartree-Fock

Ab initio methods

$$H\psi = E\psi$$

Hartree-Fock

Density functional theory (DFT)

$$E[n] = E_K[n] + E_Z[n] + E_H[n] + E_{xc}[n] = \min$$

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{KS}\right)\psi_i = \epsilon_i \psi_i$$

Ab initio methods

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Hartree-Fock

Density functional theory (DFT)

$$E[n] = E_K[n] + E_Z[n] + E_H[n] + E_{xc}[n] = \min$$

LDA
GGA

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{KS}\right)\psi_i = \epsilon_i\psi_i$$

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Hartree-Fock

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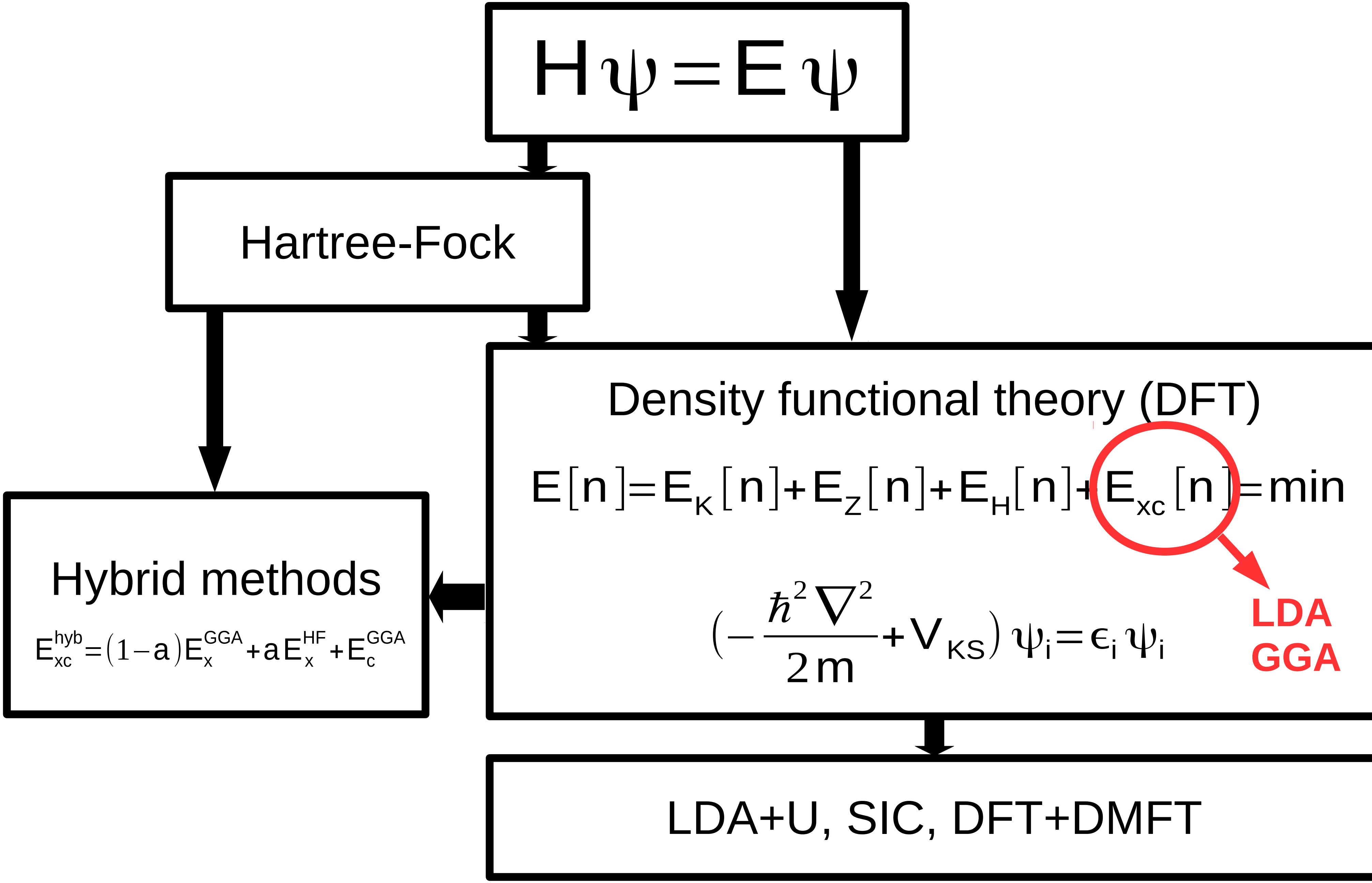
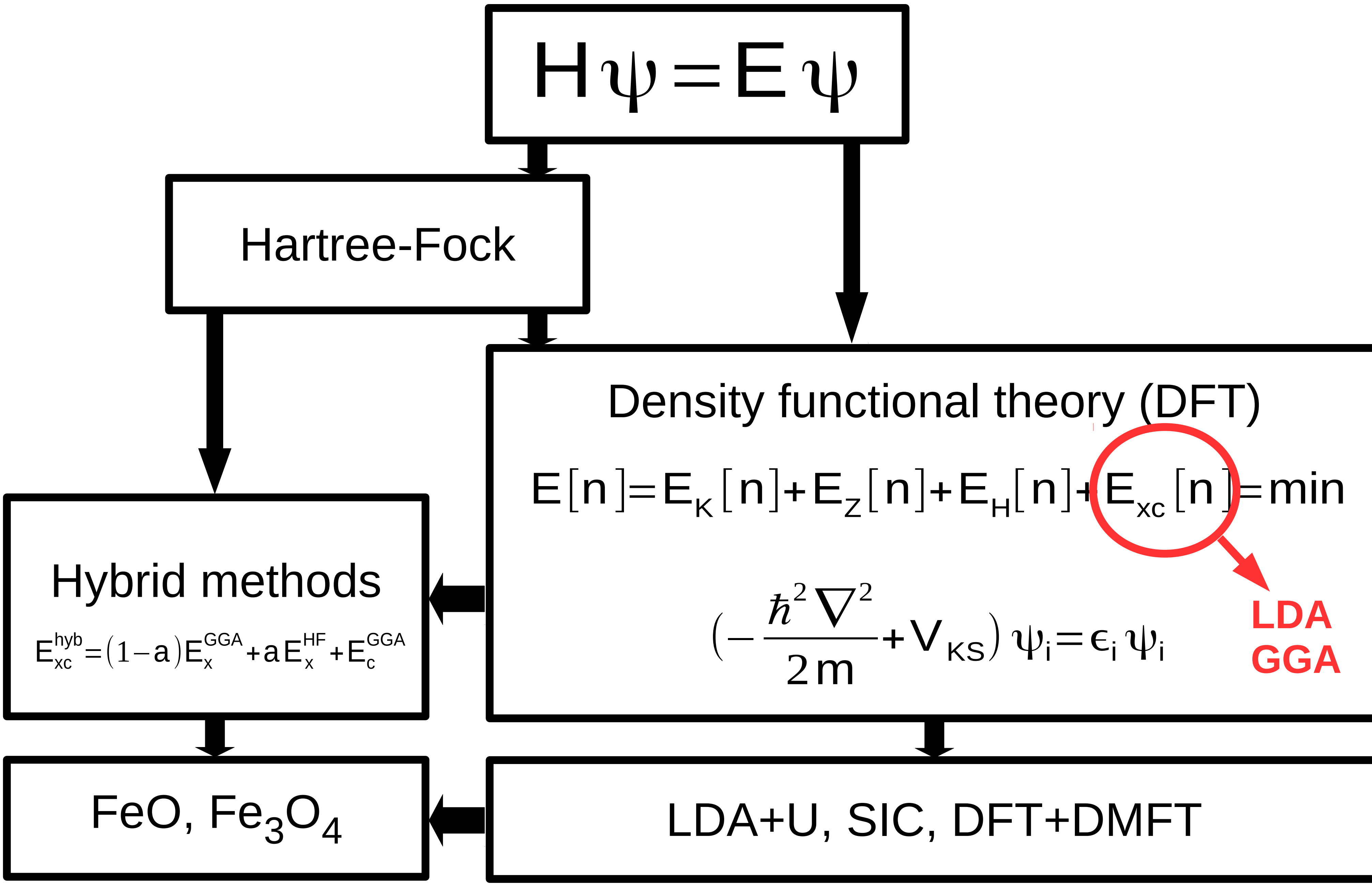
LDA
GGA

LDA+U, SIC, DFT+DMFT

Ab initio methods



Ab initio methods



Electron self-interaction

Hartree-Fock $E = E_K + E_Z + E_H + E_x$

$$E_H = \frac{1}{2} \iint dr\, dr' \frac{n(r)\, n(r')}{|r - r'|} \qquad n(r) = e \sum_i |\psi_i(r)|^2$$

$$E_x = -\frac{e^2}{2} \sum_{i,j,\sigma} \iint dr\, dr' \frac{\overline{\psi_i^\sigma}(r)\, \overline{\psi_j^\sigma}(r')\, \psi_i^\sigma(r')\, \psi_j^\sigma(r)}{|r - r'|}$$

hydrogen atom (i =j=1)

$E_H \neq 0 \quad E_x = -E_H \quad \Rightarrow \quad E_H + E_x = 0$ (no self-interaction)

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DFT $E = E_K + E_Z + E_H + E_{xc}$

hydrogen atom

$E_H \neq 0 \quad E_{xc} \neq -E_H \quad \Rightarrow \quad E_H + E_{xc} \neq 0$ (self-interaction!)

LDA+U (GGA+U)

V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991)

$$E_{tot} = E_{DFT} + E_U - E_{dc}$$

$$E_U = U \sum_{i,\alpha,\beta,\sigma} n_{i,\alpha,\sigma} n_{i,\beta,-\sigma} + (U - J) \sum_{i,\alpha \neq \beta,\sigma} n_{i,\alpha,\sigma} n_{i,\beta,\sigma}$$

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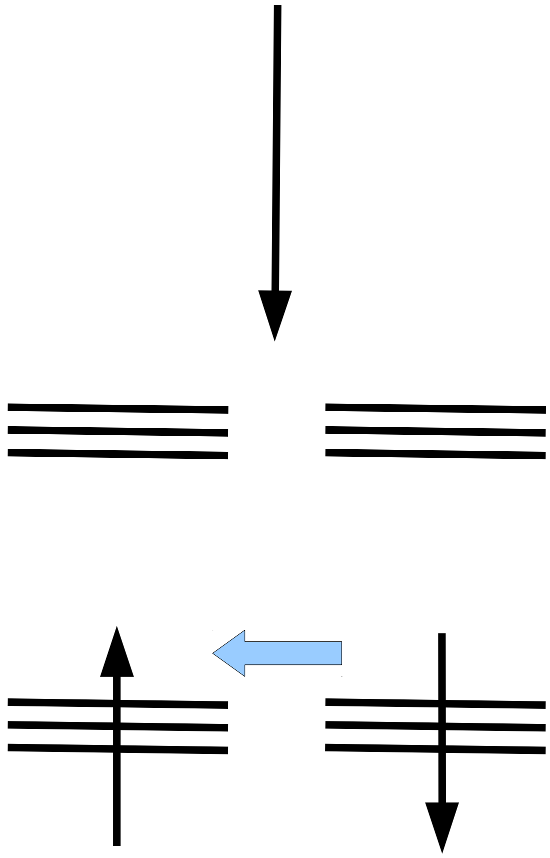

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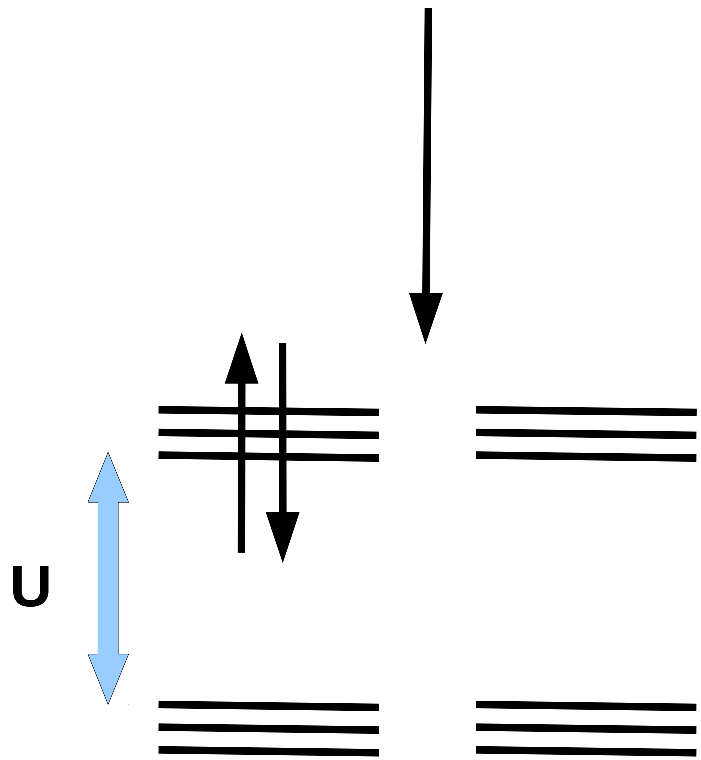

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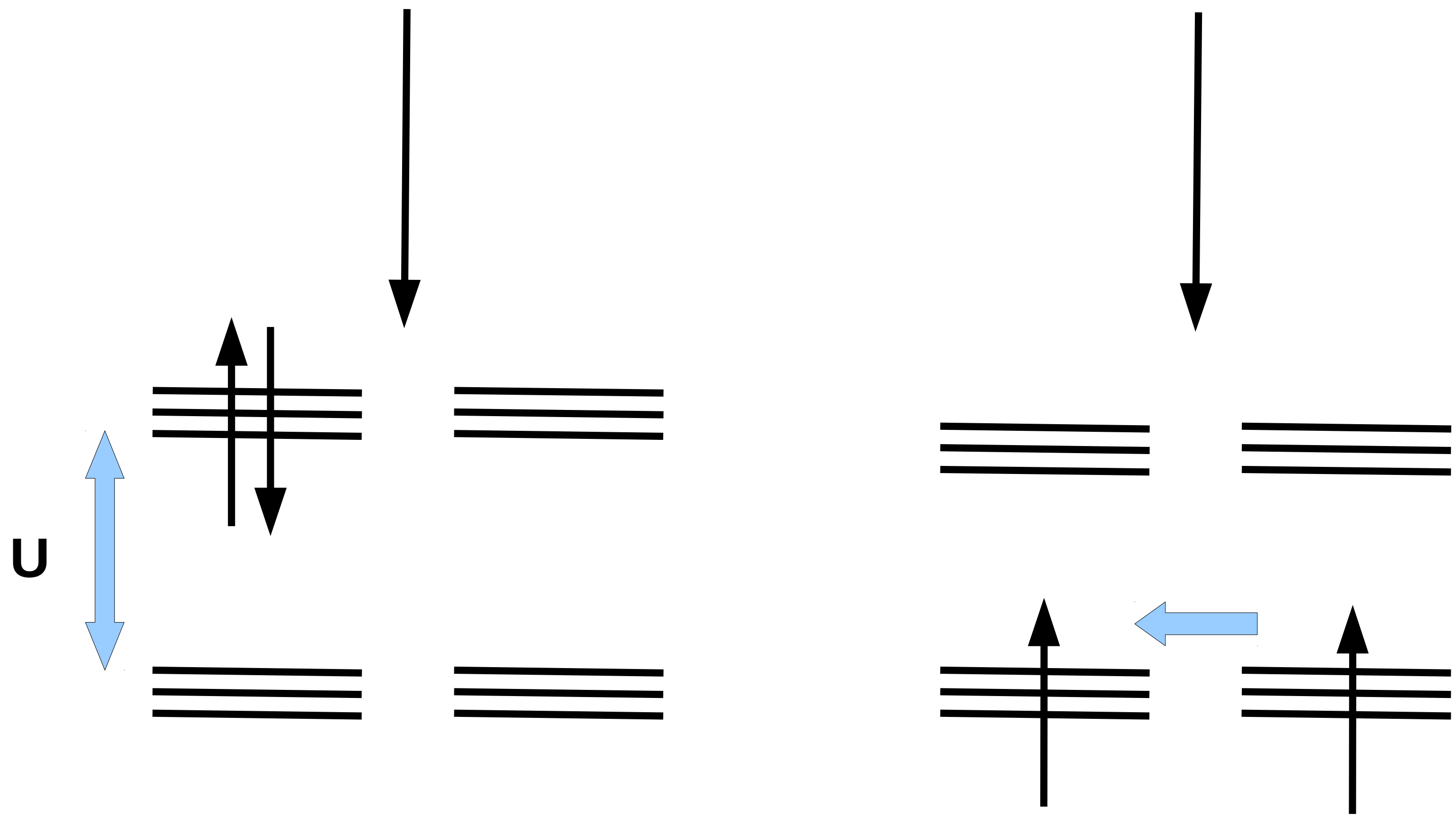

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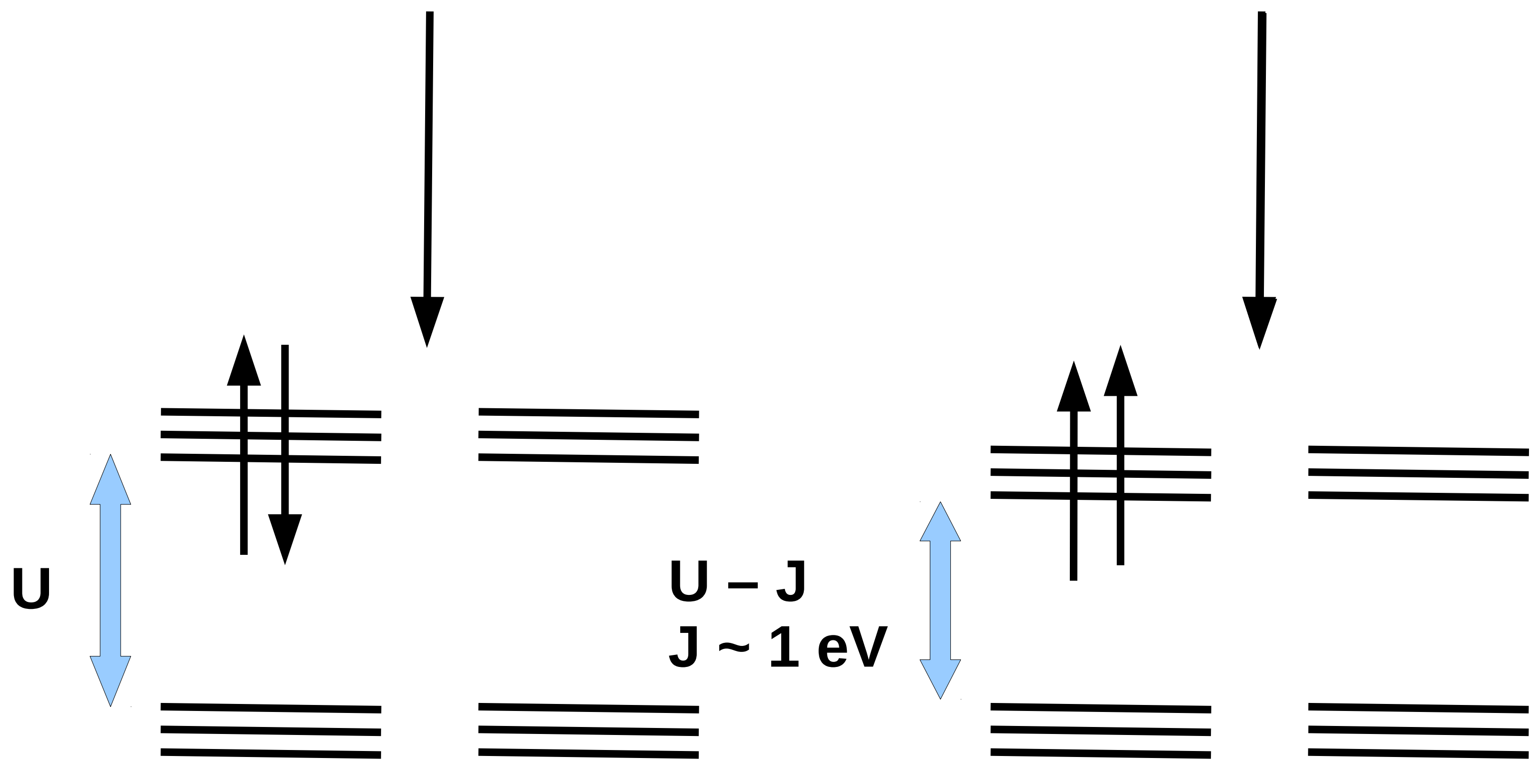


Lattice dynamics – direct method

K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett 78, 4063 (1997)

- crystal structure optimization (DFT, VASP)

  $E_{tot} = \min \quad F_i(\mu) = 0$

- Hellmann-Feynman forces

  $F_i(\mu) = - dE_{tot}/du_i(\mu)$

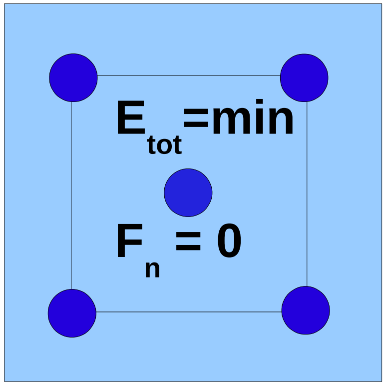
- force constants matrix (Phonon)

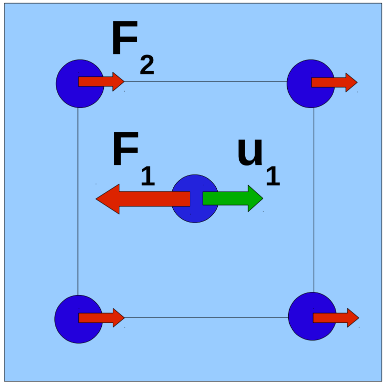
  $F_i(\mu) = - \Sigma\, \Phi_{ij}(\mu,\nu) u_j(\nu)$

- dynamical matrix $\Phi(\mu,\nu) \Rightarrow D(k,\mu,\nu)$

- dispersion curves, polarization vectors, DOS

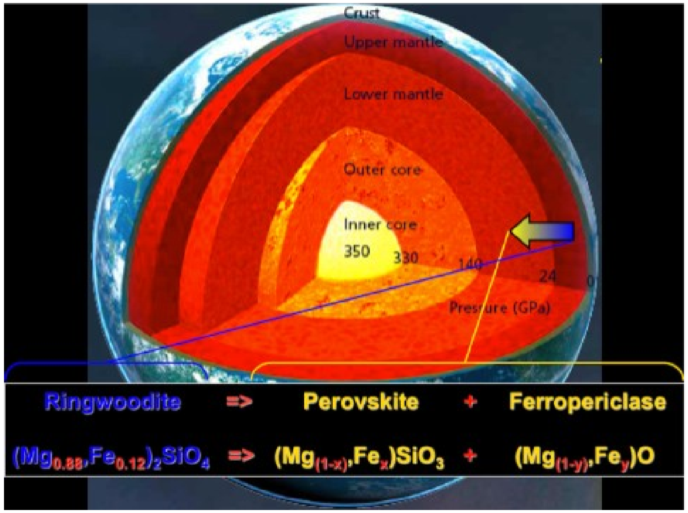
  $D(k,\mu,\nu) e(k,j) = \omega^2(k,j) e(k,j)$



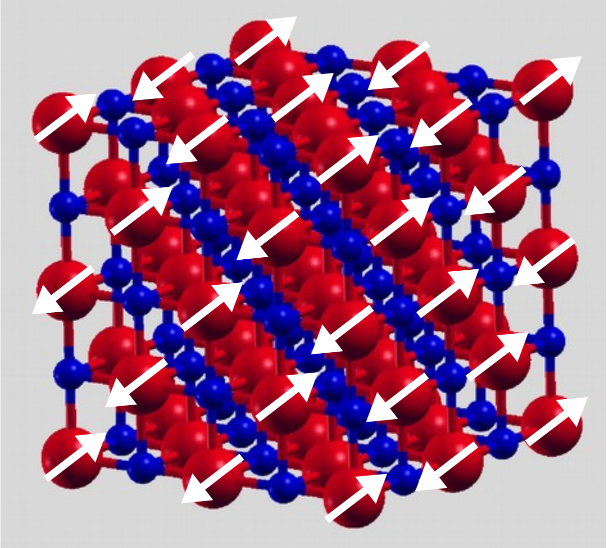


LO-TO splitting =>
$$D^{LO}_{i\alpha,j\beta} = D^{TO}_{i\alpha,j\beta} + \frac{4\pi e^2}{\Omega\sqrt{M_i M_j}} \frac{(\mathbf{q}\cdot\mathbf{Z}^*(i))_\alpha (\mathbf{q}\cdot\mathbf{Z}^*(j))_\beta}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}$$

FeO wüstite



$Fe_{1-x}O$ x = 0.05-0.15



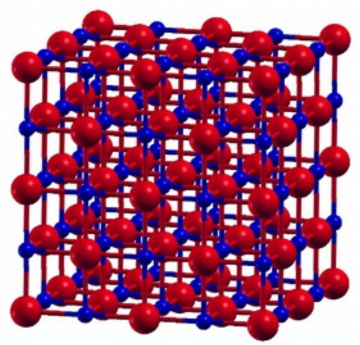
T_N = 198 K
AF order: alternating FM (111) planes
magnetic moments parallel to [111]
W. L. Roth, Phys. Rev. 110, 1333 (1958)

T > T_N => NaCl (Fm-3m)
T < T_N => rhomboedral distortion (R-3m)
1% elongation along [111]

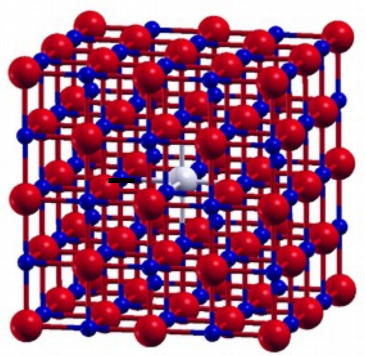
Band structure – effect of Fe vacancies

$Fe_{1-x}O$

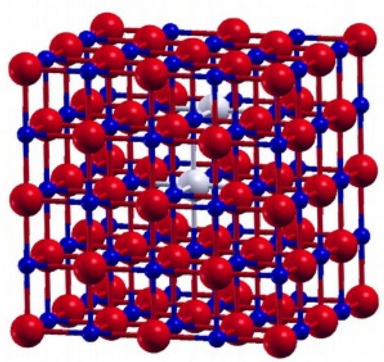
64 atoms
32 Fe + 32 O
x = 0

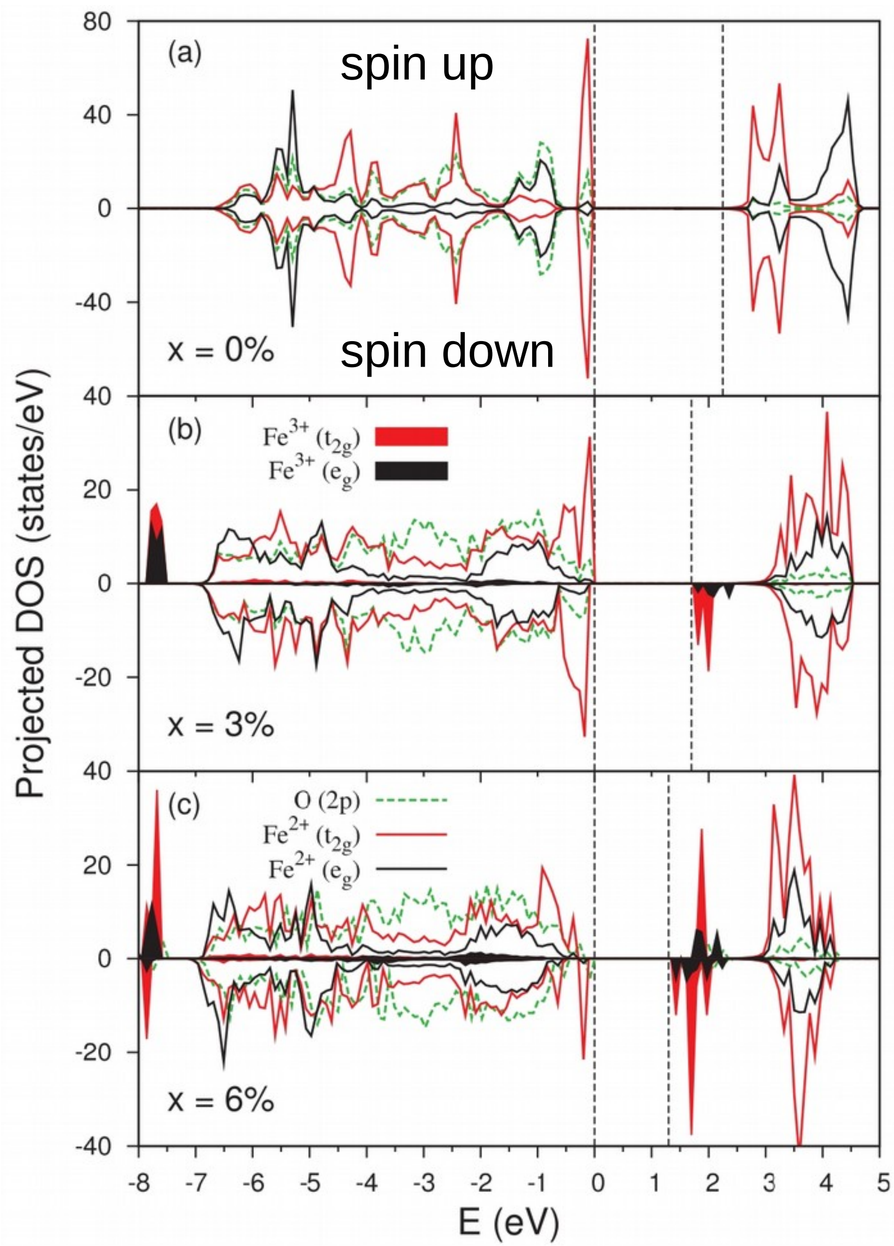


63 atoms 1 V_{Fe} $2Fe^{3+}$
31 Fe + 32 O
x ~ 3%



62 atoms 2 V_{Fe} $4Fe^{3+}$
30 Fe + 32 O
x ~ 6%

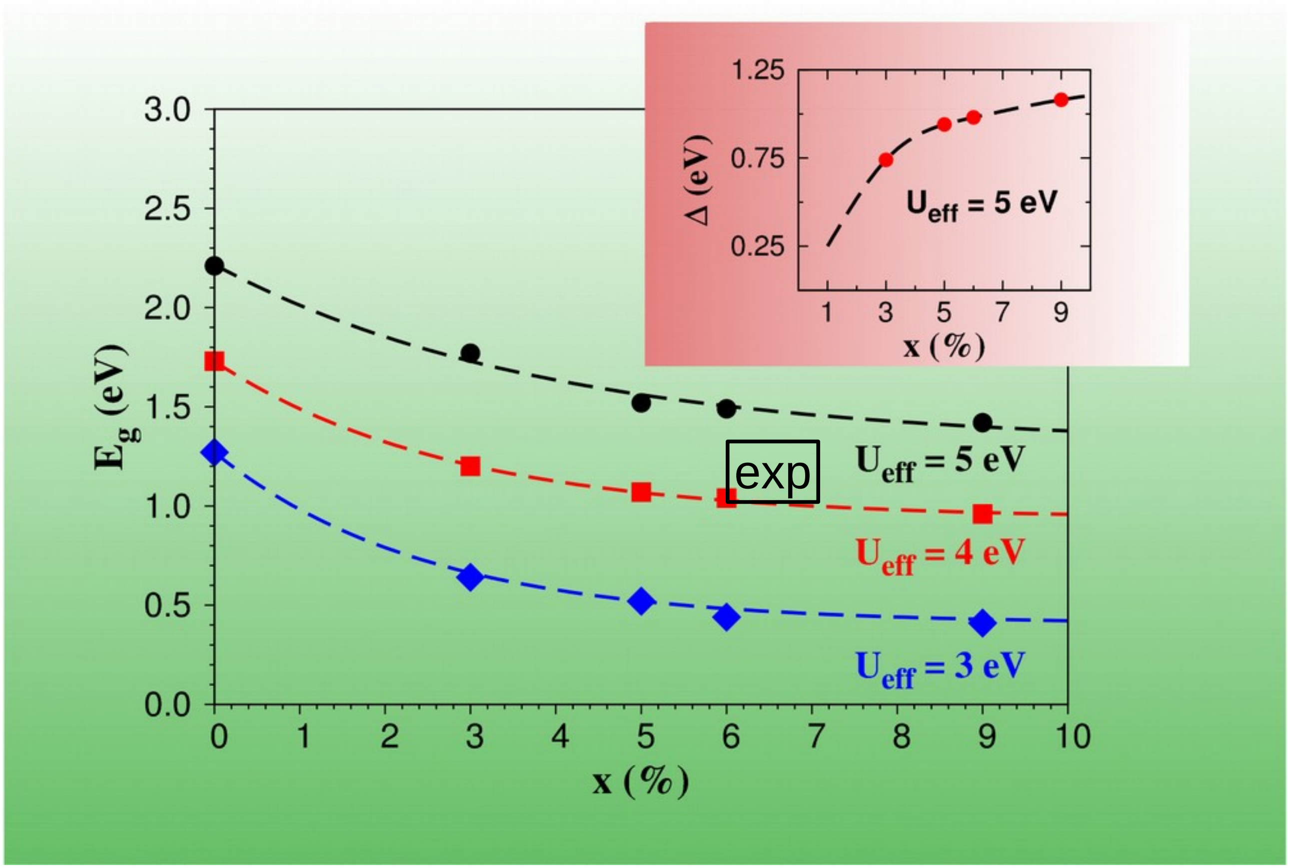




Band gap $E_g(x)$

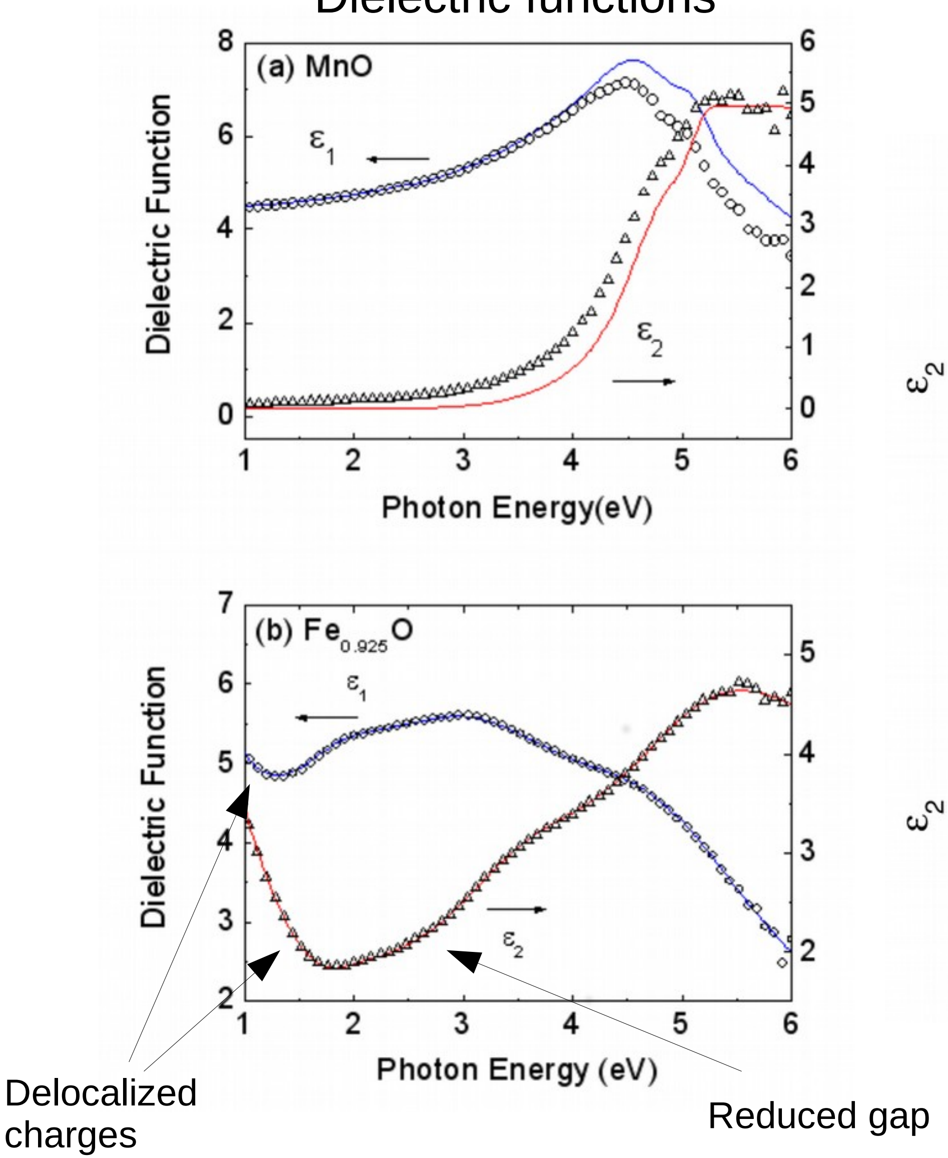
The gap is reduced due to Fe^{3+} states

$U_{eff} = U – J \sim 2$ eV
insulator => metal



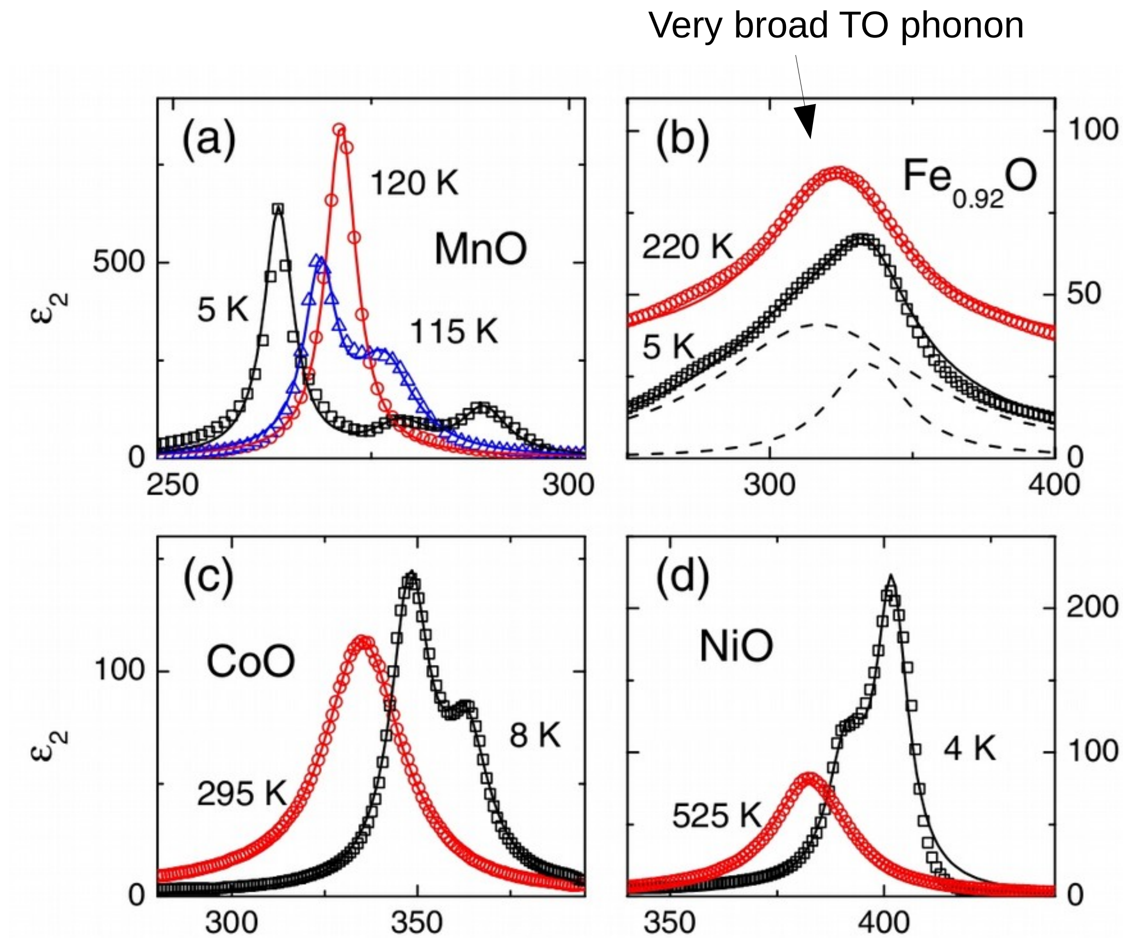
Peculiar dielectric properties

Dielectric functions



J.-W. Park, S. Kim, S.-H. Choi, and H. Lee, New Physics: Sae Mulli 63, 818 (2013)

Infrared TO phonon mode



C. Kant, M. Schmidt, Z. Wang, F. Mayr, V. Tsurkan, J. Deisenhofer, and A. Loidl, Phys. Rev. Lett. 108, 177203 (2012)

Dielectric functions

$$\vec{D}(\vec{x},\omega) = \varepsilon(\omega)\vec{E}(\vec{x},\omega) = \varepsilon_0[1+\chi(\omega)]\vec{E}(\vec{x},\omega)$$

Dielectric properties are studied within the independent electron approach taking into account only direct transitions between the occupied and unoccupied states. Energy dependent complex dielectric tensor:

$$\varepsilon_{\mu\nu}(\omega) = \varepsilon^{(1)}_{\mu\nu}(\omega) + i\varepsilon^{(2)}_{\mu\nu}(\omega)$$

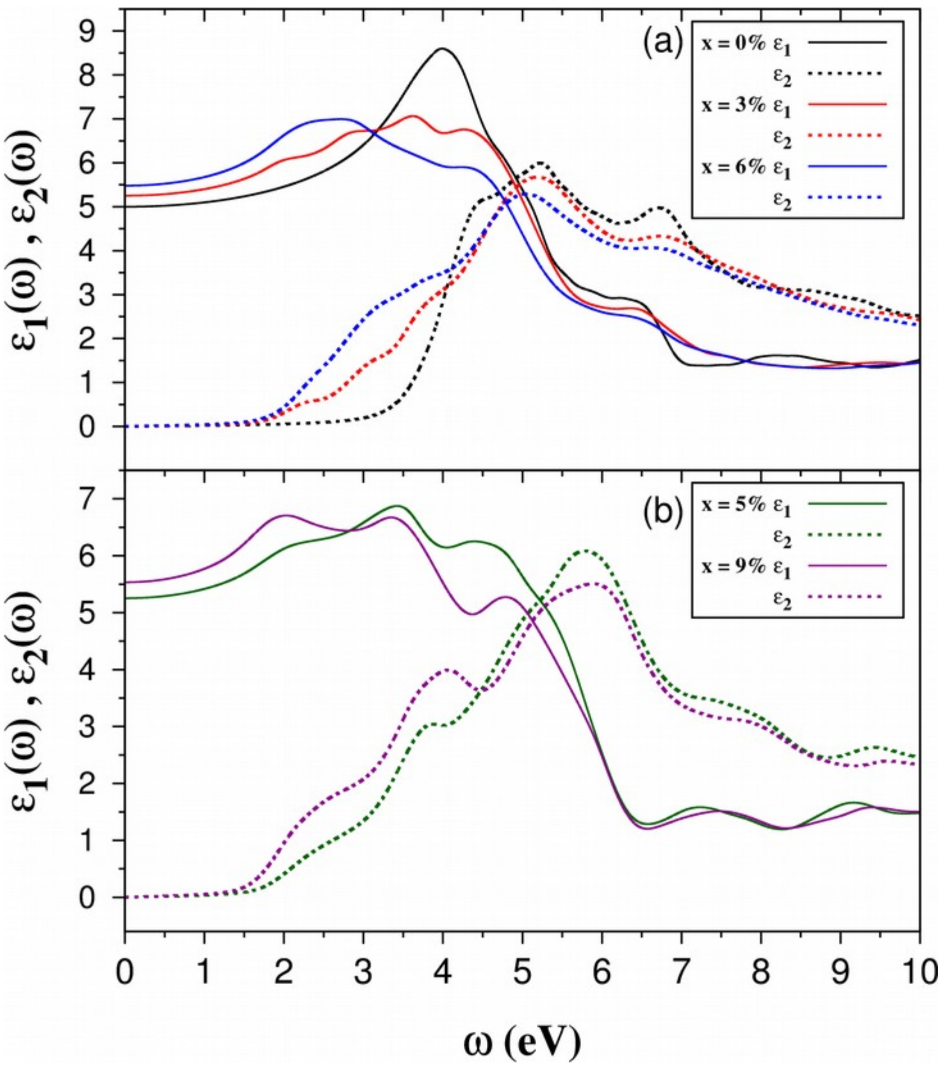
the imaginary part is given by

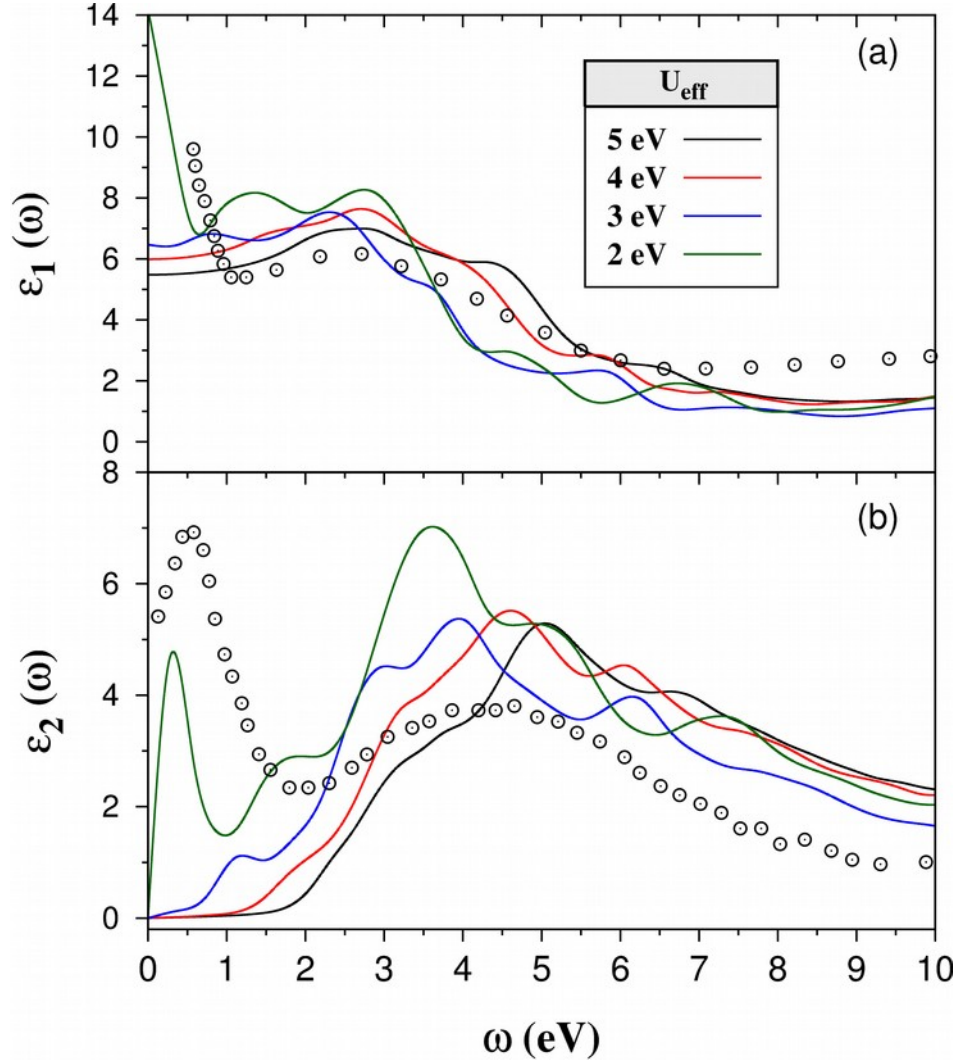
$$\varepsilon^{(2)}_{\mu\nu}(\omega) = \frac{4\pi^2 e^2}{V}\lim_{q\to 0}\frac{1}{q^2}\sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}}\delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$
$$\times\langle u_{c\mathbf{k}+\mathbf{e}_\mu q}|u_{v\mathbf{k}}\rangle\langle u_{c\mathbf{k}+\mathbf{e}_\nu q}|u_{v\mathbf{k}}\rangle^*$$

the real part is obtained by the Kramers-Kronig transformation

$$\varepsilon^{(1)}_{\mu\nu}(\omega) = 1 + \frac{2}{\pi}\mathcal{P}\int_0^\infty d\omega' \frac{\varepsilon^{(2)}_{\mu\nu}(\omega')\,\omega'}{\omega'^2 - \omega^2 + i\eta}$$

Dielectric functions





Optical properties

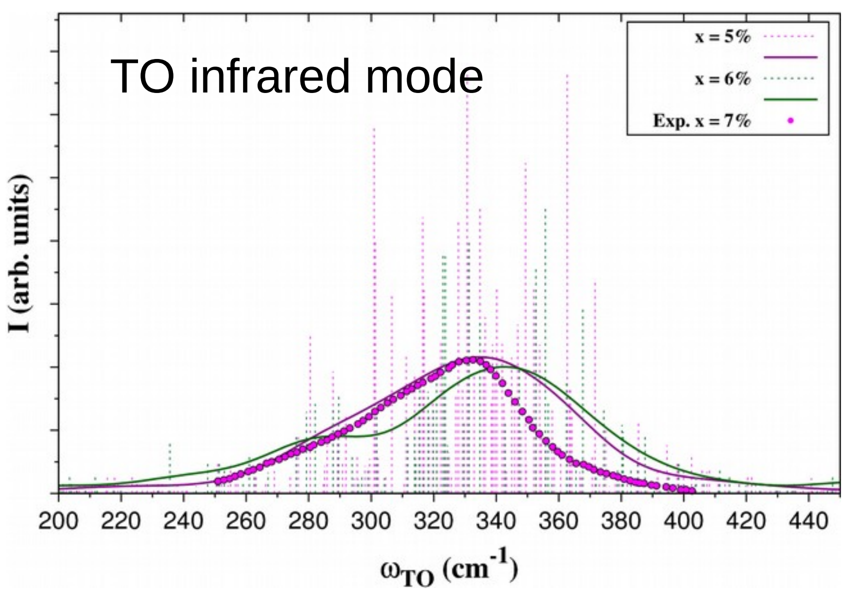
Reflectivity

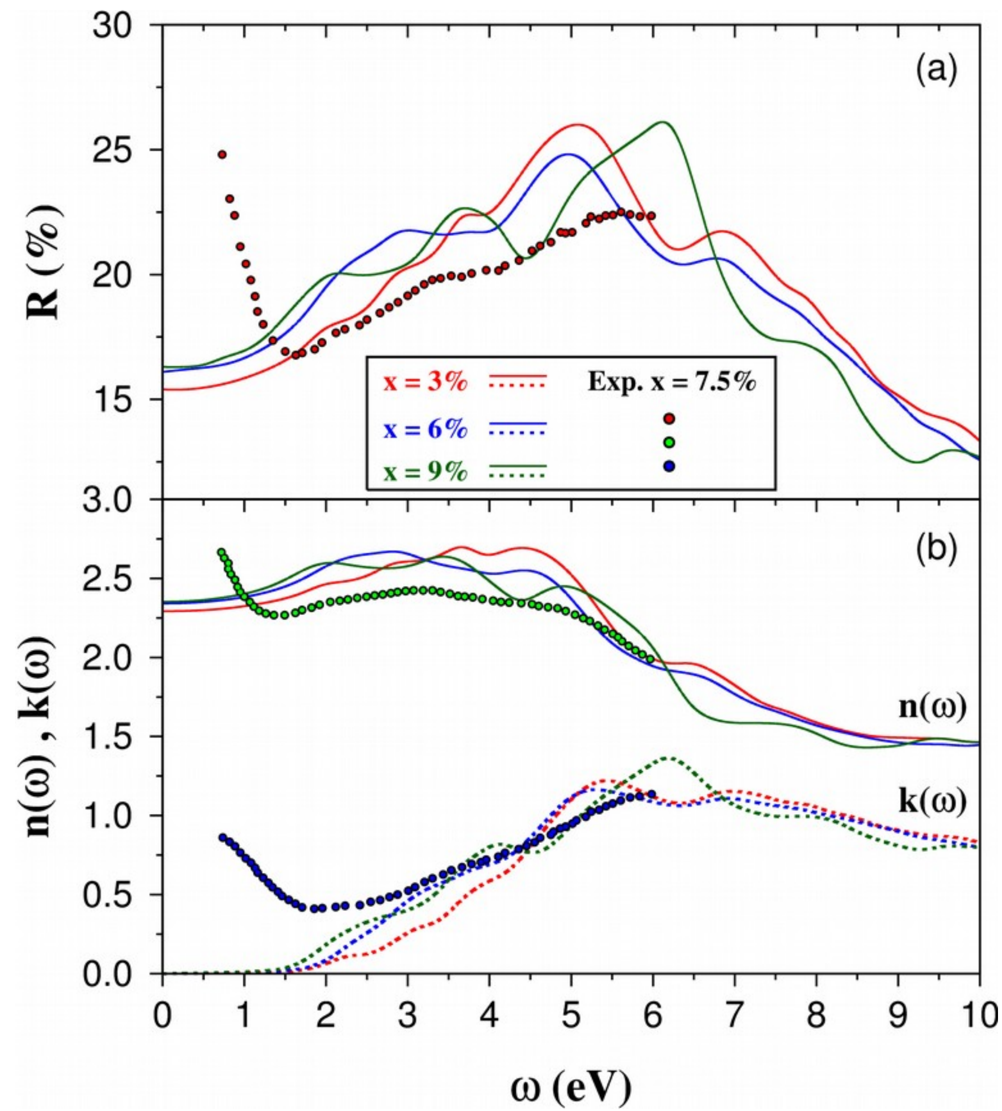
$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1)}{\sqrt{\varepsilon(\omega)} + 1)} \right|^2 = \frac{[n(\omega) - 1]^2 + k^2(\omega)}{[n(\omega) + 1]^2 + k^2(\omega)}$$

Refractive and extinction coefficients

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \varepsilon_1(\omega)}{2}}$$

$$k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \varepsilon_1(\omega)}{2}}$$

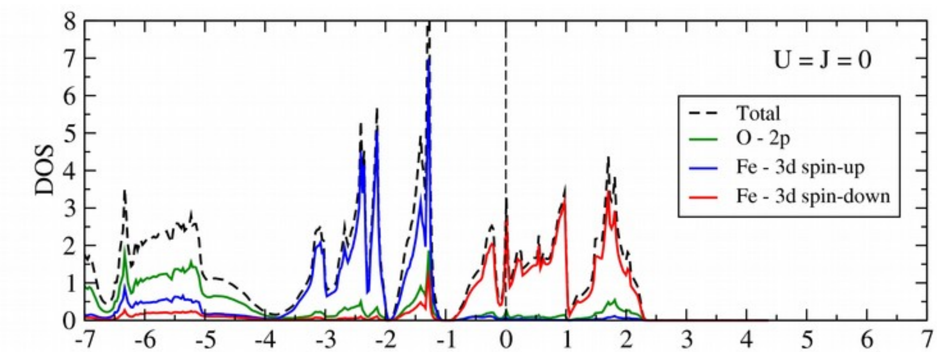


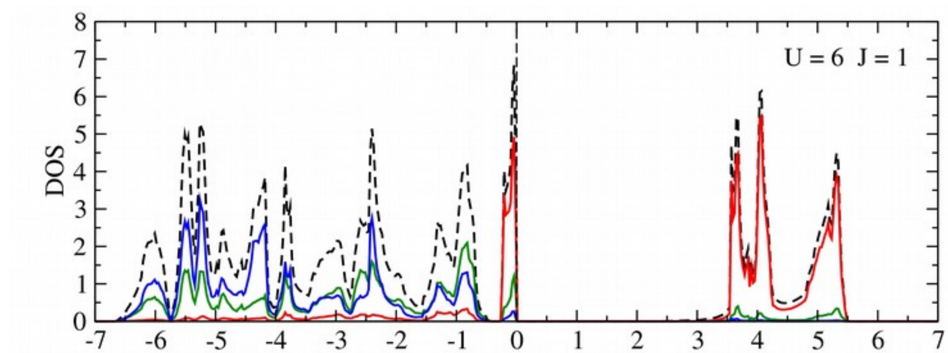


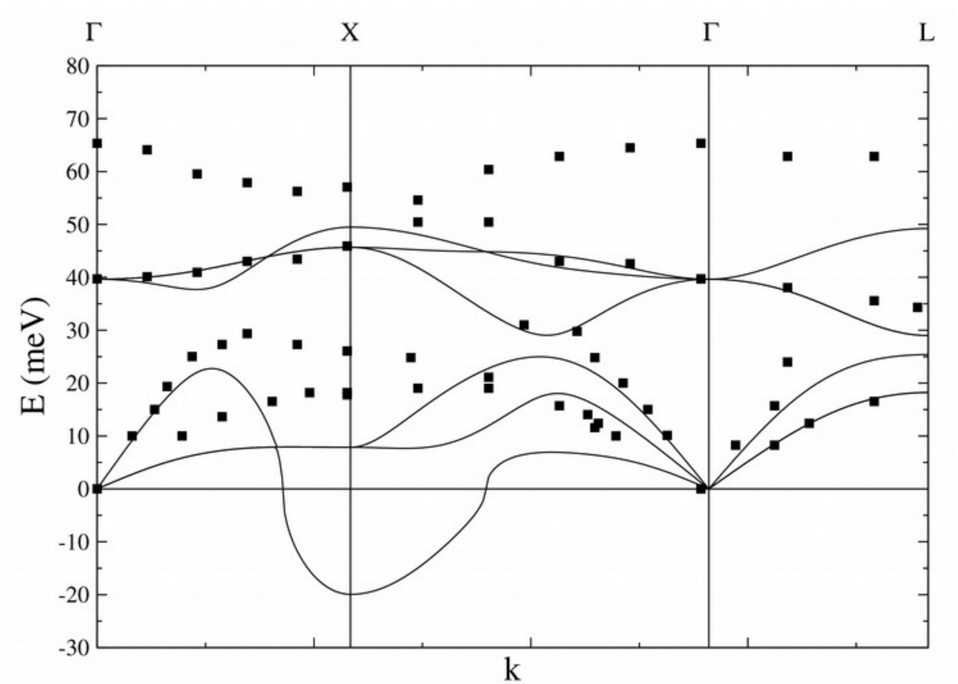
Phonon dispersion curves

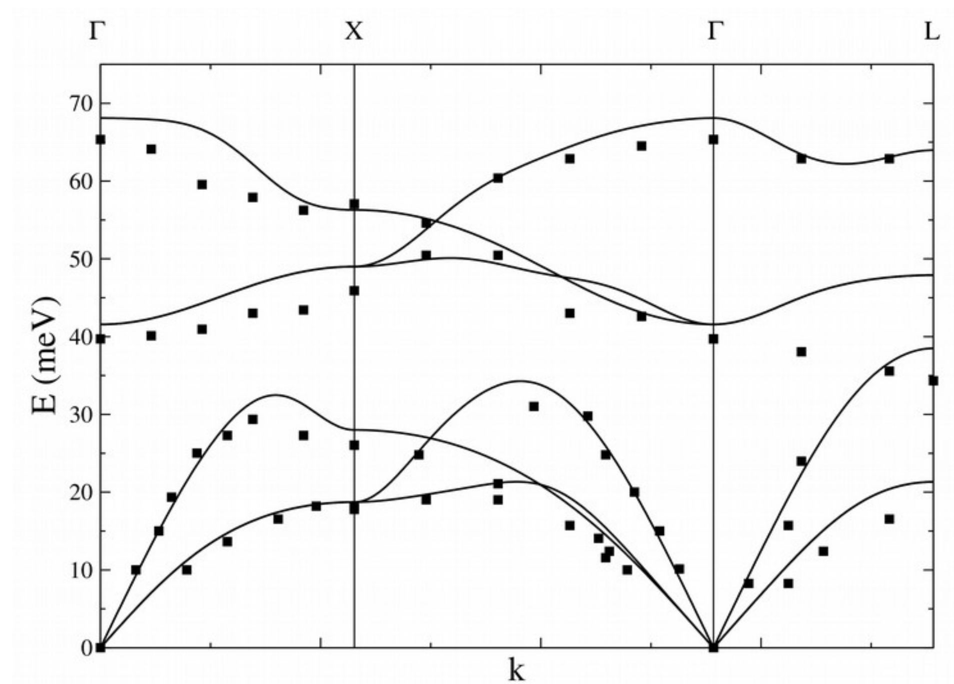
U = 0

U = 6 eV



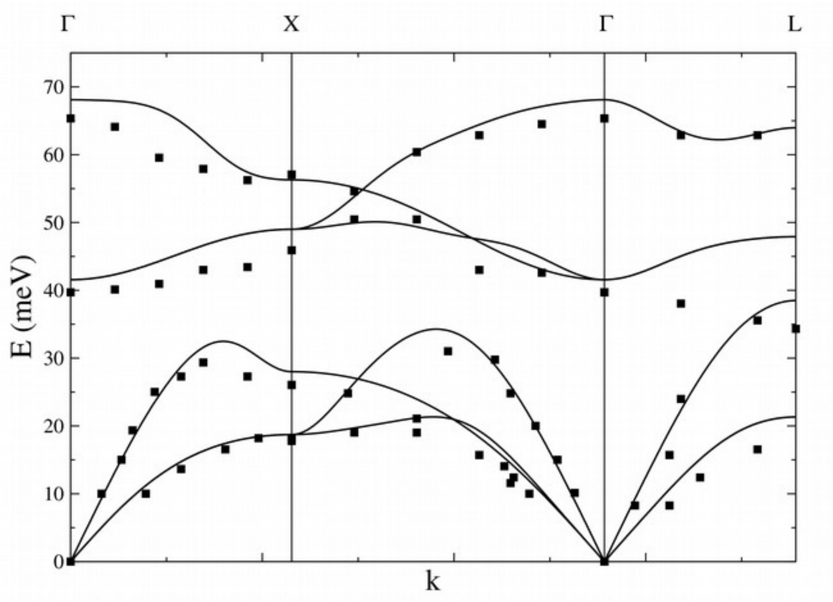






Phonon dispersion curves

x=0 Fm-3m 2 disp. 6 branches



Inelastic neutron scattering $Fe_{0.93}O$

G. Kugel et al., Phys. Rev. B 16, 378 (1977)

Phonon dispersion curves

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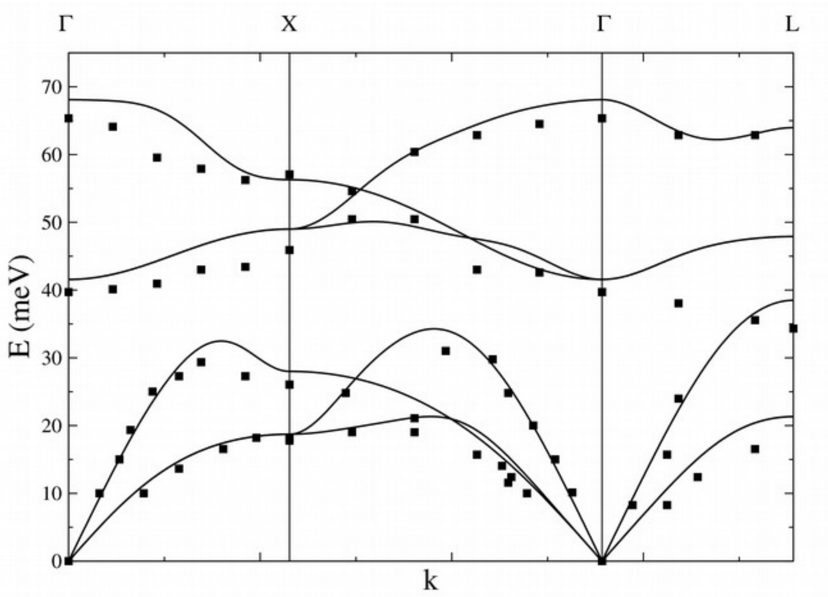
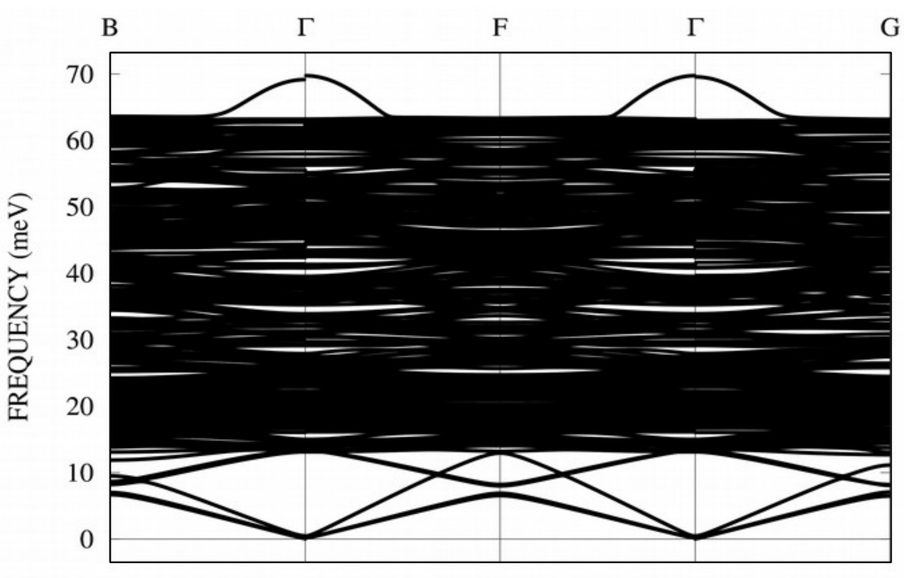


x=3% P1 378 disp. 189 branches



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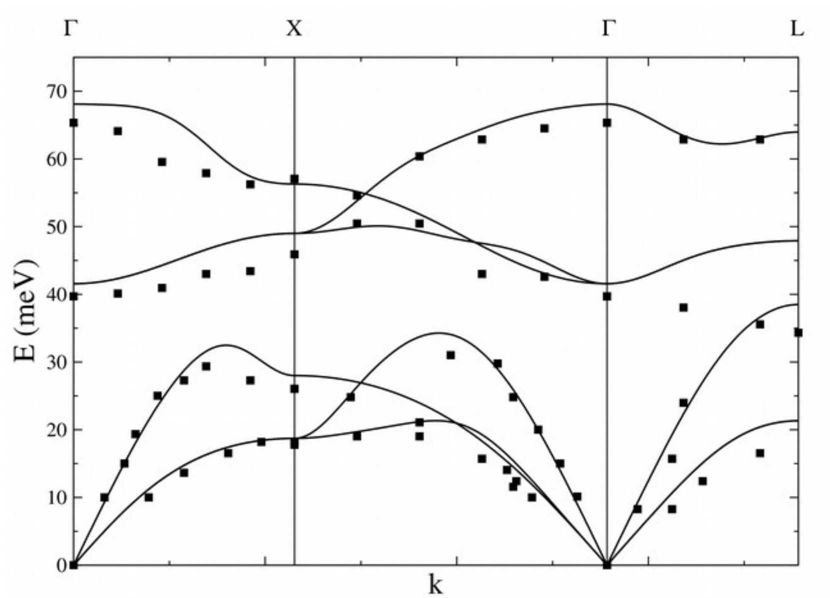

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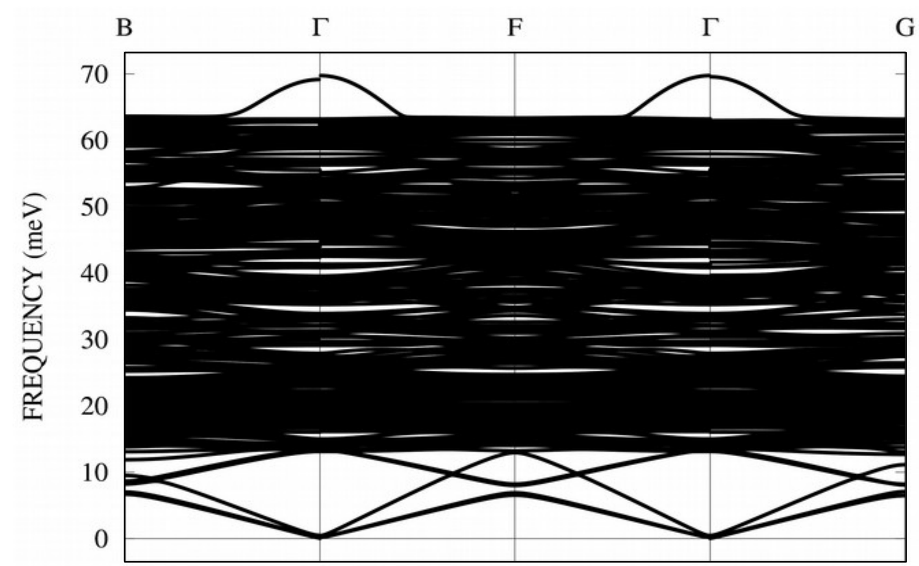
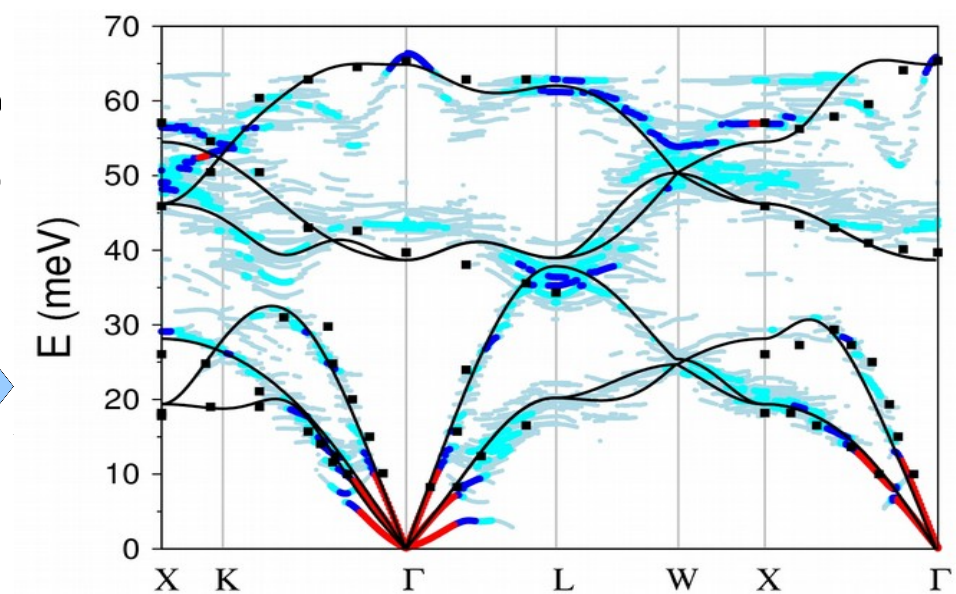


Inelastic neutron scattering $Fe_{0.93}O$

G. Kugel et al., Phys. Rev. B 16, 378 (1977)

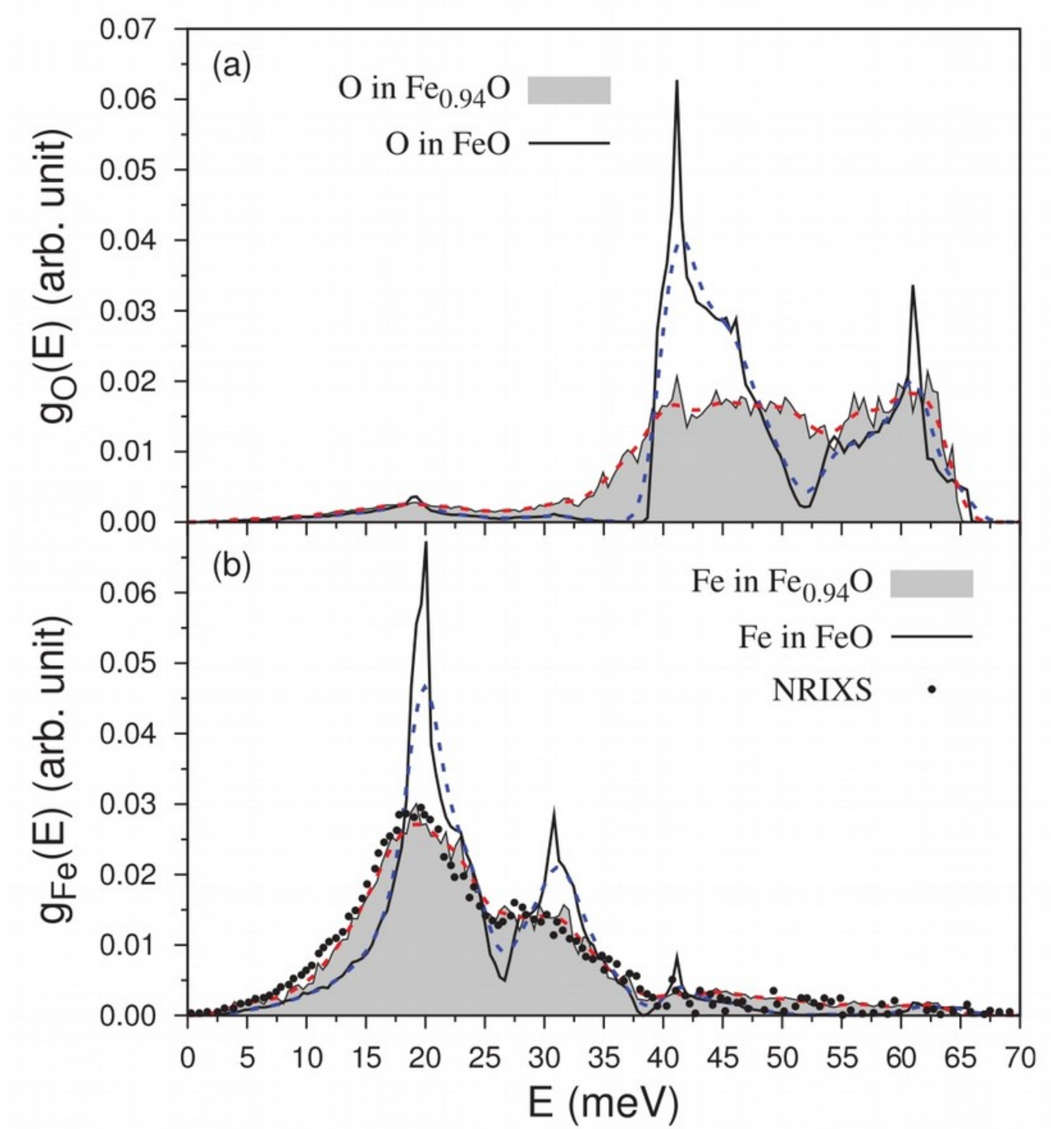
Intensity filter

$$\left| \sum_{\mu,i} \frac{\mathbf{e}_i(\mathbf{k}, j; \mu)}{\sqrt{M_\mu}} \right|^2$$



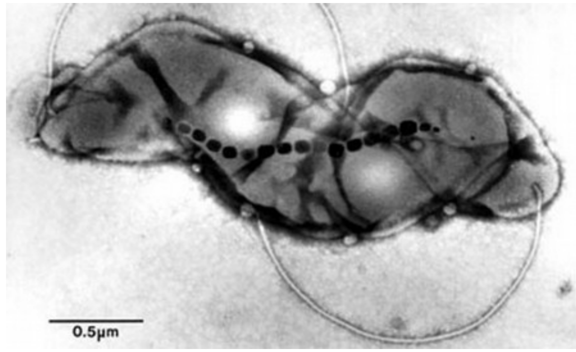
Phonon density of states

Substantial broadening of phonon DOS
=> good agreement with inelastic nuclear scattering on $Fe_{0.95}O$
V. V. Struzhkin *et al.*, PRL 87, 255501 (2001)

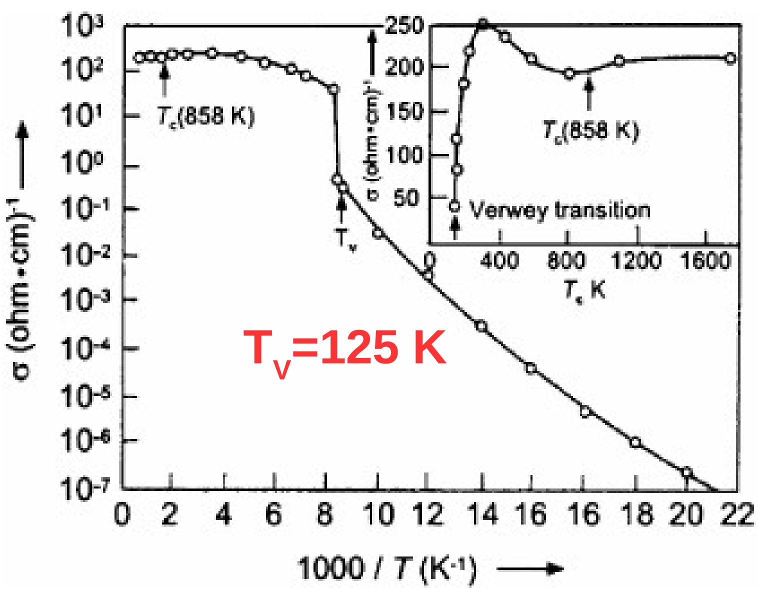


U. D. Wdowik, P. Piekarz, K. Parlinski, A. M. Oleś, J. Korecki, Phys. Rev. B 87, 121106 (2013)
U. D. Wdowik, P. Piekarz, P. T. Jochym, K. Parlinski, A. M. Oleś, Phys. Rev. B 91, 195111 (2015)

Magnetite Fe_3O_4

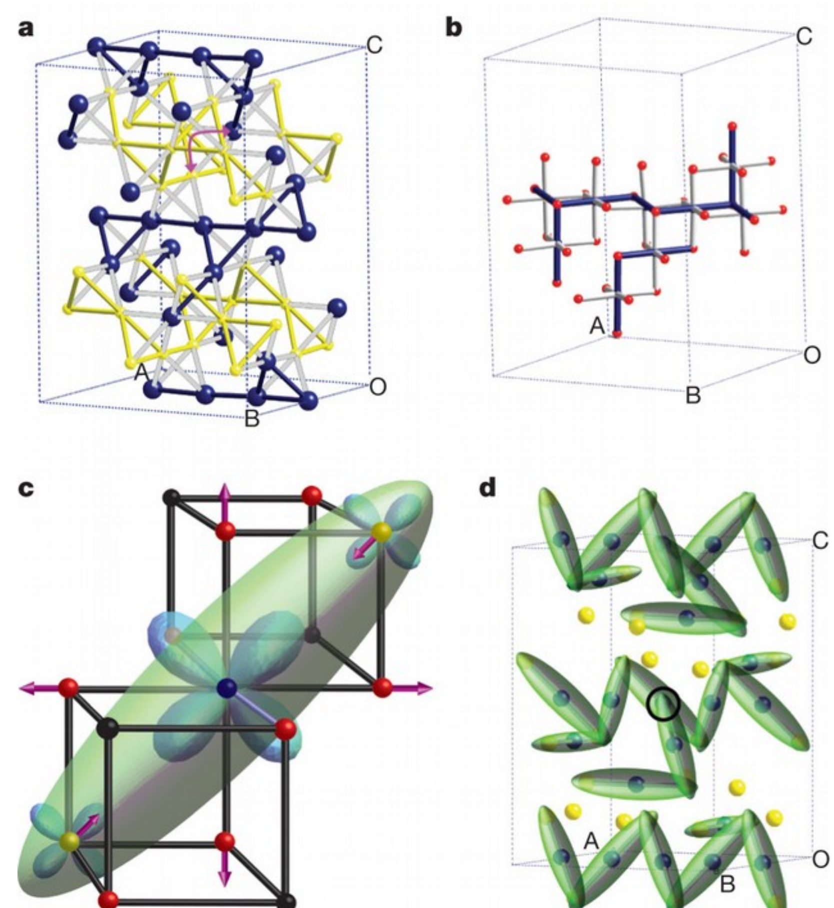


E. J. W. Verwey, Nature 144, 327 (1939)



$Fe_2(B)^{2.5+}Fe(A)^{3+}O_4$ => $Fe(B)^{2+}Fe(B)^{3+}Fe(A)^{3+}O_4$

Fd-3m => Cc

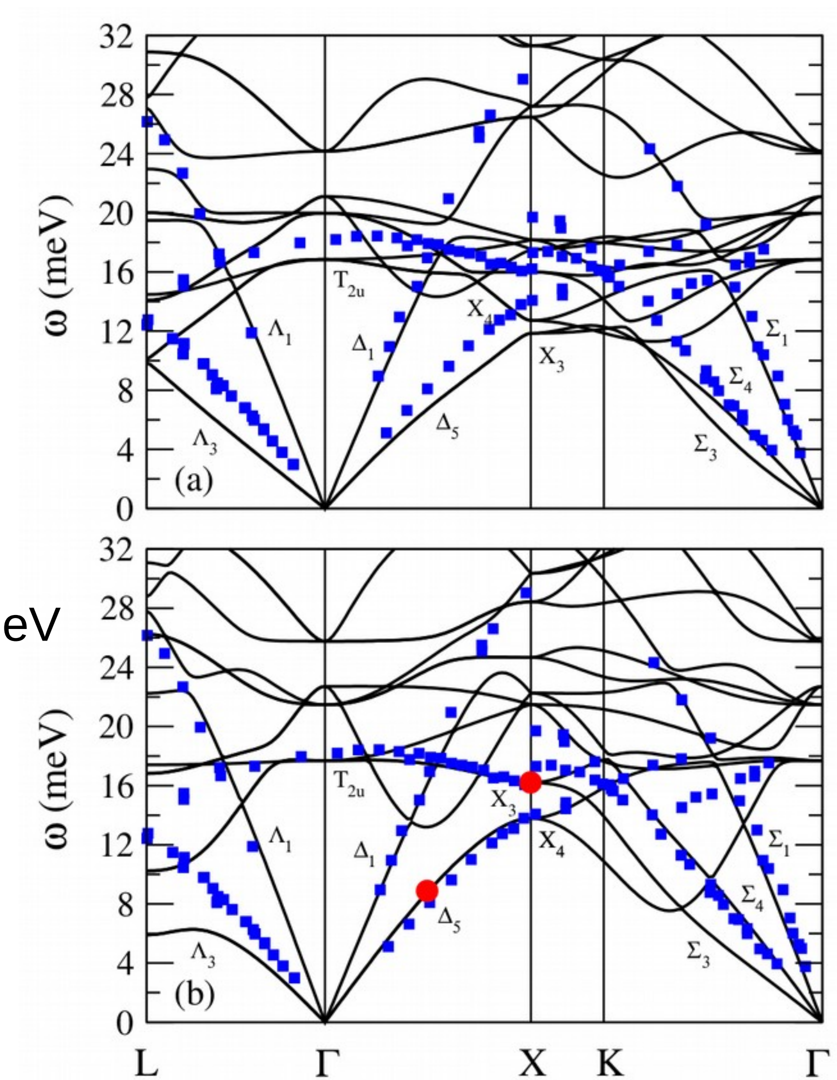


M.R. Senn, J.P. Wright, and J. P. Attfield
Nature 481, 173 (2012)

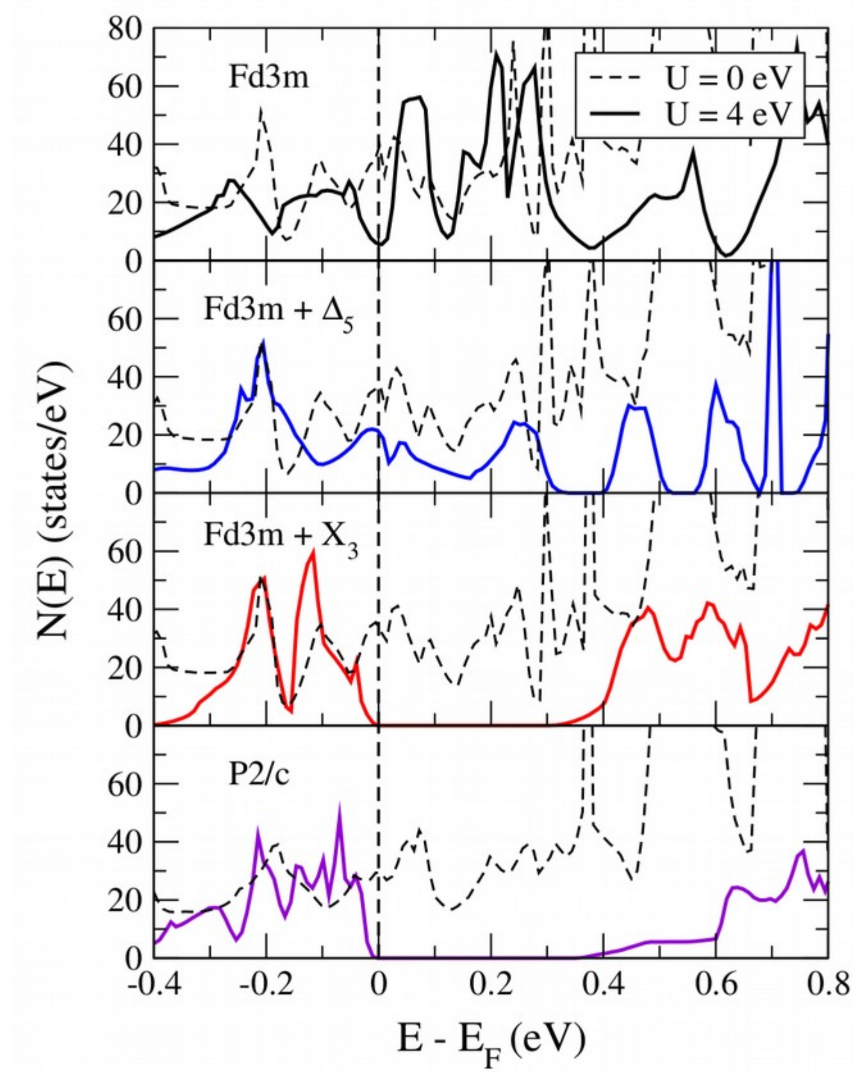
Magnetite Fe_3O_4

U = 0

U = 4 eV



P. Piekarz, K. Parlinski, A. M. Oleś,
Phys. Rev. B 76, 165124 (2007)



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

The European Synchrotron ESRF Grenoble

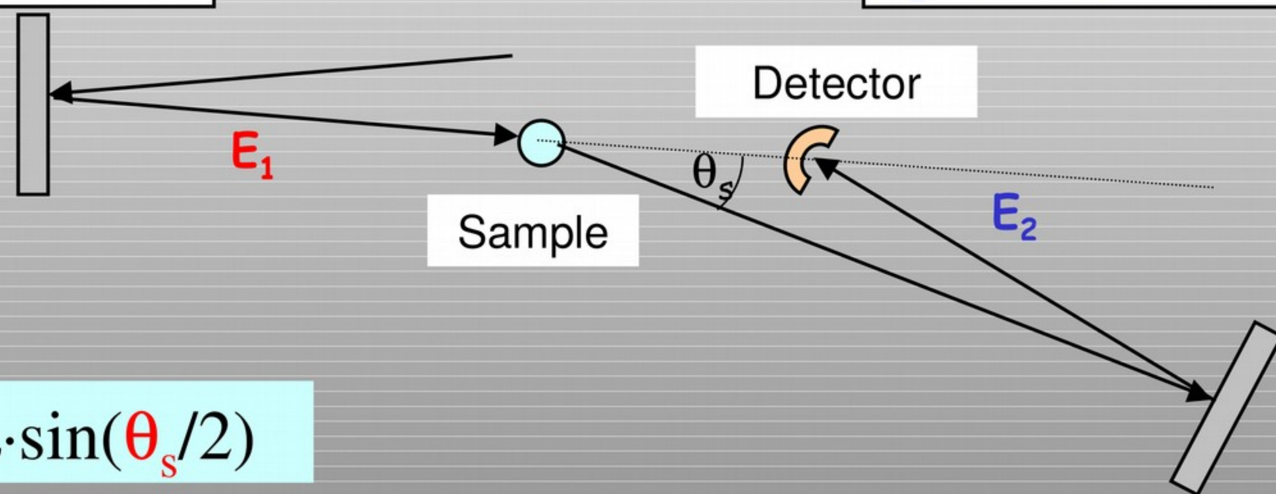
Blas Cabrera 2016

Inelastic X-ray scattering ID28 ESRF

Experimental set-up

Monochromator:
Si(n,n,n), θ_b = 89.98º
n=7-13
λ_1 **tunable**

Analyser:
Si(n,n,n), θ_b = 89.98º
n=7-13
λ_2 **constant**

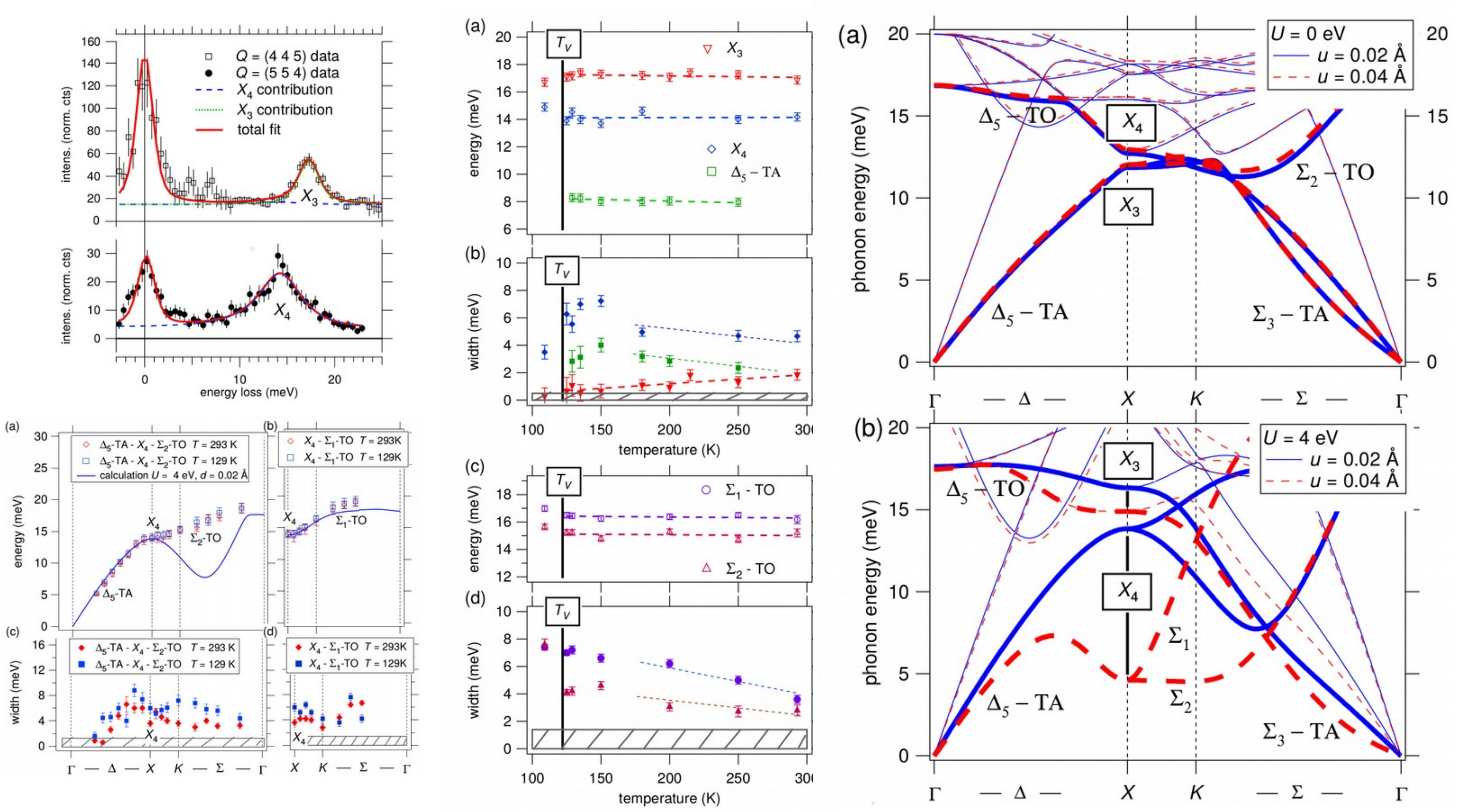


$Q = 4\pi/\lambda \cdot \sin(\theta_s/2)$

$\lambda = 2 \cdot d(T) \sin\theta_B$
$\Delta d/d = \Delta E/E = -\alpha(T) \cdot \Delta T$ ($\alpha = 2.58 \cdot 10^{-6}$ at RT)

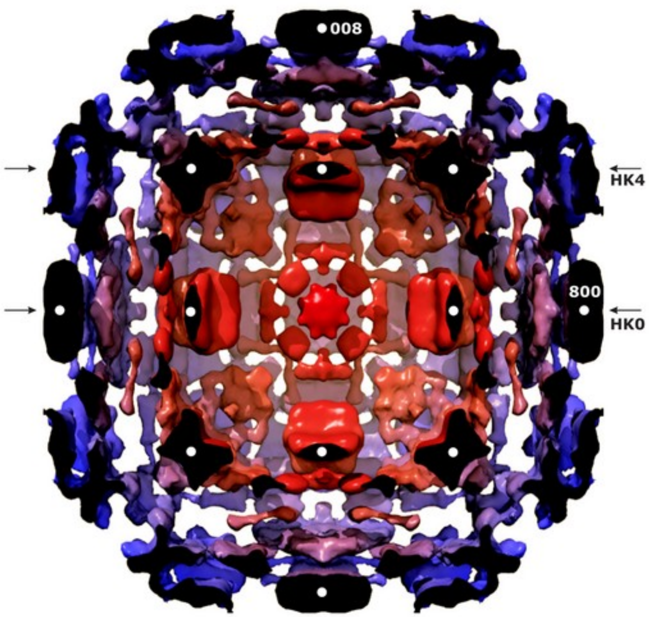
Beam size: 30 (250) x 70 μm^2 (hor. x vert.)

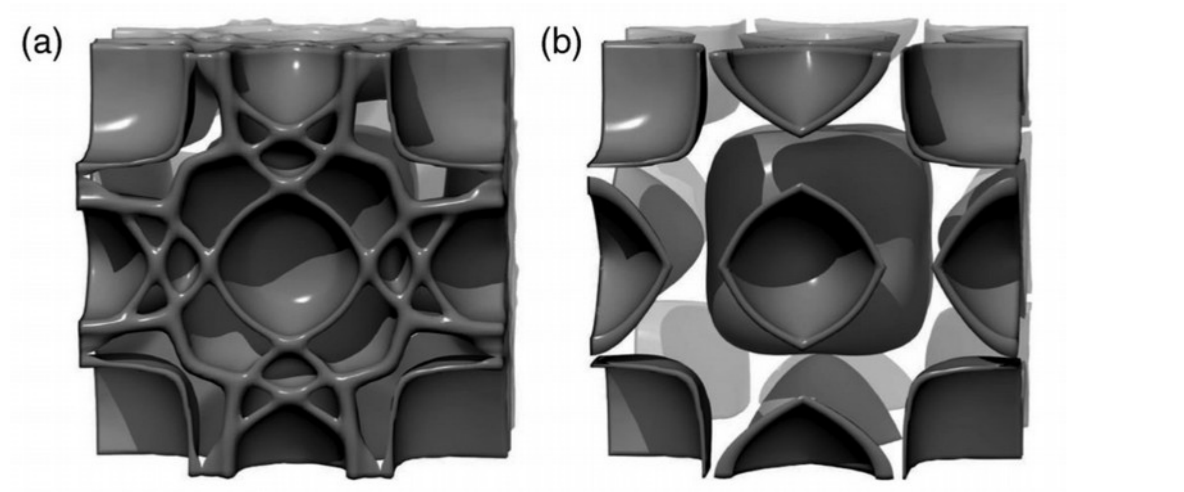
Electron-phonon interaction in magnetite

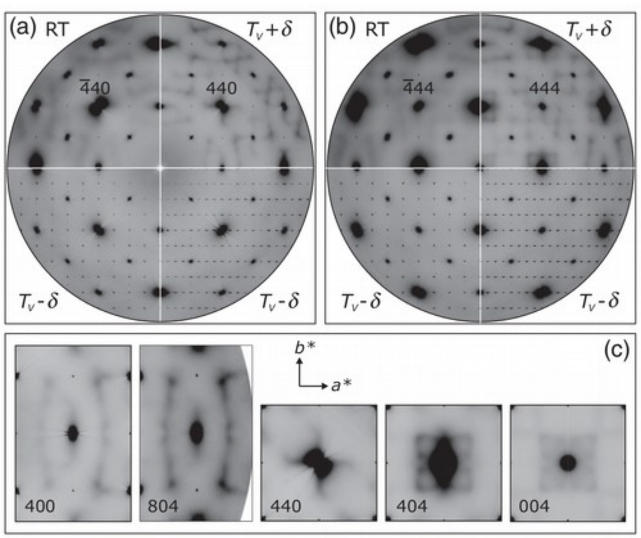


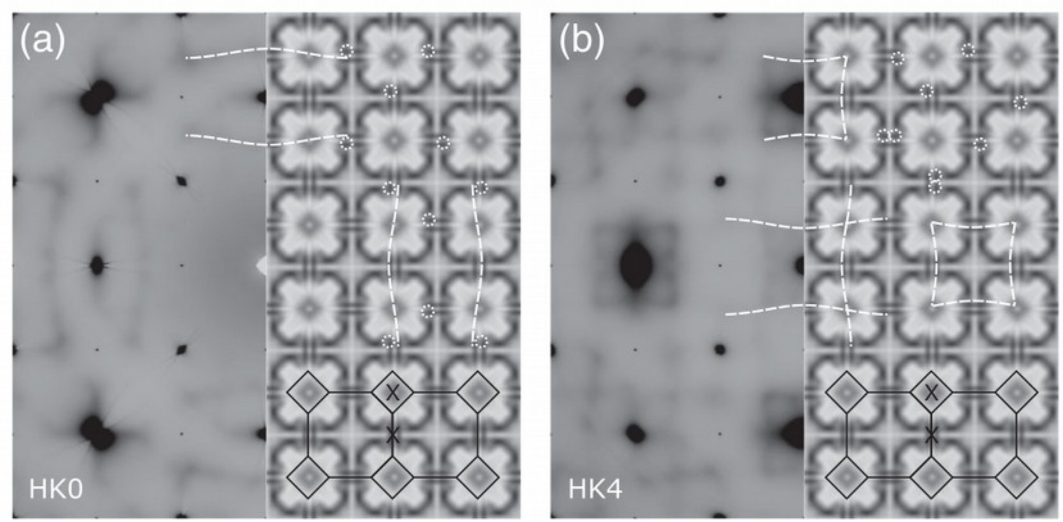
M. Hoesch, P. Piekarz, A. Bosak, M. Le Tacon, M. Krisch, A. Kozłowski, A. M. Oleś, K. Parlinski
Phys. Rev. Lett. 110, 207204 (2013)

X-ray diffuse scattering in magnetite









A. Bosak, D. Chernyshov, M. Hoesch, P. Piekarz, M. Le Tacon, M. Krisch, A. Kozłowski, A. M. Oleś, and K. Parlinski, Phys. Rev. X 4, 011040 (2014)

EuO

Structure: fcc NaCl a = 0.51 nm

Mott insulator with FM order!
$E_g \sim 1$ eV, m ~ 7 μ_B

N.J.C. Ingle and I.S. Elfimov, PRB 77, 121202 (2008)

GGA+U, U=8.3 eV, J=0.77 eV

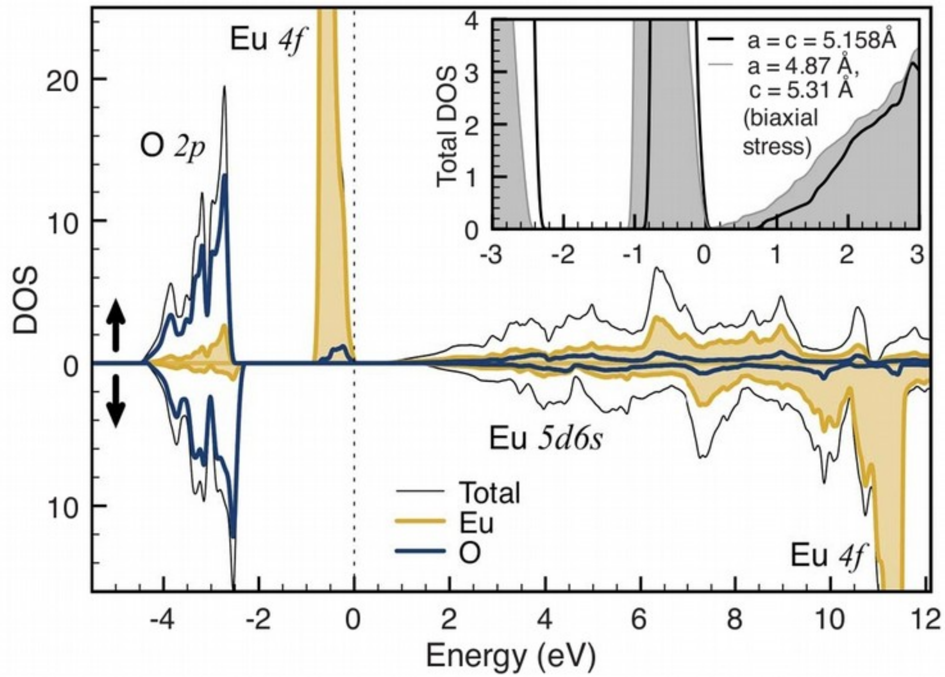
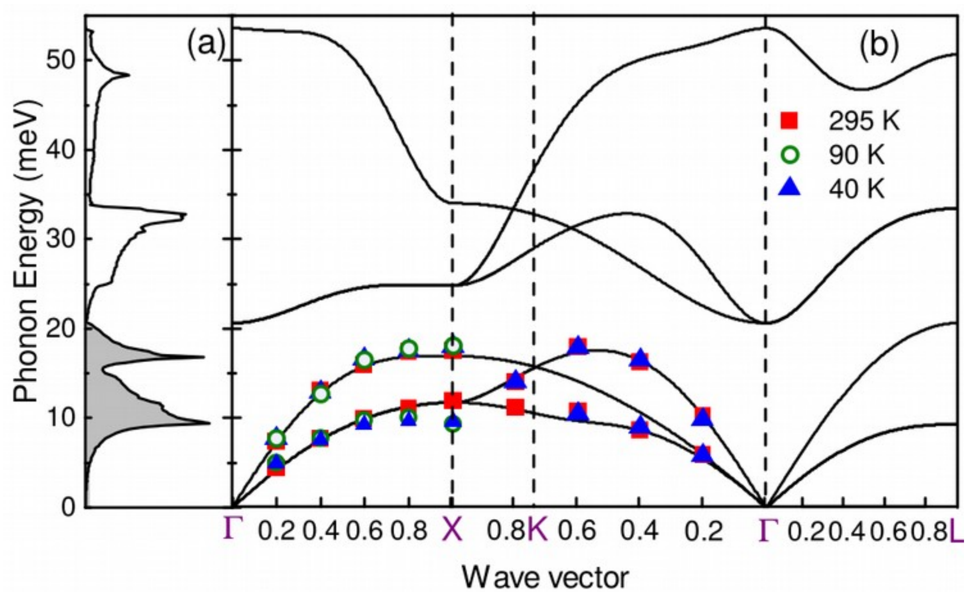


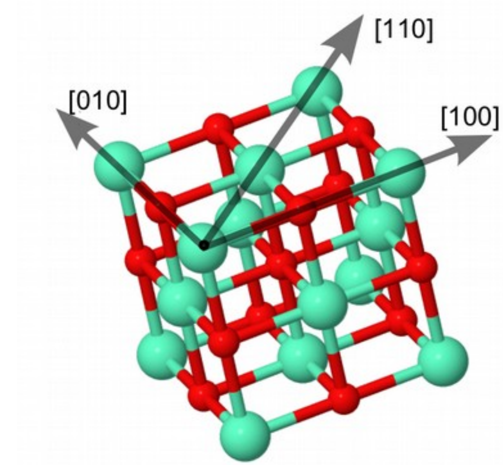
TABLE I.

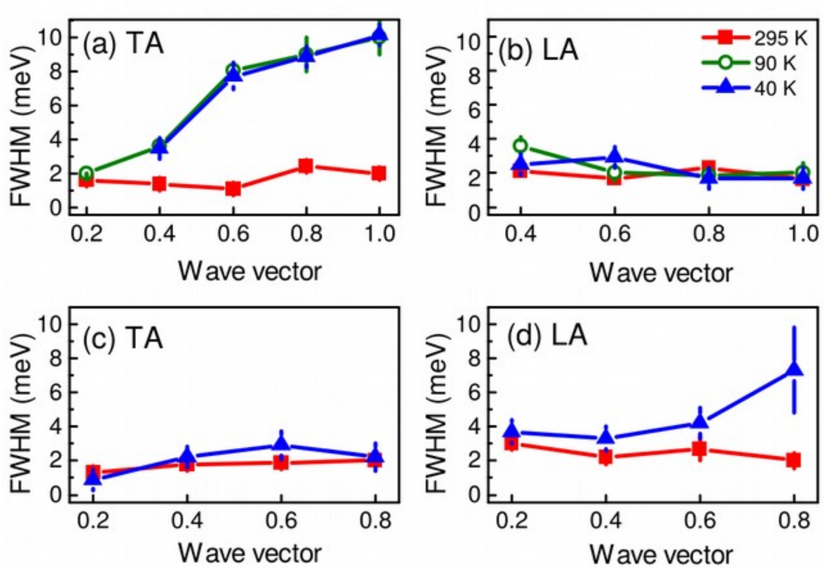
U (eV)	$U_f = 0$, $U_p = 0$	$U_f = 8.3$, $U_p = 0$	$U_f = 8.3$, $U_p = 4.6$	Exp.
J (eV)	$J_f = 0$, $J_p = 0$	$J_f = 0.77$, $J_p = 0$	$J_f = 0.77$, $J_p = 1.2$	
a (Å)	5.077	5.181	5.172	5.144
m (μ_B)	6.834	6.997	7.004	6.9
E_g (eV)	0	1.10	1.11	1.12
ϵ_∞	-	3.563	4.364	3.85, 4.6, 5.0
Z^*(Eu)	-	2.625	2.638	
Z^*(O)	-	-2.671	-2.680	
TO (meV)	27.23	19.59	19.25	22.57, 24.71, 43.41
LO (meV)	27.23	57.87	53.15	42.94, 52.92, 53.93

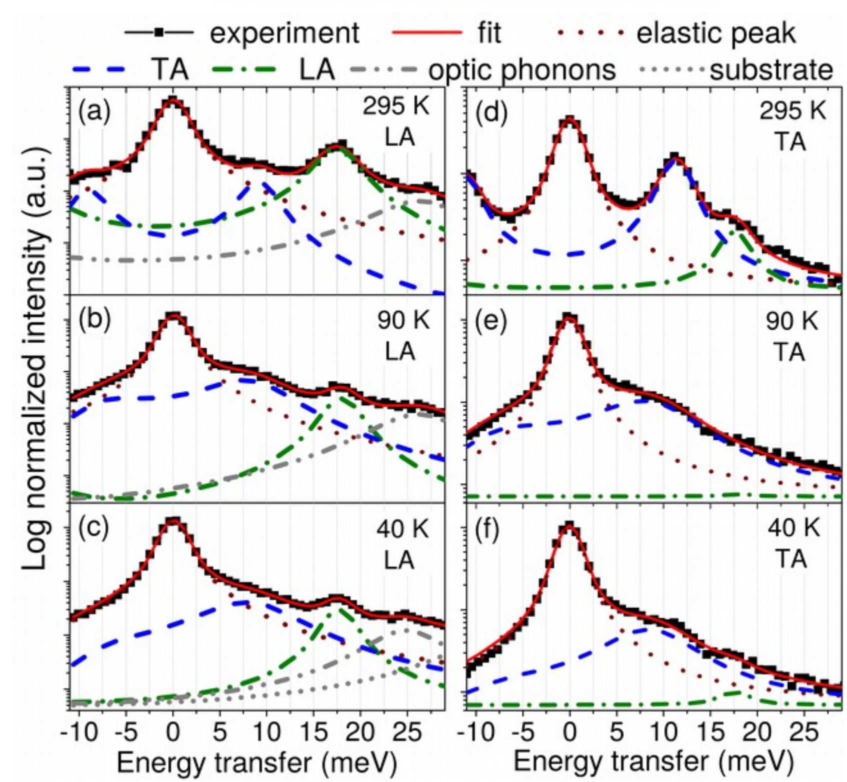
Phonons in EuO

R. Pradip, P. Piekarz, A. Bosak, D. G. Merkel, O. Waller, A. Seiler, A. I. Chumakov, R. Rüffer, A. M. Oleś, K. Parlinski, M. Krisch, T. Baumbach, S. Stankov, Phys. Rev. Lett. 116, 185501 (2016)





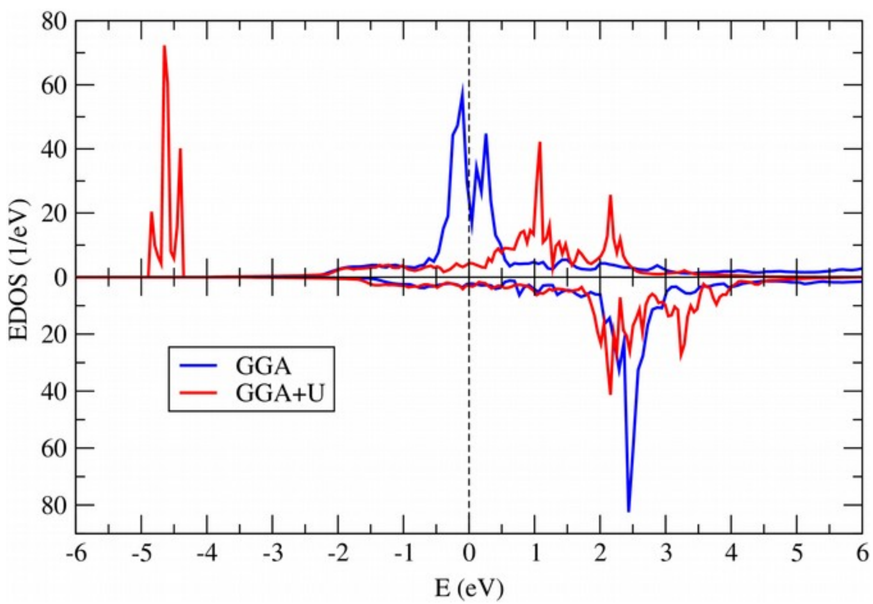




Lattice dynamics in Nd

O. Waller, P. Piekarz, A. Bosak, P. T. Jochym, S. Ibrahimkutty, A. Seiler, M. Krisch, T. Baumbach, K. Parlinski, and S. Stankov, Phys. Rev. B 94, 014303 (2016)

Property	GGA_0	GGA	GGA+U(SOC)	Expt.
a (Å)	3.690	3.528	3.669 (3.670)	3.658[a]
c (Å)	11.870	11.277	11.804 (11.824)	11.797[a]
V (Å^3/atom)	34.997	30.389	34.398 (34.470)	34.18[a]
B (GPa)	34.7	18.6	31.4 (32.15)	31.8[a]
B' (GPa)	3.09	2.41	3.05 (3.04)	2.9[b]
c_{11} (GPa)	59.9	31.4	55.2	58.78[c]
c_{33} (GPa)	72.2	39.1	65.1	65.13[c]
c_{12} (GPa)	29.8	14.9	27.9	24.58[c]
c_{13} (GPa)	16.5	11.1	14.2	16.20[c]
c_{44} (GPa)	18.8	6.3	18.5	16.20[c]
C_V (J/mol K)	24.67	24.75	24.69	24.68[d]



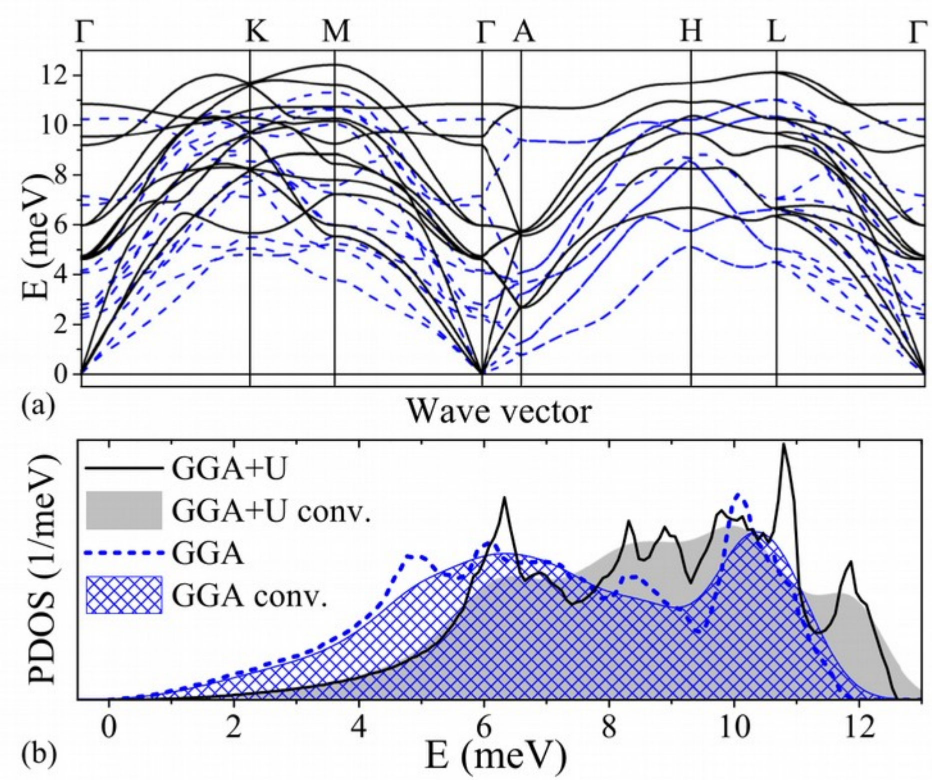
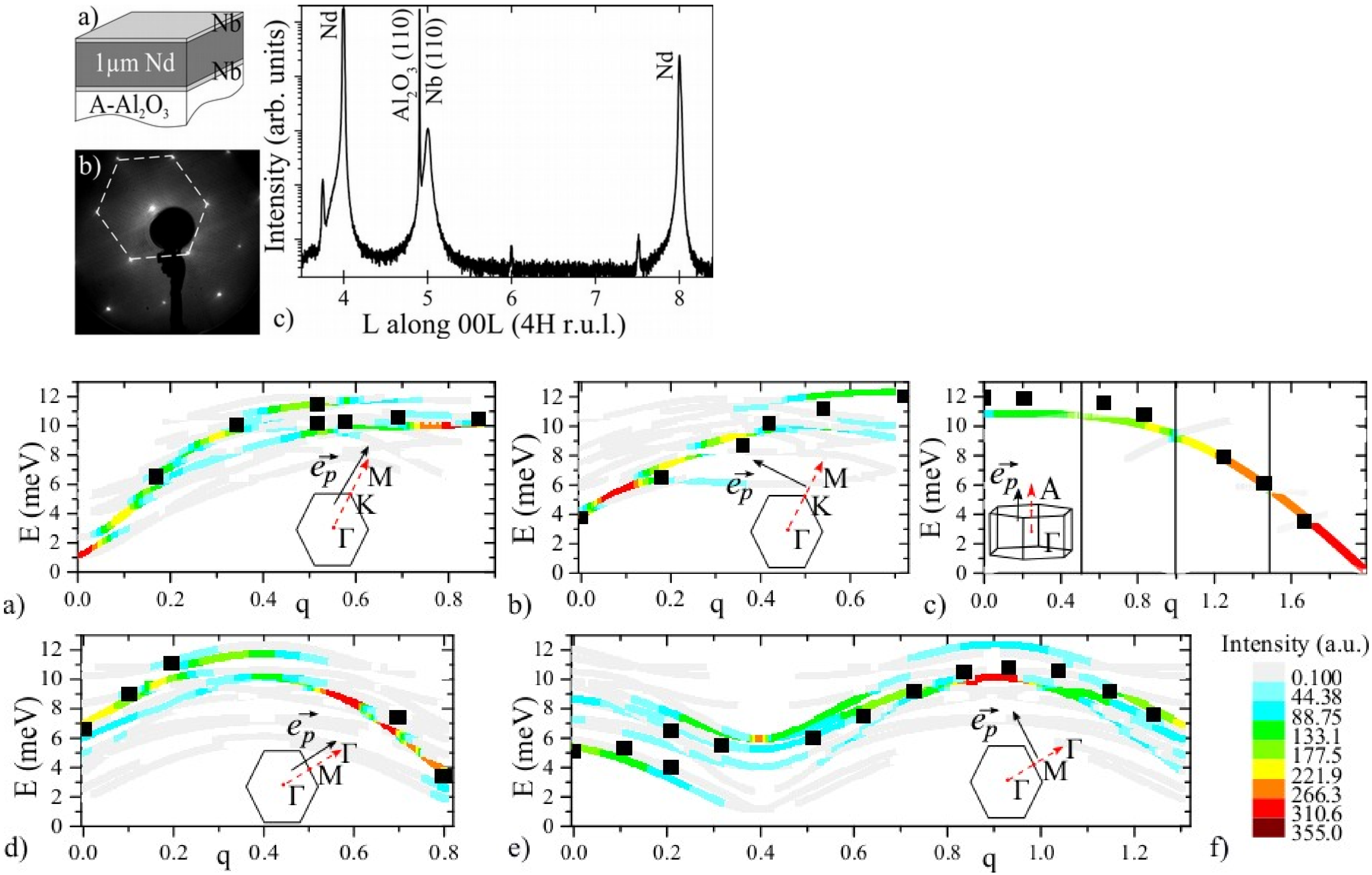


FIG. 1. *Ab initio* calculated (a) dispersion relations and (b) PDOS of Nd within GGA and GGA+U using the optimized lattice constants. The high-symmetry points in units of $2\pi/a$ are $\Gamma = (0,0,0)$, $K = (\frac{1}{3},\frac{1}{3},0)$, $M = (\frac{1}{2},0,0)$, $A = (0,0,\frac{1}{2})$, $H = (\frac{1}{3},\frac{1}{3},\frac{1}{2})$, and $L = (\frac{1}{2},0,\frac{1}{2})$. Shaded areas correspond to the Gauss convolution with FWHM = 1 meV.

Inelastic X-ray scattering (ESRF)



$$F(\mathbf{k}, j) = \left| \sum_{\mu} f_0^{(\mu)}(\mathbf{k}) \exp[-W_\mu(2\pi\mathbf{k})] \frac{2\pi\mathbf{k}\cdot\mathbf{e}(\mathbf{k}, j; \mu)}{\sqrt{M_\mu}} \right|^2$$

Conclusions

1) Standard DFT approximations (LDA, GGA) do not describe properly electronic structure of the open shell d- and f-electron systems with strong on-site Coulomb interactions

2) In transition-metal oxides, electron localization induced by Coulomb interactions leads to insulating state (Mott insulator)

3) It has impact on inter-atomic forces and phonon energies, which are enhanced due to long-range forces

4) In iron oxide (FeO), the electronic, optical, and phonon properties are determined by local Coulomb interactions and cation vacancies

5) In magnetite, local Coulomb interactions induce charge-orbital ordering and increase electron-phonon coupling – the mechanism of the Verwey transition

6) Recent studies revealed that local interactions between 4f electrons have strong impact on phonon energies and elastic properties in rare-earth metal Nd