The Henryk Niewodniczański
Institute of Nuclear Physics
Polish Academy of Sciences

# Przejście Verweya w magnetycie
# - dynamika sieci i fluktuacje krytyczne

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***Zakład Komputerowych Badań Materiałów***
***Instytut Fizyki Jądrowej PAN***

# Collaboration

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*Massachusetts Institute of Technology, Cambridge, USA*

# Magnetic susceptibility

## Die anfängliche Suszeptibilität von Eisen und Magnetit in Abhängigkeit von der Temperatur

VON DER

EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE IN ZÜRICH

ZUR ERLANGUNG DER WÜRDE EINES

DOKTORS DER TECHNISCHEN WISSENSCHAFTEN

GENEHMIGTE PROMOTIONSARBEIT

VORGELEGT VON

KARL RENGER

DIPL. MASCH.-ING.

AUS BÖHM.-KAMNITZ (ÖSTERREICH)

REFERENT:

HERR PROF. DR P. WEISS

KORREFERENT:

HERR PROF. DR A. EINSTEIN

ZÜRICH 1913

Buch- und Kunstdruckerei Jean Frey

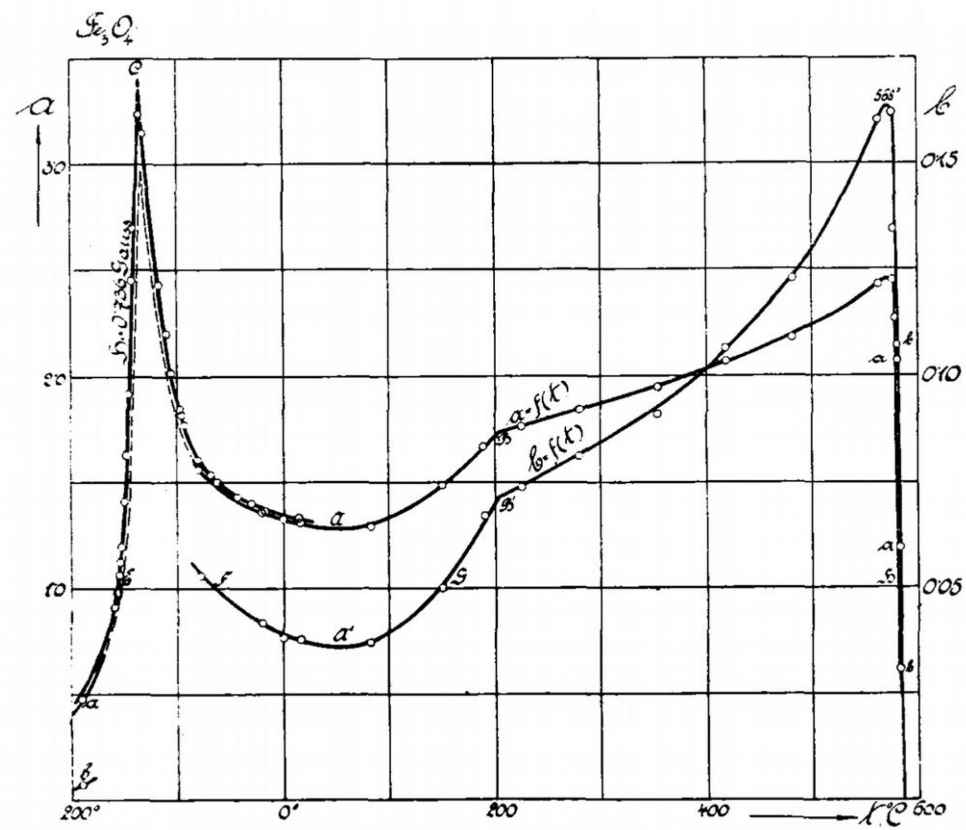
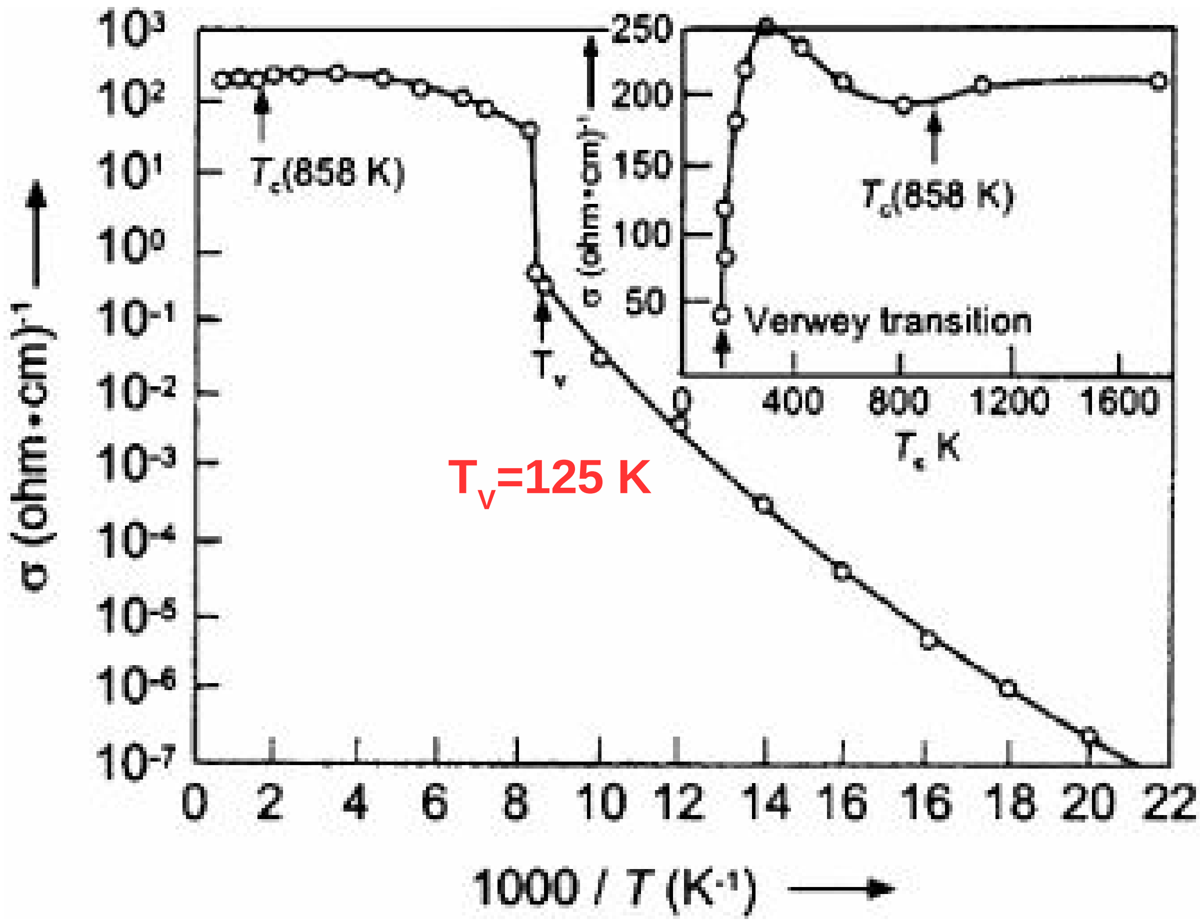



Fig. 14

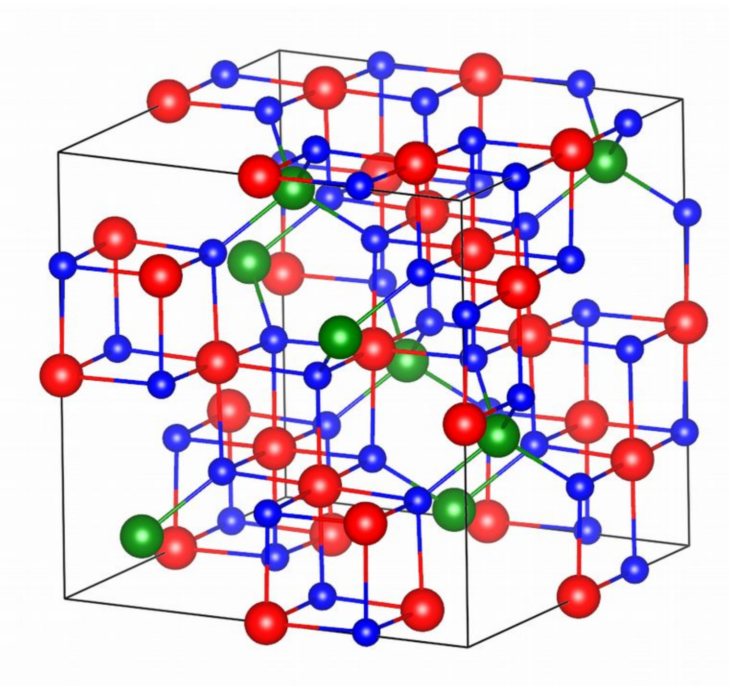
# Verwey transition in magnetite $Fe_3O_4$

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

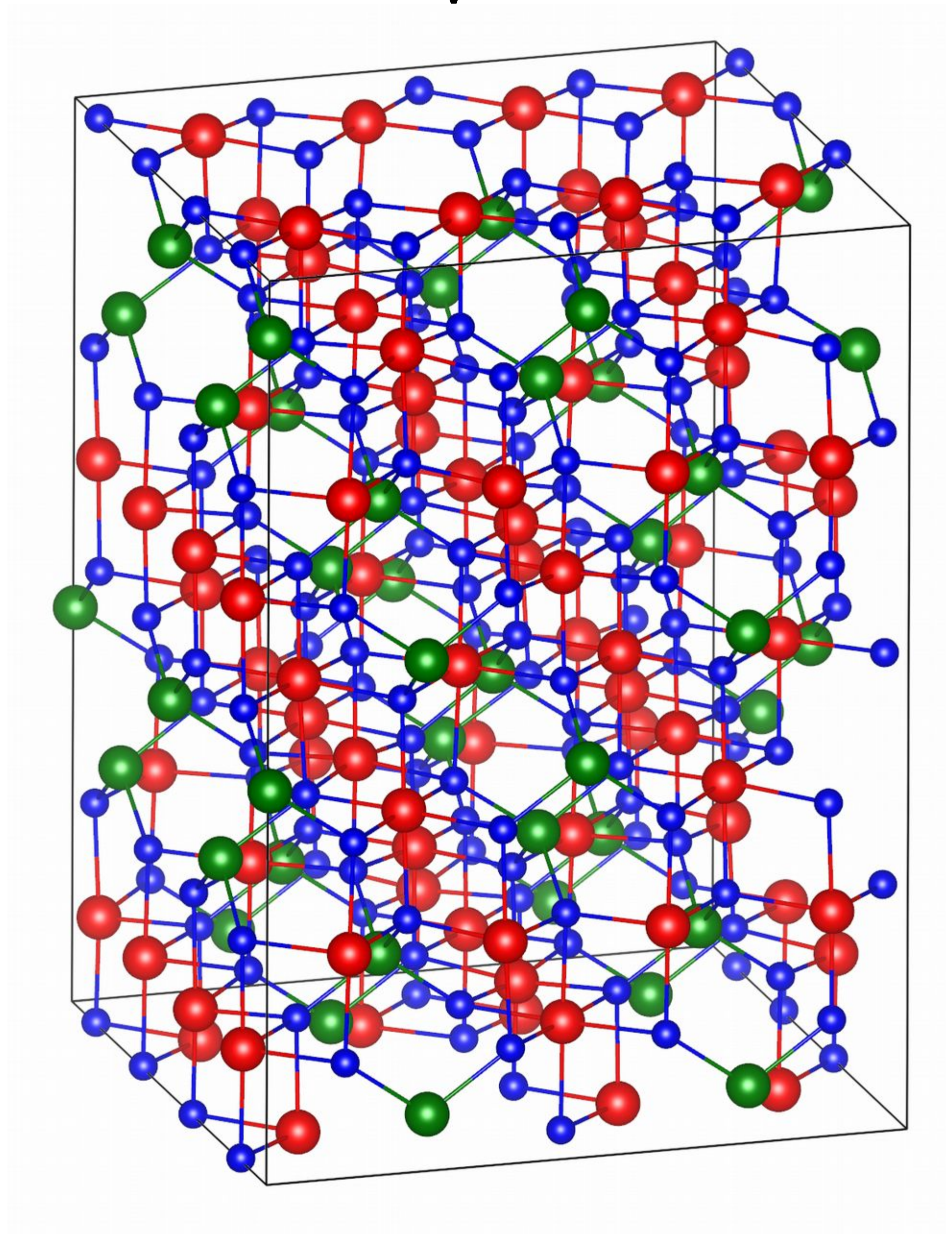


# Structural phase transition

**Fd-3m  $T > T_V = 125$ K**

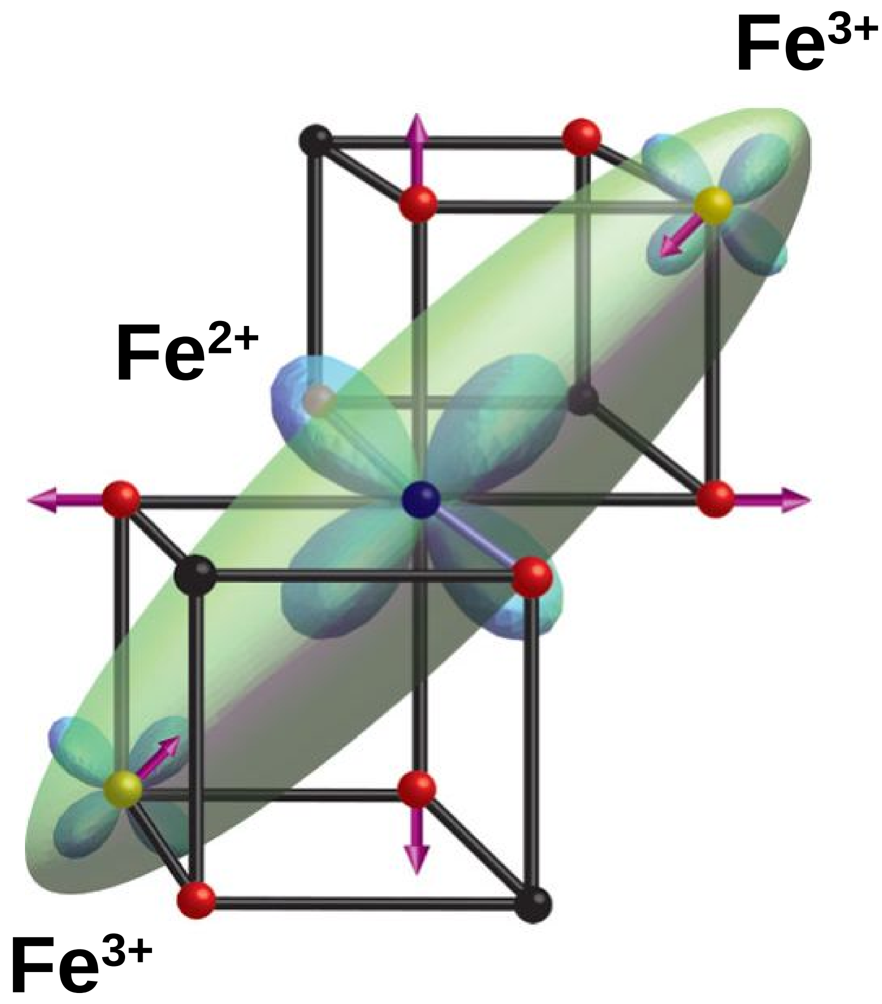


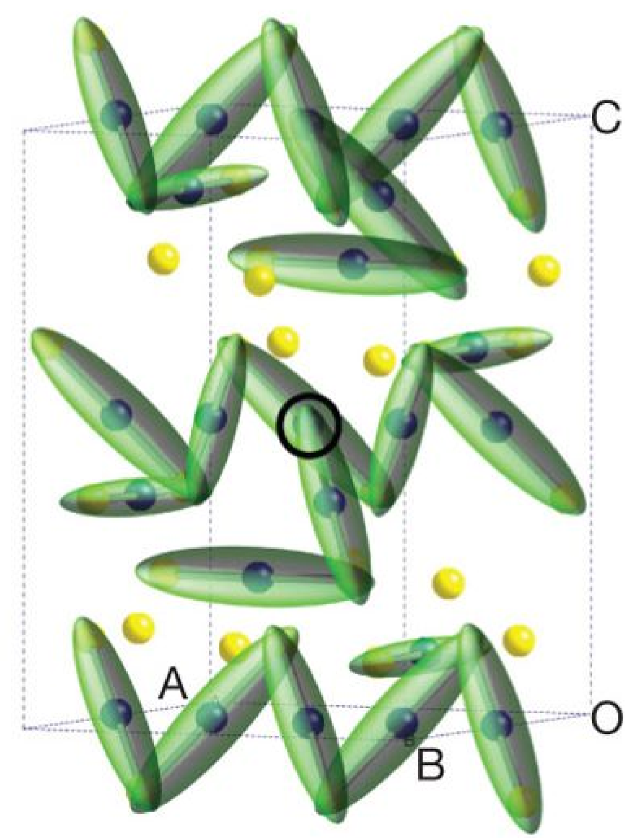
**Cc  $T < T_V = 125$ K**



**$Fe(A)^{3+}$ - tetrahedral position**
**$Fe(B)^{2.5+}$ - octahedral position**
**O - oxygen**

# Trimerons

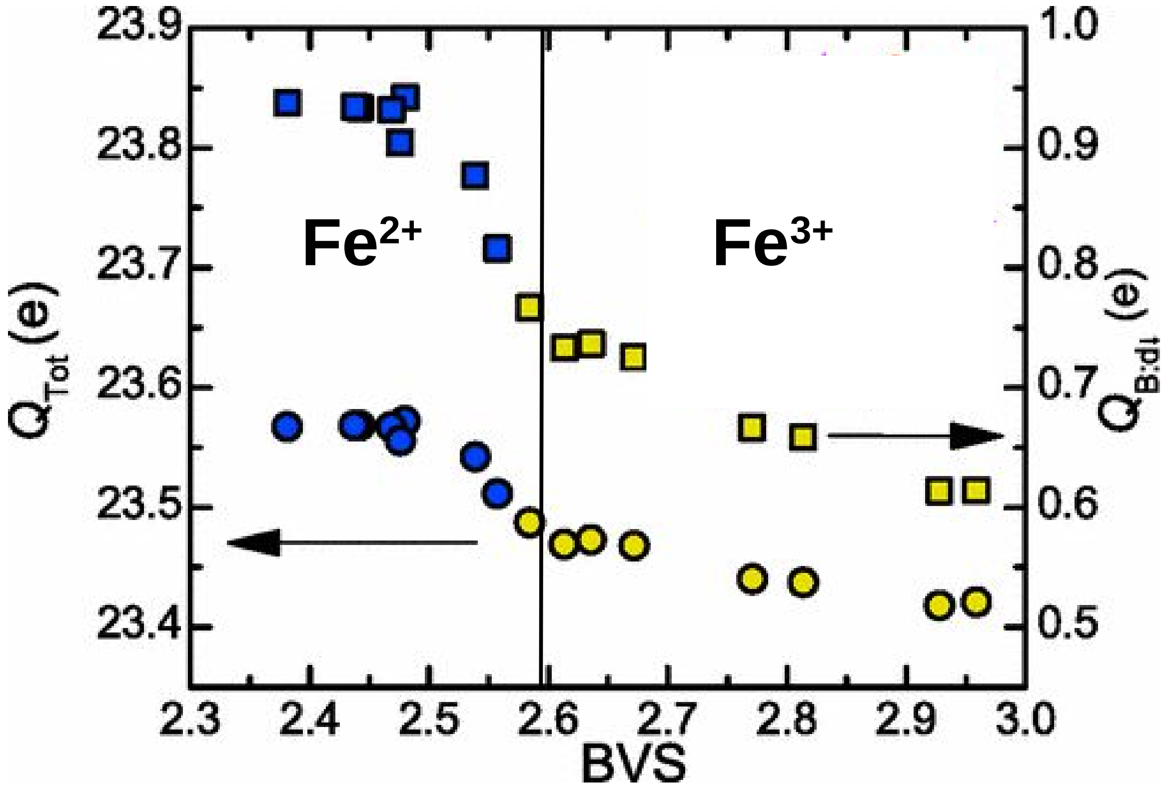


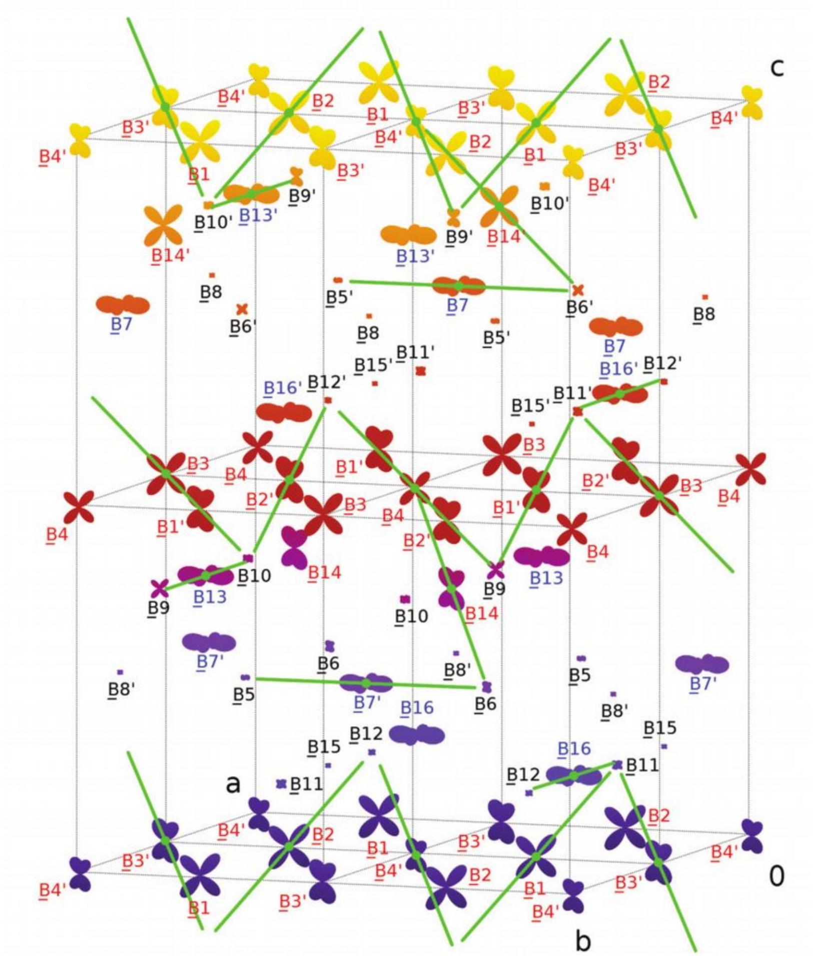

M. R. Senn, J. P. Wright, and J. P. Attfield, Nature 481, 173 (2012)

# Charge-orbital order

**Fe(B) – 16 different crystallographic sites (charges) in Cc**



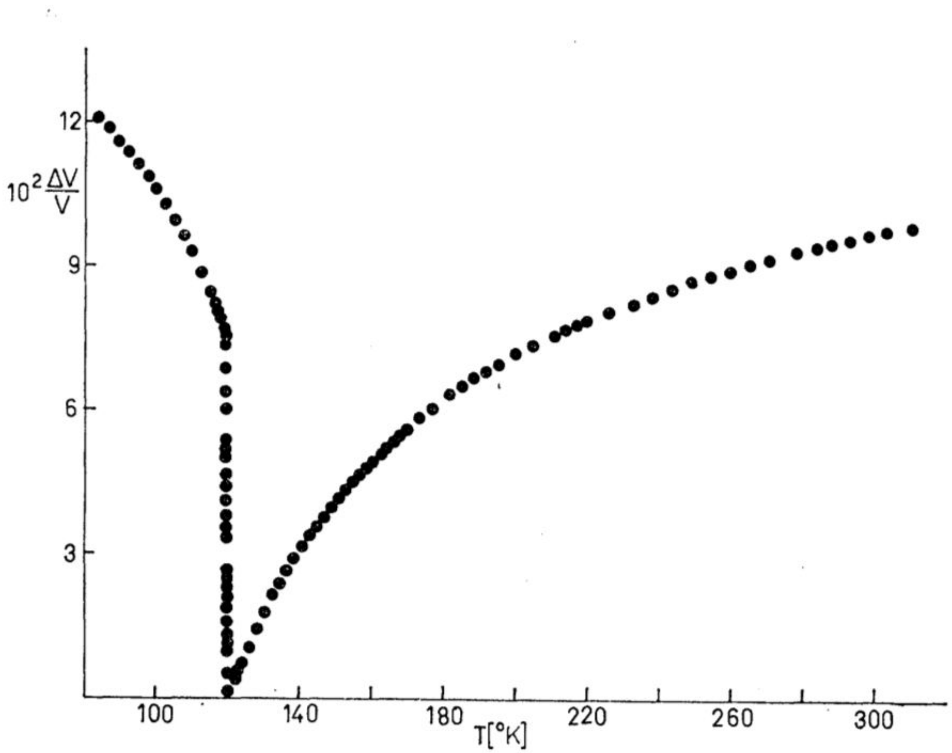

M. S. Senn et al., Phys. Rev. B 85, 125119 (2012)

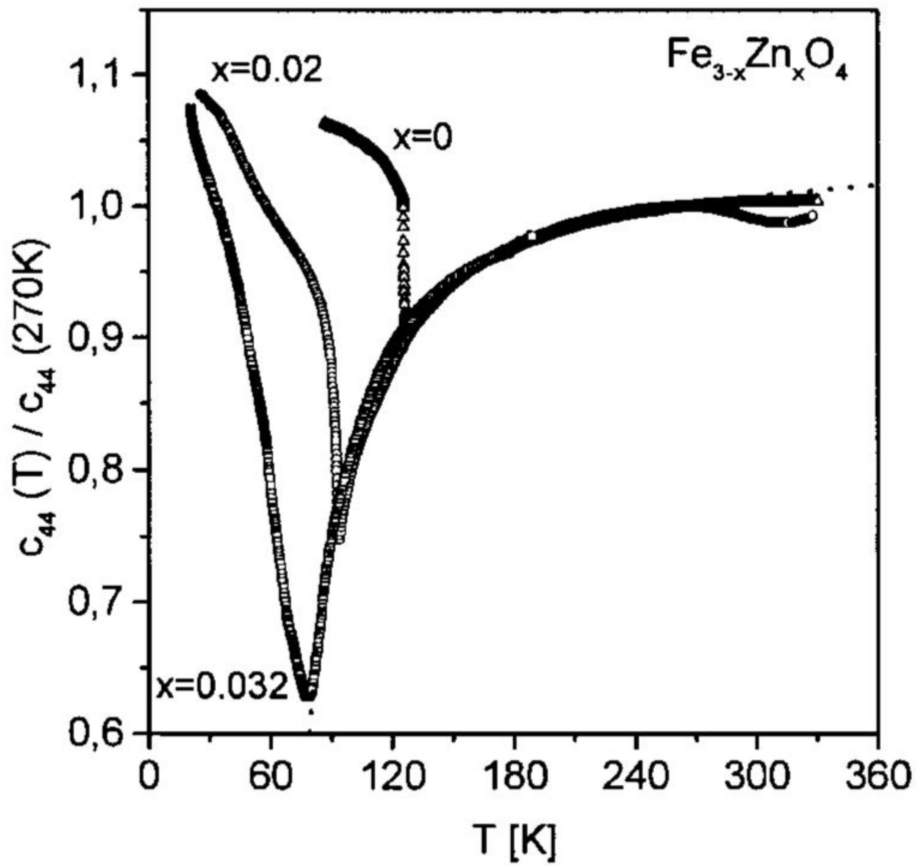


R. Reznicek et al., Phys. Rev. B 91, 125134 (2015)

# Critical softening of $c_{44}$ above $T_V$

T. J. Moran and B. Luthi, Phys. Rev. 187, 710 (1969)



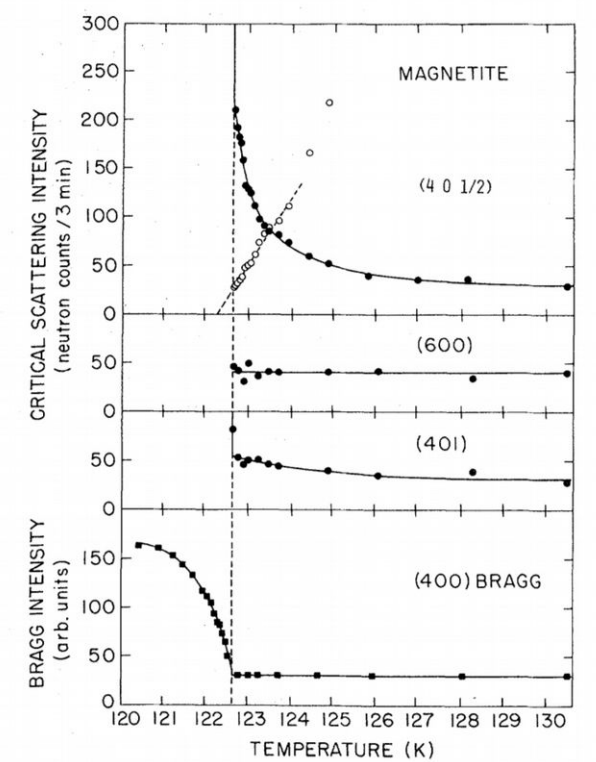

H. Schwenk, S. Bareiter, C. Hinkel, B. Luthi, Z. Kakol, A. Koslowski, and J. M. Honig, Eur. Phys. J. B 13, 491 (2000)

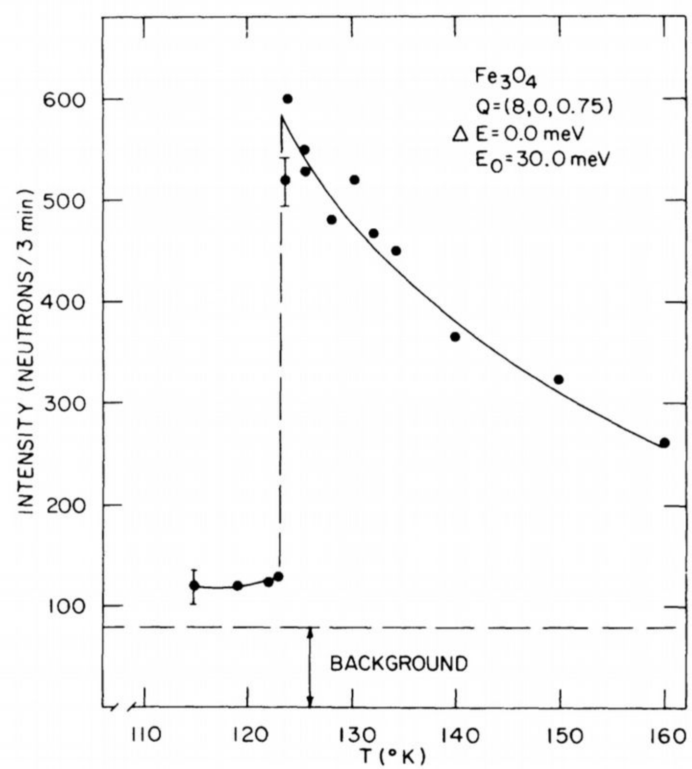
**The critical behavior of elastic constant $c_{44}$ was explained in terms of bilinear coupling of the elastic strain to a fluctuation mode of the charge ordering field of $T_{2g}$ symmetry**

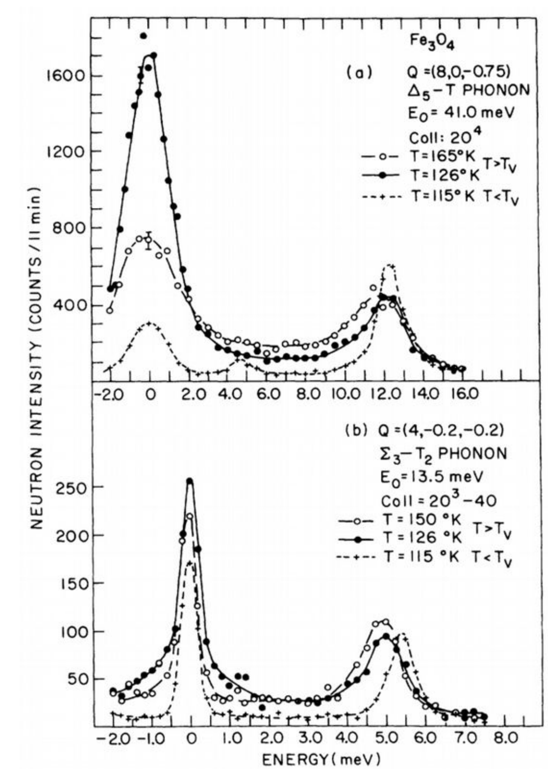
# Critical neutron scattering above $T_V$

Diffuse scattering at the same wave vectors as the superlattice reflections of the monoclinic phase

Diffuse scattering at incommensurate q vectors is observed in broad temperature range



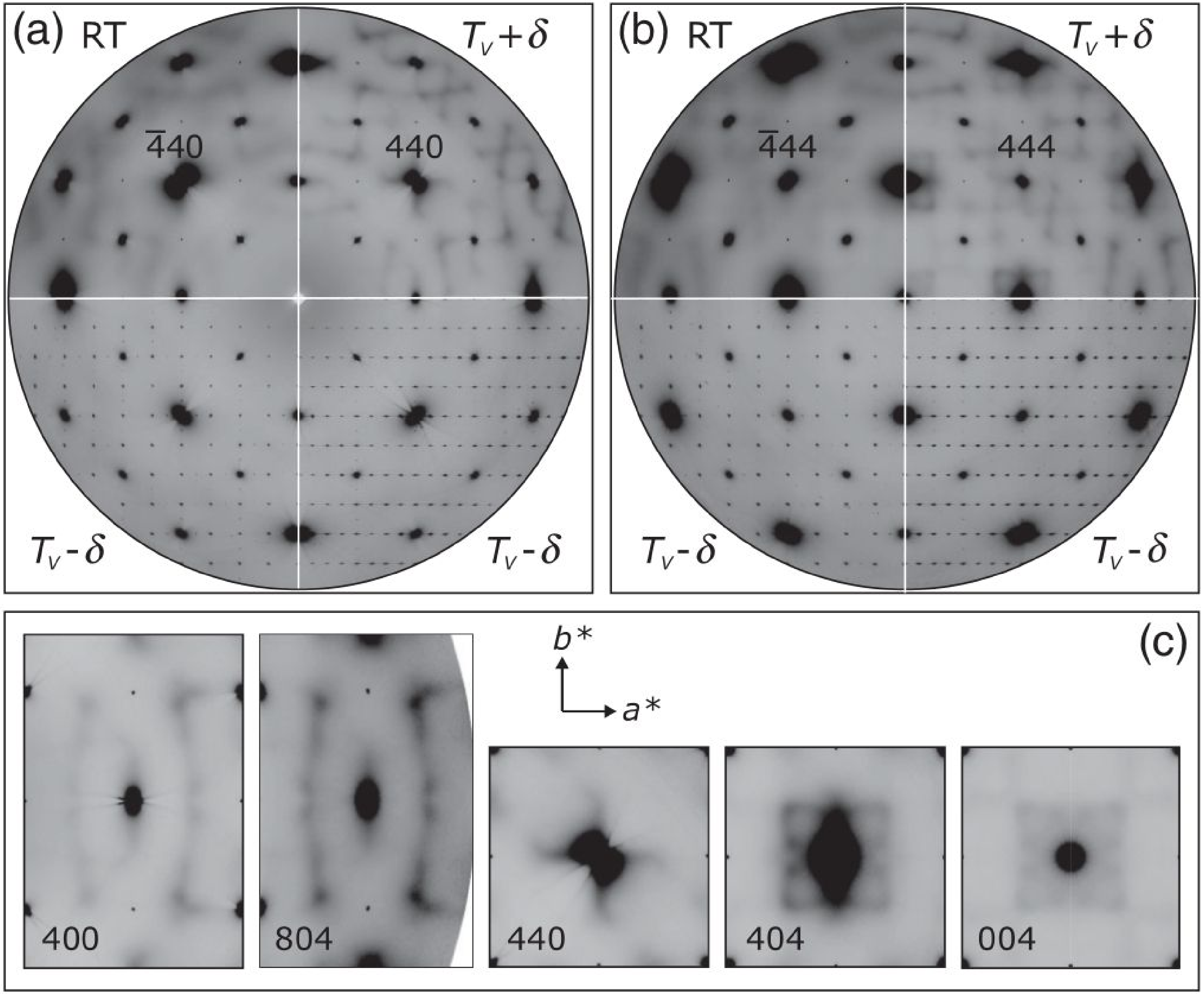




Y. Fujii, G. Shirane, and Y. Yamada, Phys. Rev. B 11, 2036 (1975)

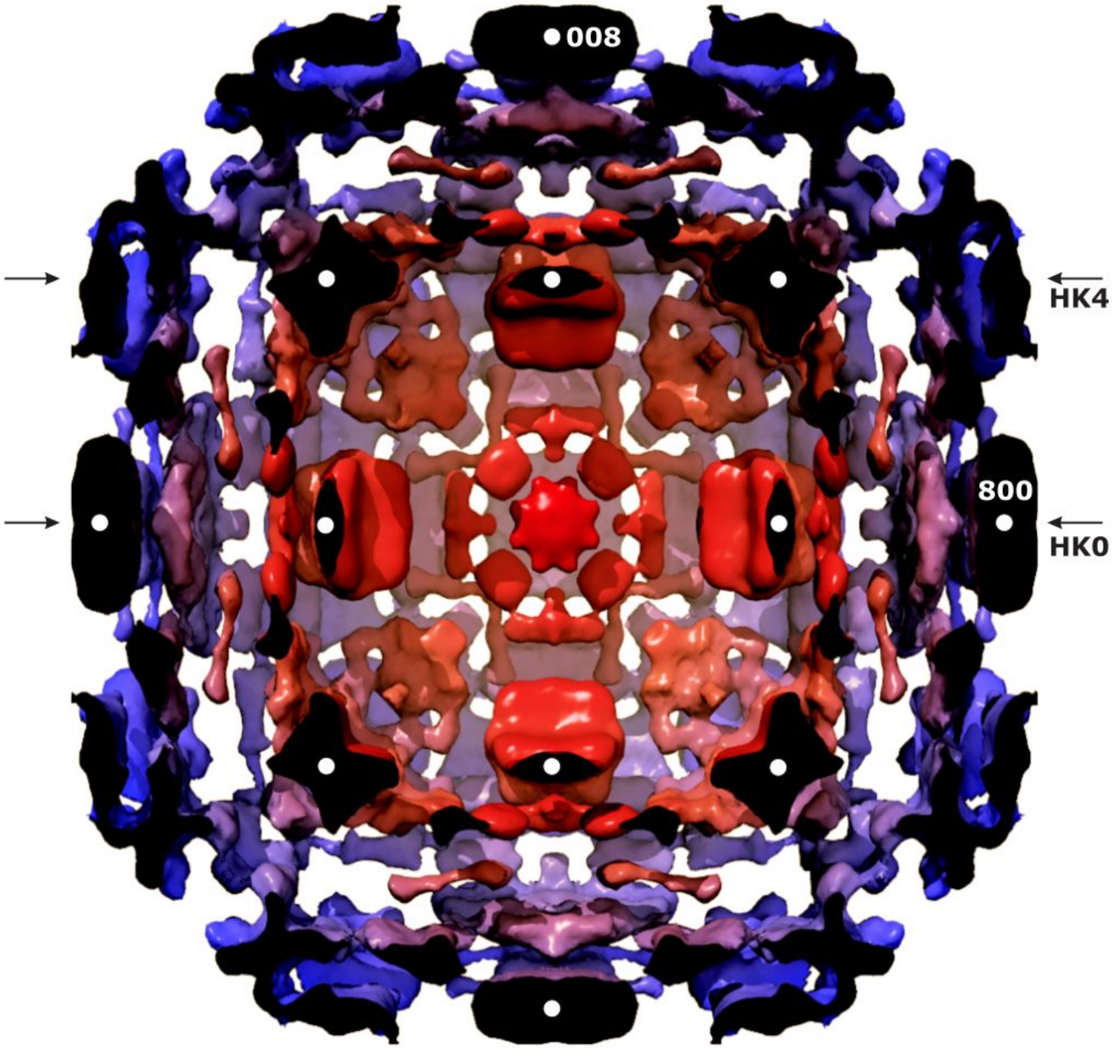
S. M. Shapiro, M. Iizumi, and G. Shirane, Phys. Rev. B 14, 200 (1976)

**Neutron diffuse scattering centered at zero energy (central peak) is coupled with transverse acoustic (TA) phonons**

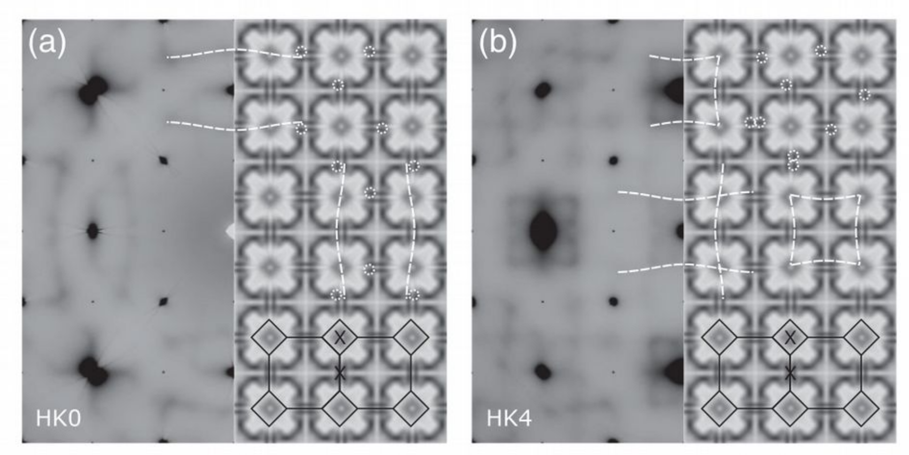
# X-ray diffuse scattering (ID28, ESRF)



# X-ray diffuse scattering (ID28, ESRF)



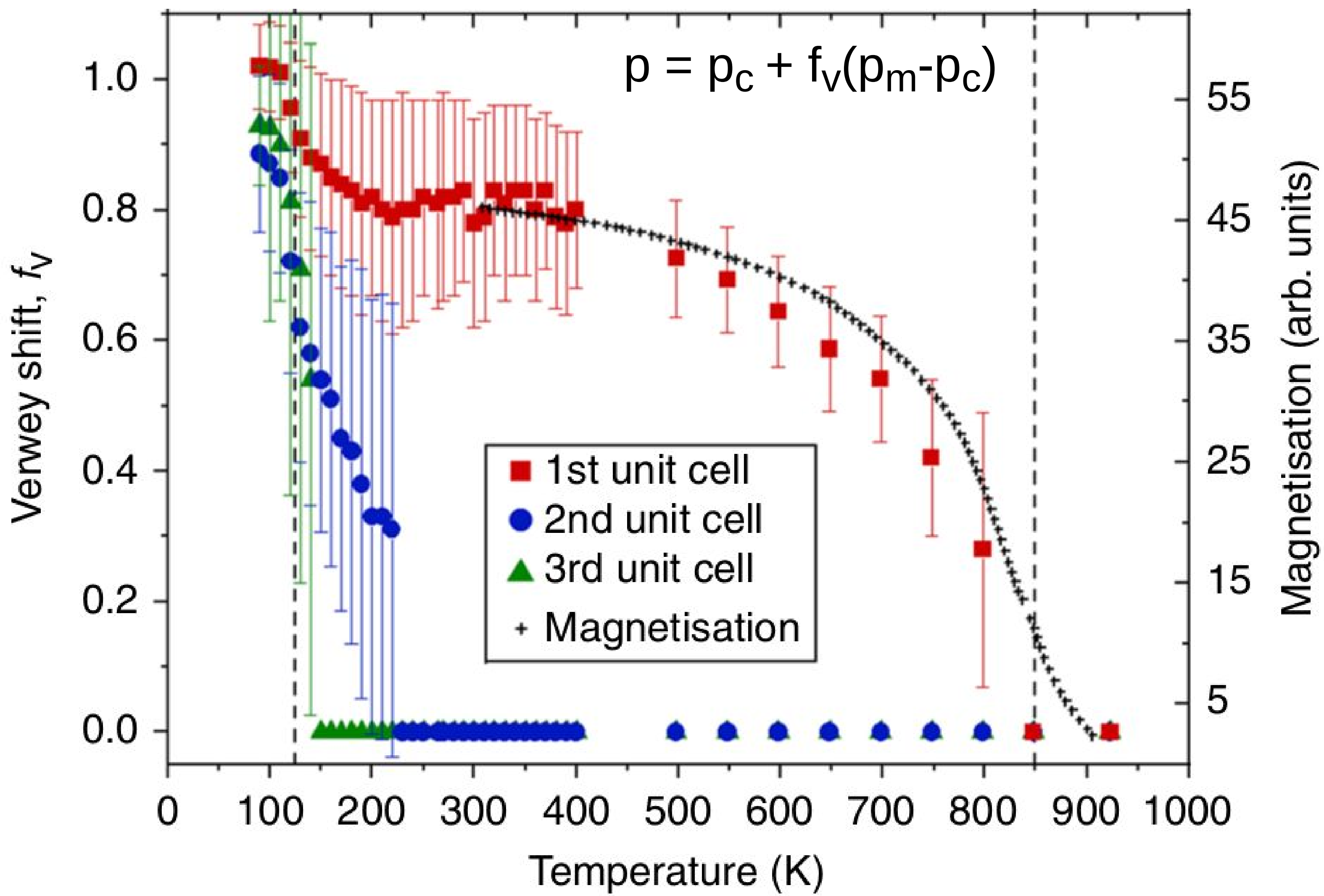

$q = 2k_F$




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)

# Short-range fluctuations up to $T_C$

**The structural fluctuations responsible for the Verwey transition emerge with the long-range magnetic order below the Curie transition and scale with the magnetisation**




G. Perversi, E. Pachoud, J. Cumby, J. M. Hudspeth, J. P. Wright, S. A.J. Kimber and J. P. Attfield, Nature Communications 10, 2857 (2019)

# Lattice dynamics

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

- crystal structure optimization (DFT, VASP)

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

- Hellmanna-Feynman forces

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

- force constants matrix (Phonon)

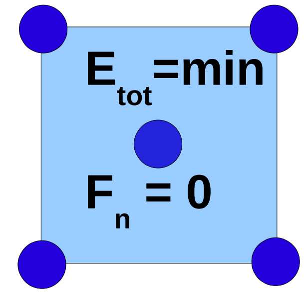
  $F_i(\mu) = - \Sigma\, \Phi_{ij}(\mu,\nu)u_j(\nu)$

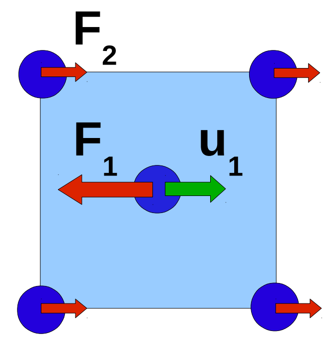
- dynamical matrix $\Phi(\mu,\nu) \Rightarrow D(k,\mu,\nu)$

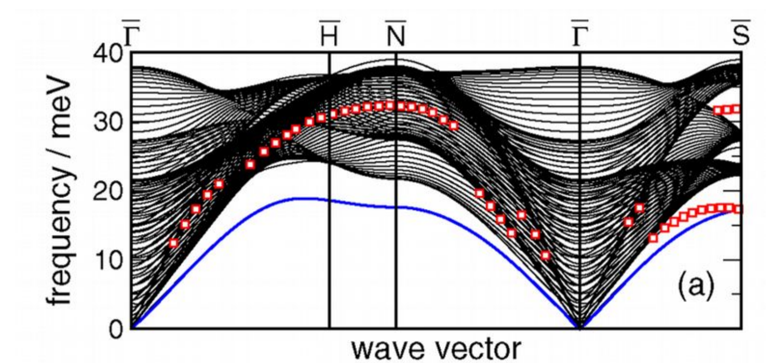
- dispersion curves, polarisation vectors, DOS

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

Method has been applied to bulk crystals, surfaces, nanostructures, disordered systems




Phonon dispersions at Fe(110) surface

# Phonons in magnetite

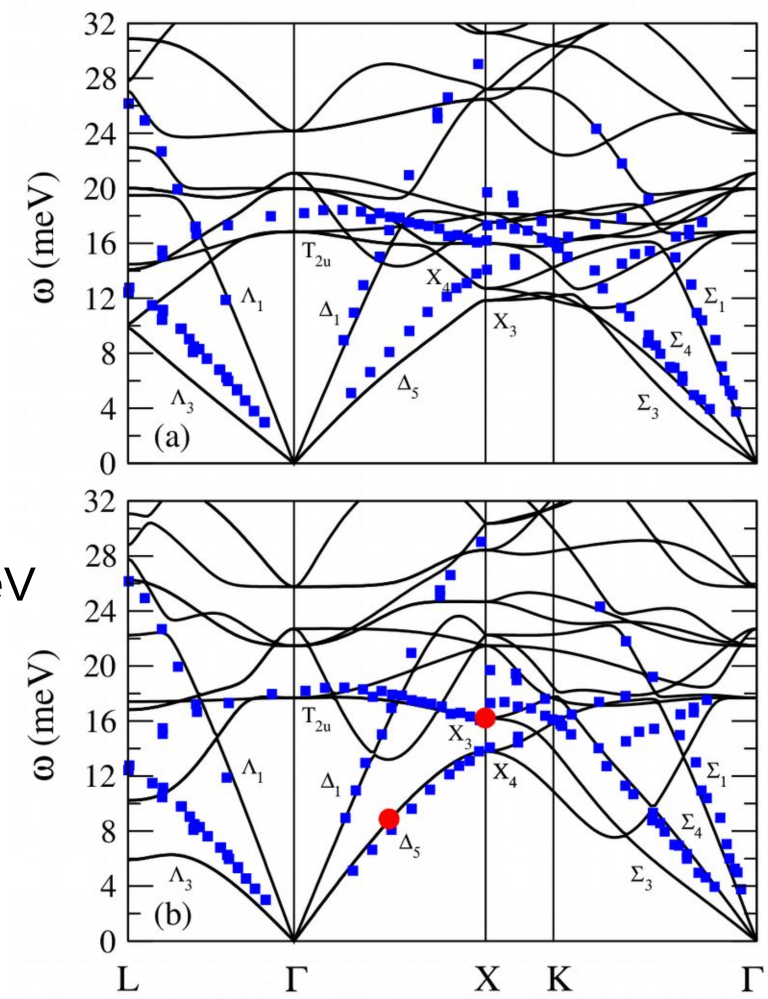
P. Piekarz, K. Parlinski, A. M. Oleś, Phys. Rev. Lett. 97, 156402 (2006), Phys. Rev. B 76, 165124 (2007)

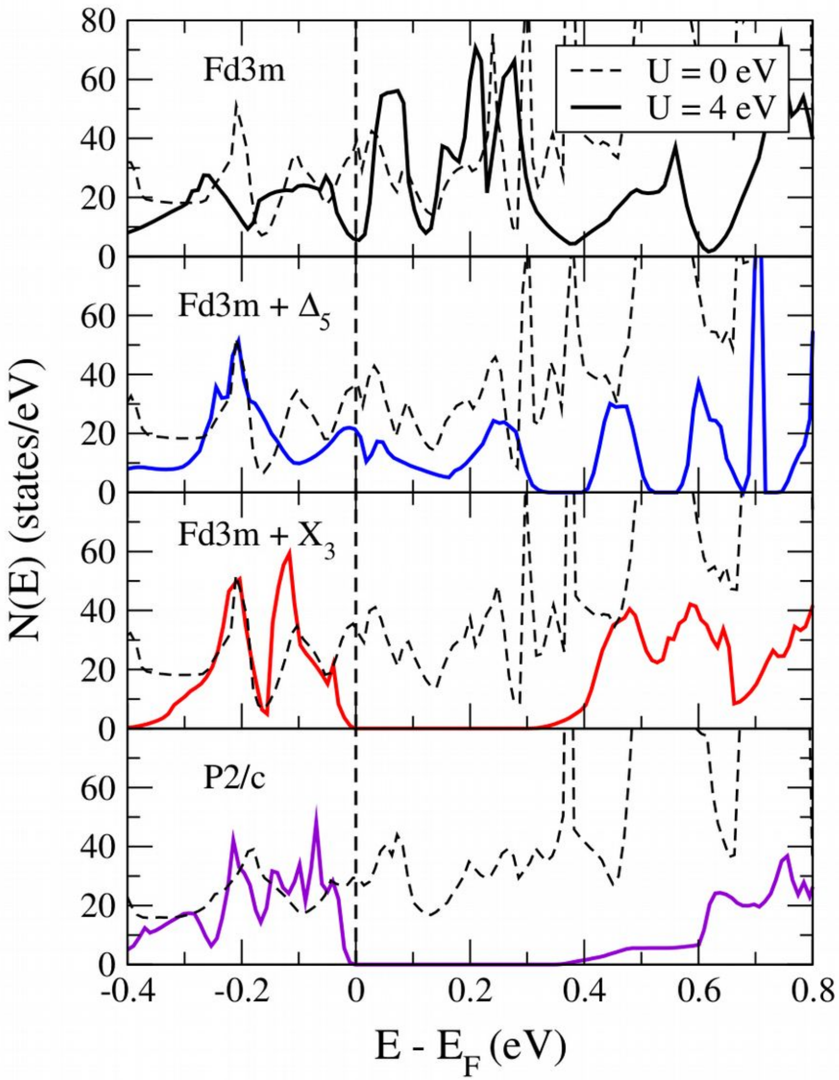
DFT, VASP, LDA+U, U = 4 eV, J = 0.8 eV

Fd-3m → $X_3 + \Delta_5$ → P2/c

U = 0

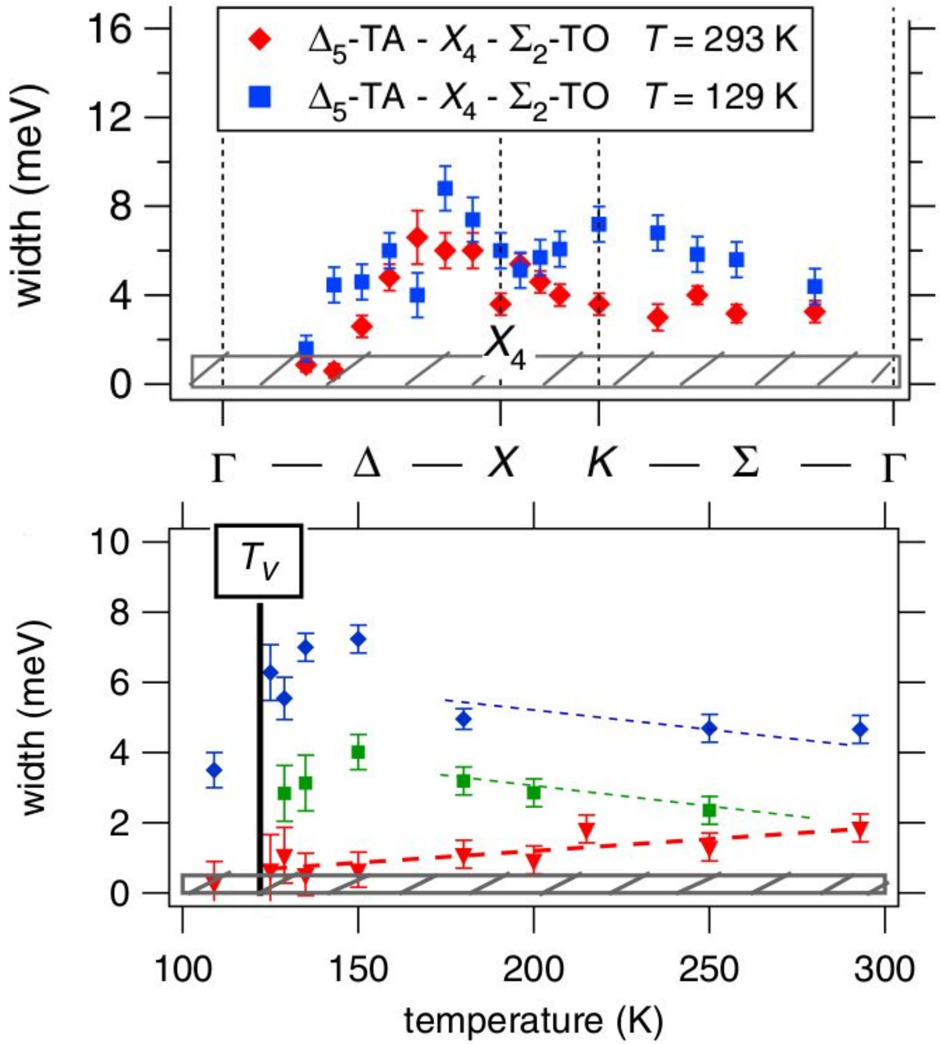
U = 4 eV

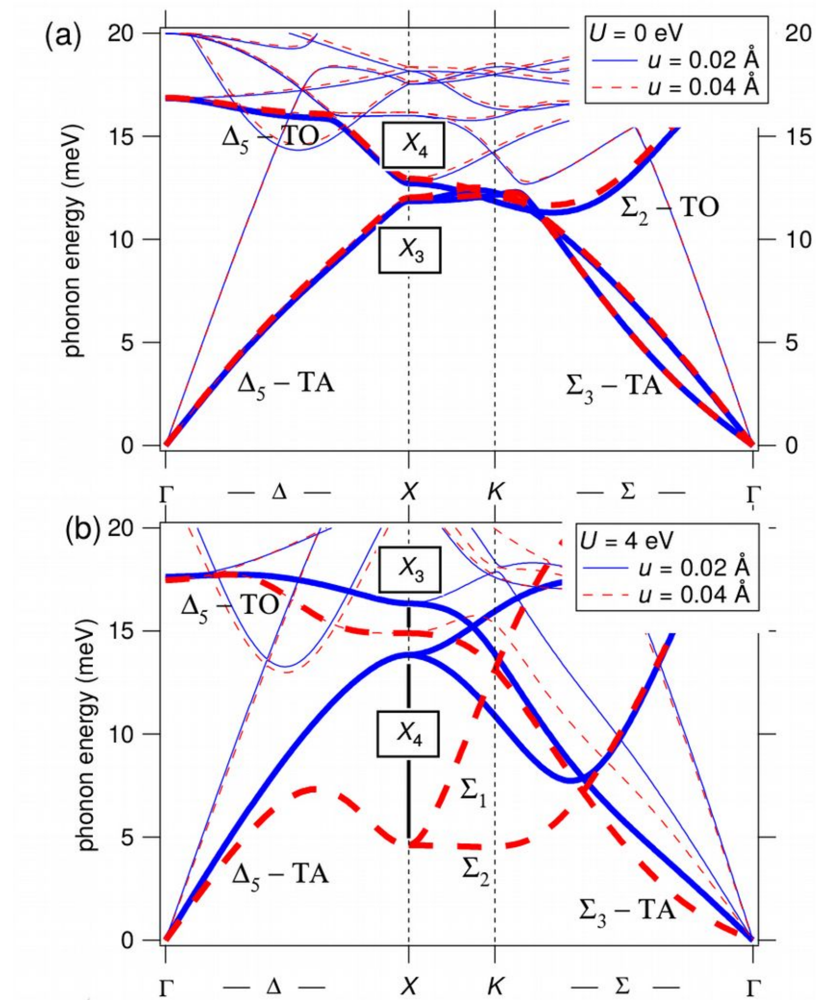



INS E. J. Samuelsen and O. Steinsvoll, Phys. Status Solidi B 61, 615 (1974)

# Inelastic X-ray scattering (ID28, ESRF)



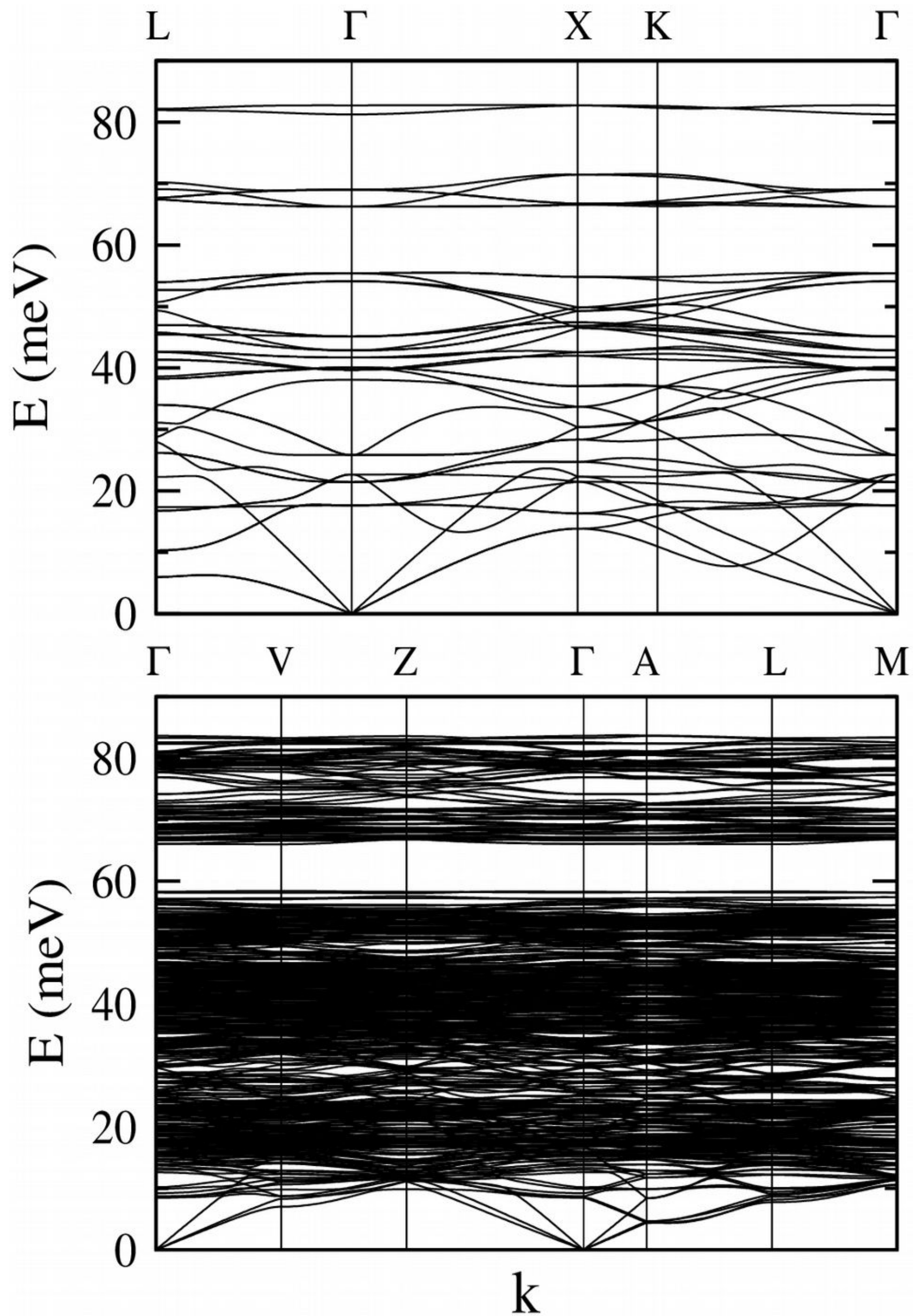




**anomalous phonon broadening**

**strong anharmonicity induced by electron-phonon coupling**

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

# Dispersion relations in Cc structure



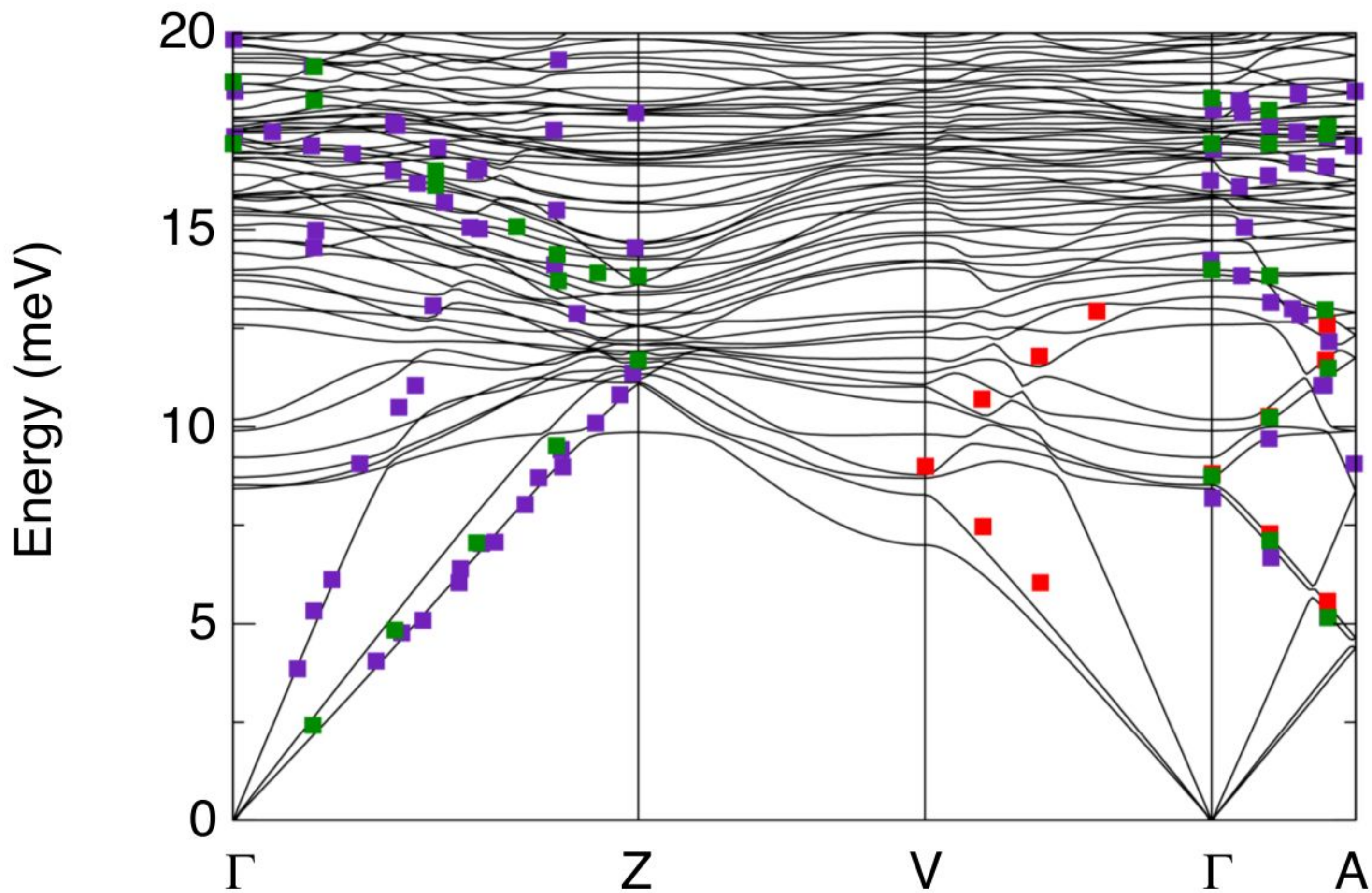

**Fd-3m**

56 atoms in supercell
14 atoms in primitive cell
42 phonon dispersions

**Cc**

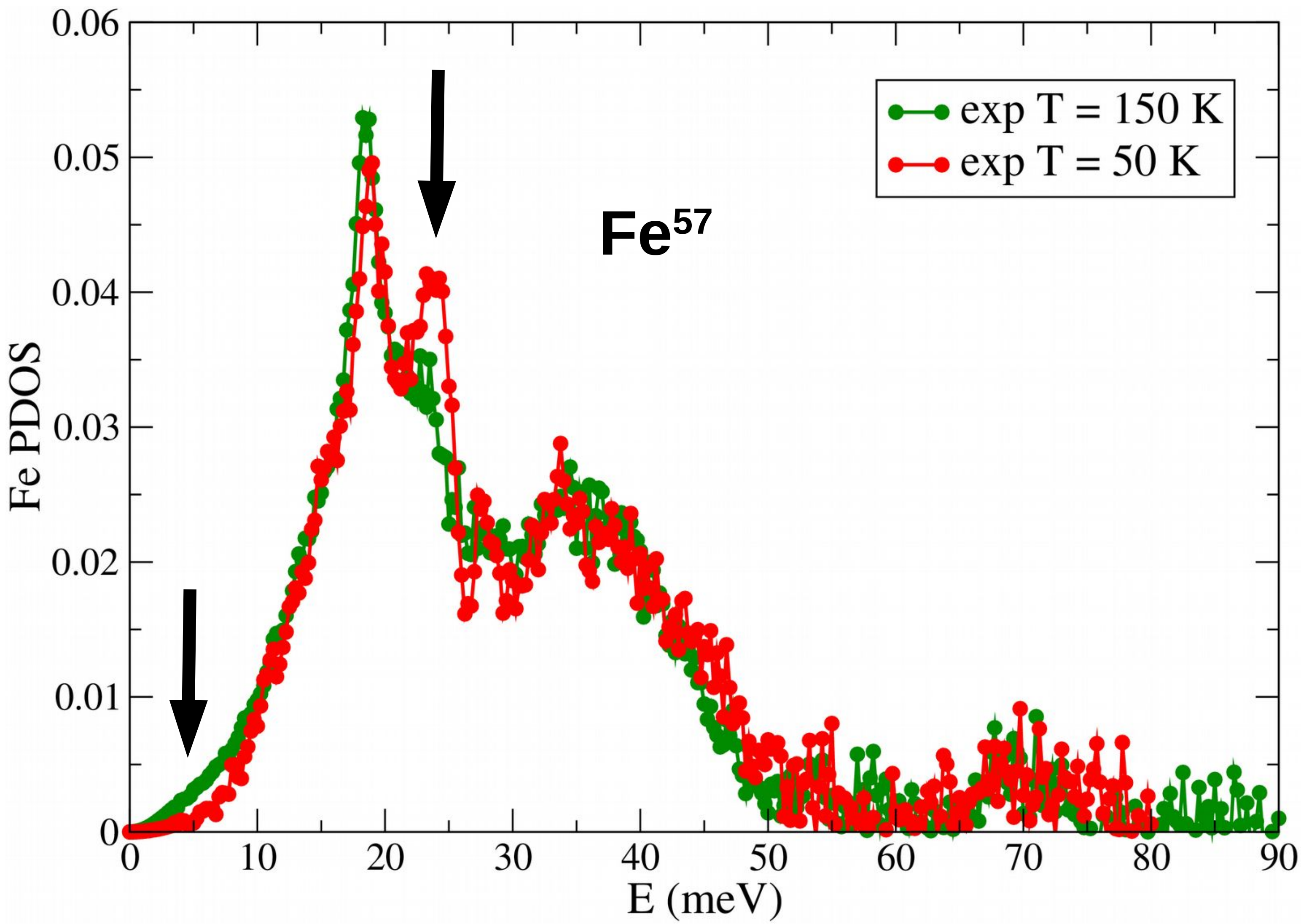
224 atoms in supercell
112 atoms in primitive cell
336 phonon dispersions

# Dispersion relations in Cc structure




INS T>$T_V$ (violet)  E. J. Samuelsen and O. Steinsvoll, Phys. Status Solidi B 61, 615 (1974)
INS T<$T_V$ (red)  S. Borroni, et al., New J. Phys. 19, 103013 (2017)
IXS T>$T_V$ (green)  M. Hoesch, et al., Phys. Rev. Lett. 110, 207204 (2013)

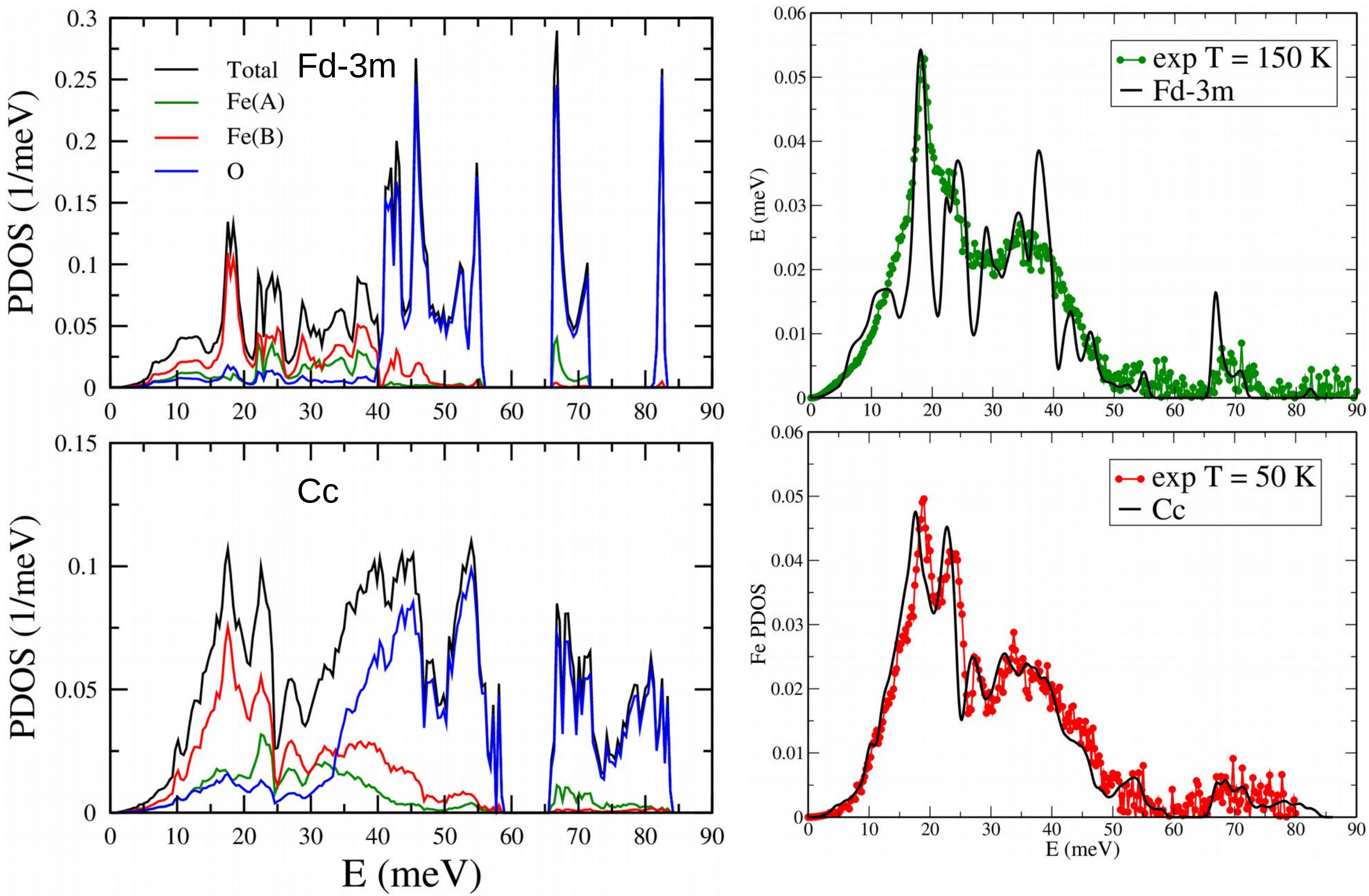
# Nuclear inelastic scattering (ID18, ESRF)



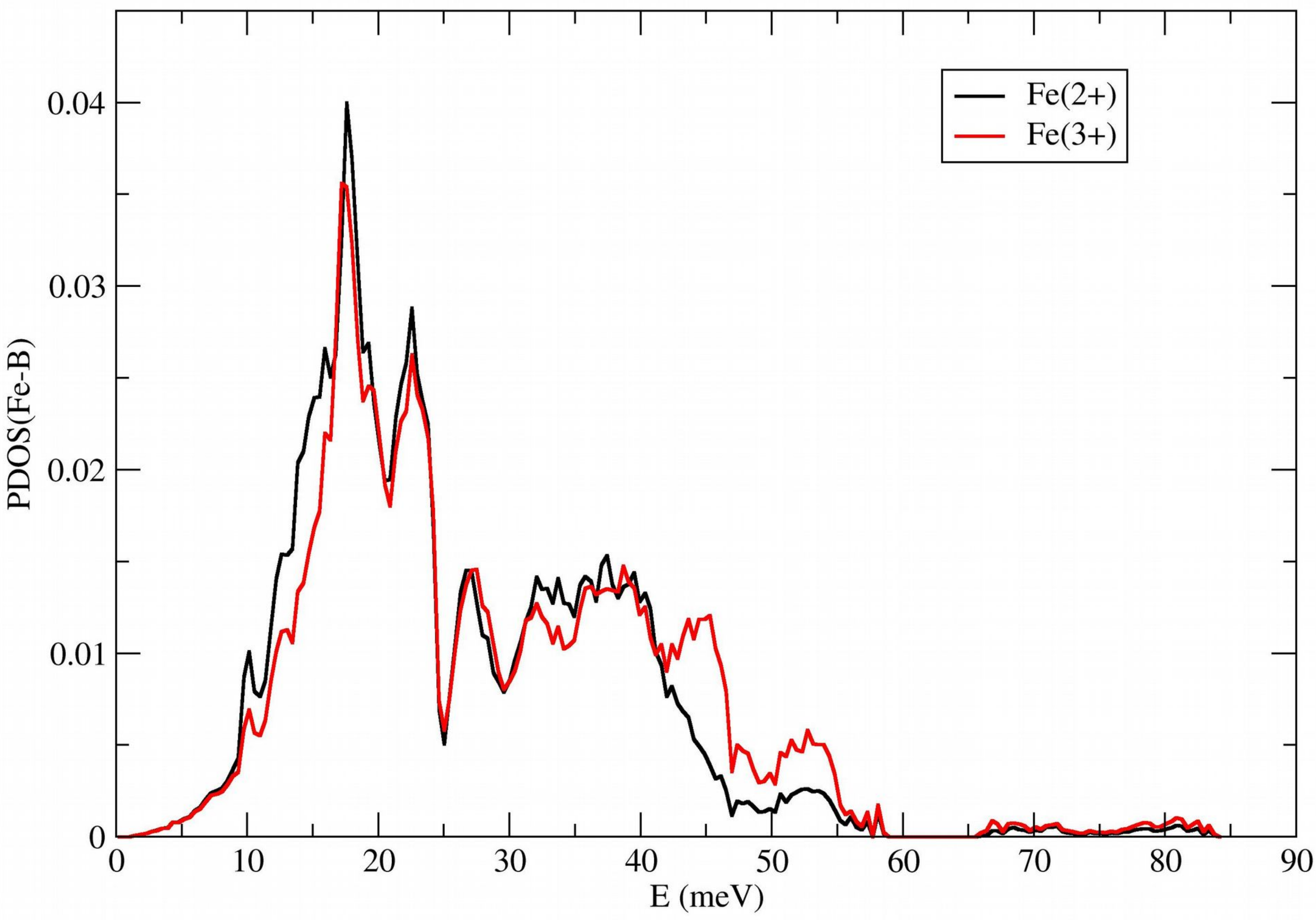

B. Handke, A. Kozłowski, K. Parlinski, J. Przewoźnik, T. Ślęzak, A. I. Chumakov, L. Niesen, Z. Kąkol, and J. Korecki, Phys. Rev. B 71, 144301 (2005)

T. Kołodziej, A. Kozłowski, P. Piekarz, W. Tabiś, Z. Kąkol, M. Zając, Z. Tarnawski, J. M. Honig, A. M. Oleś, K. Parlinski, Phys. Rev. B 85, 104301 (2012)

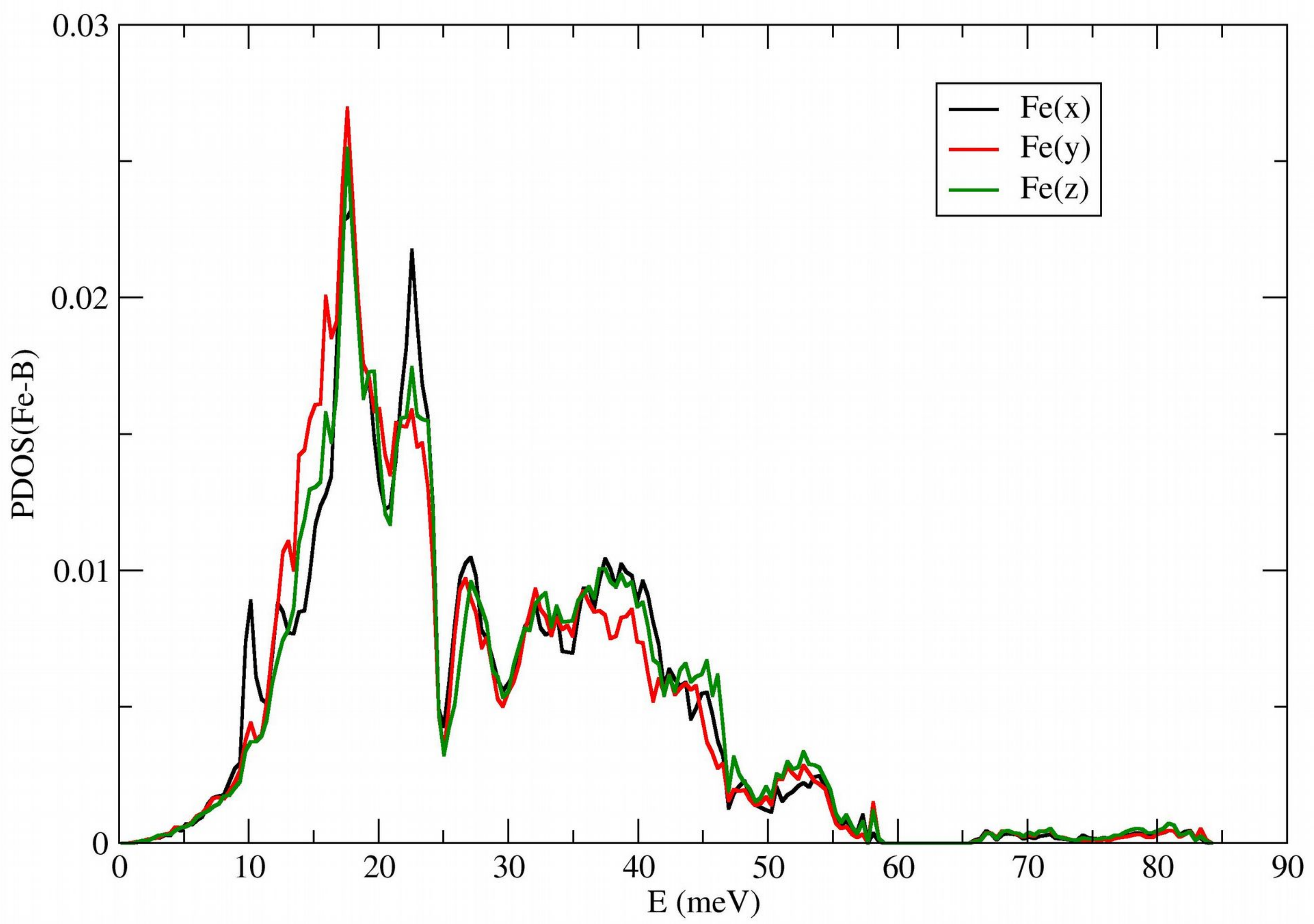
# Phonon Fe DOS Fd-3m vs Cc



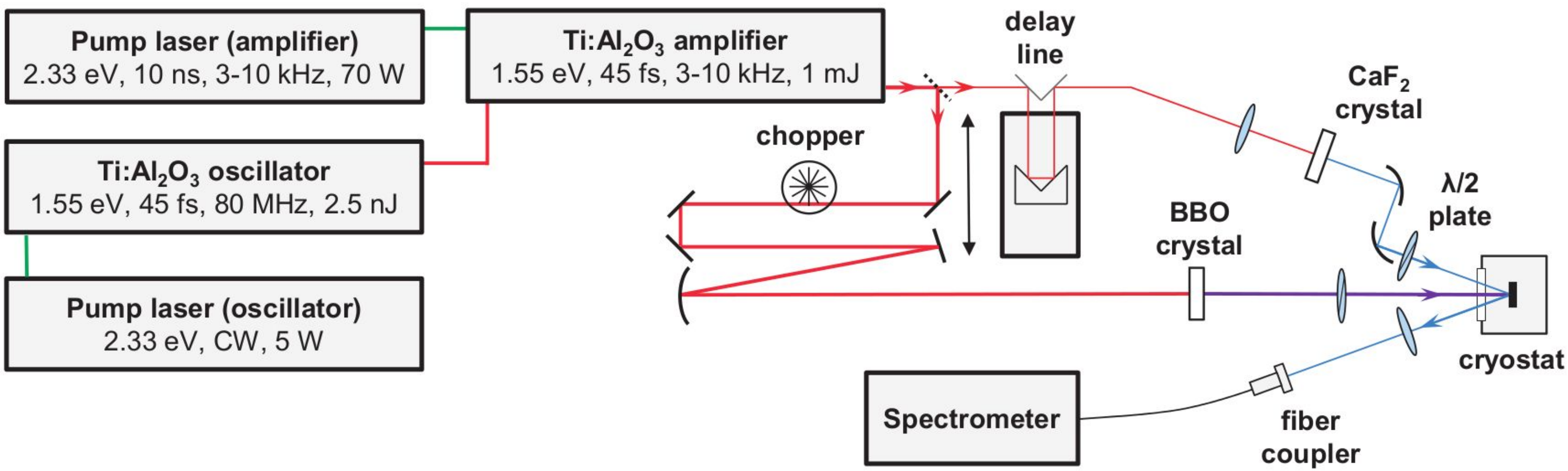
# Phonon Fe DOS Cc Fe2+ vs Fe3+



# Phonon Fe DOS Cc x, y, z



# Pump-probe experiment (EPFL)

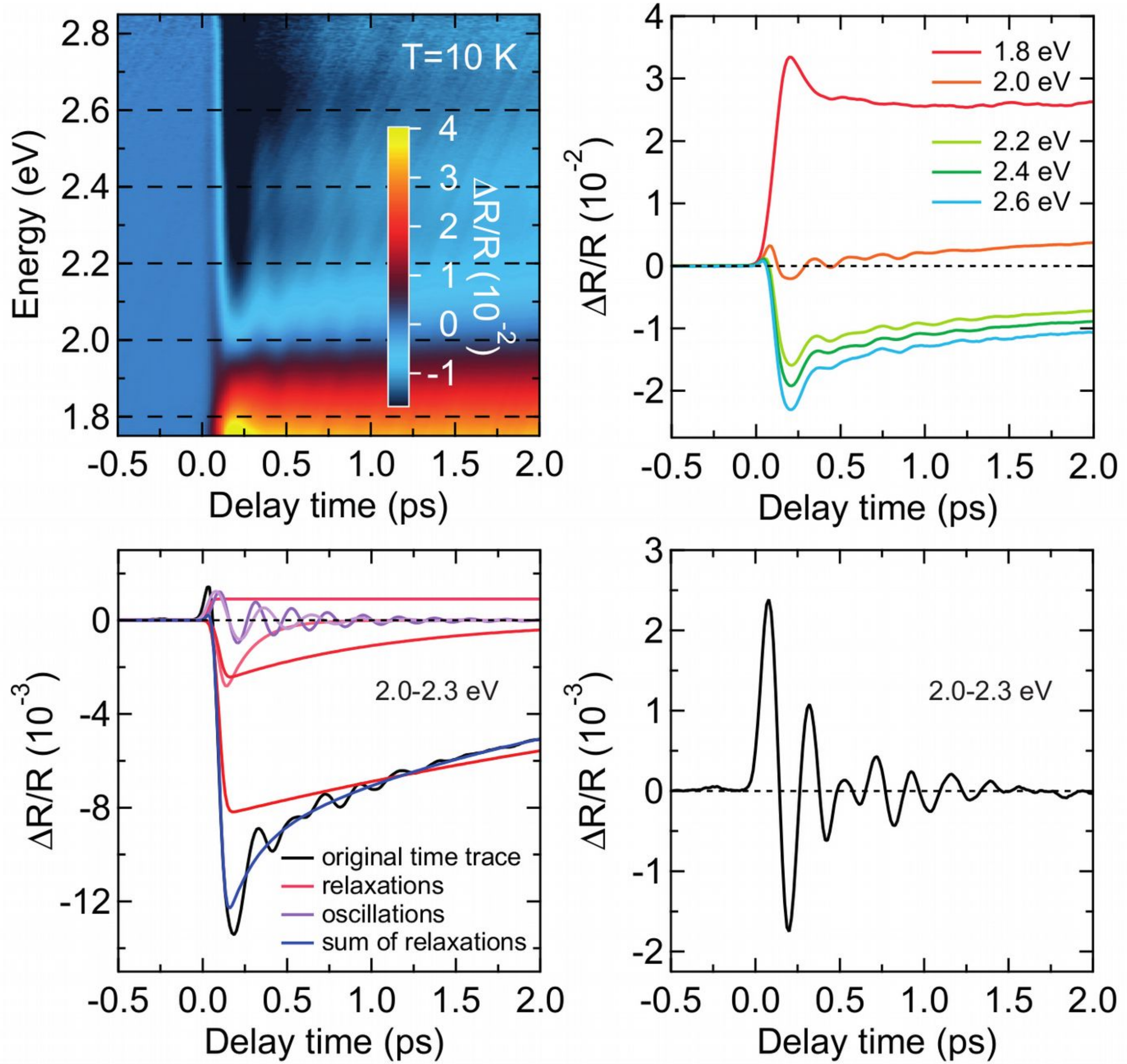



**The pump-probe ultrafast spectroscopy scheme.**
A sequence of laser pulses, the pump pulses, is sent to the sample. To measure the consequent response, delayed replica of the pump pulses, the probe pulses, are also sent to the sample, in a small spot wherein the intensity of the pump pulses is homogeneous. The repetition rate and the fluence, i.e. the energy per unit area, of the pump pulses are chosen so that the sample returns to equilibrium between consecutive pump pulses. Therefore, for a given time delay between pump and probe pulses, all probe pulses measure an identical state of the sample. After enough statistics on the probe pulses is collected, the time delay between pump and probe pulses is changed, to progressively construct a sequence of data points, representative of the dynamics upon impulsive photoexcitation.

Simone Borroni, Ph.D. Thesis, “New Insights into the Verwey Transition in Magnetite” (2018)

# Pump-probe experiment (EPFL)

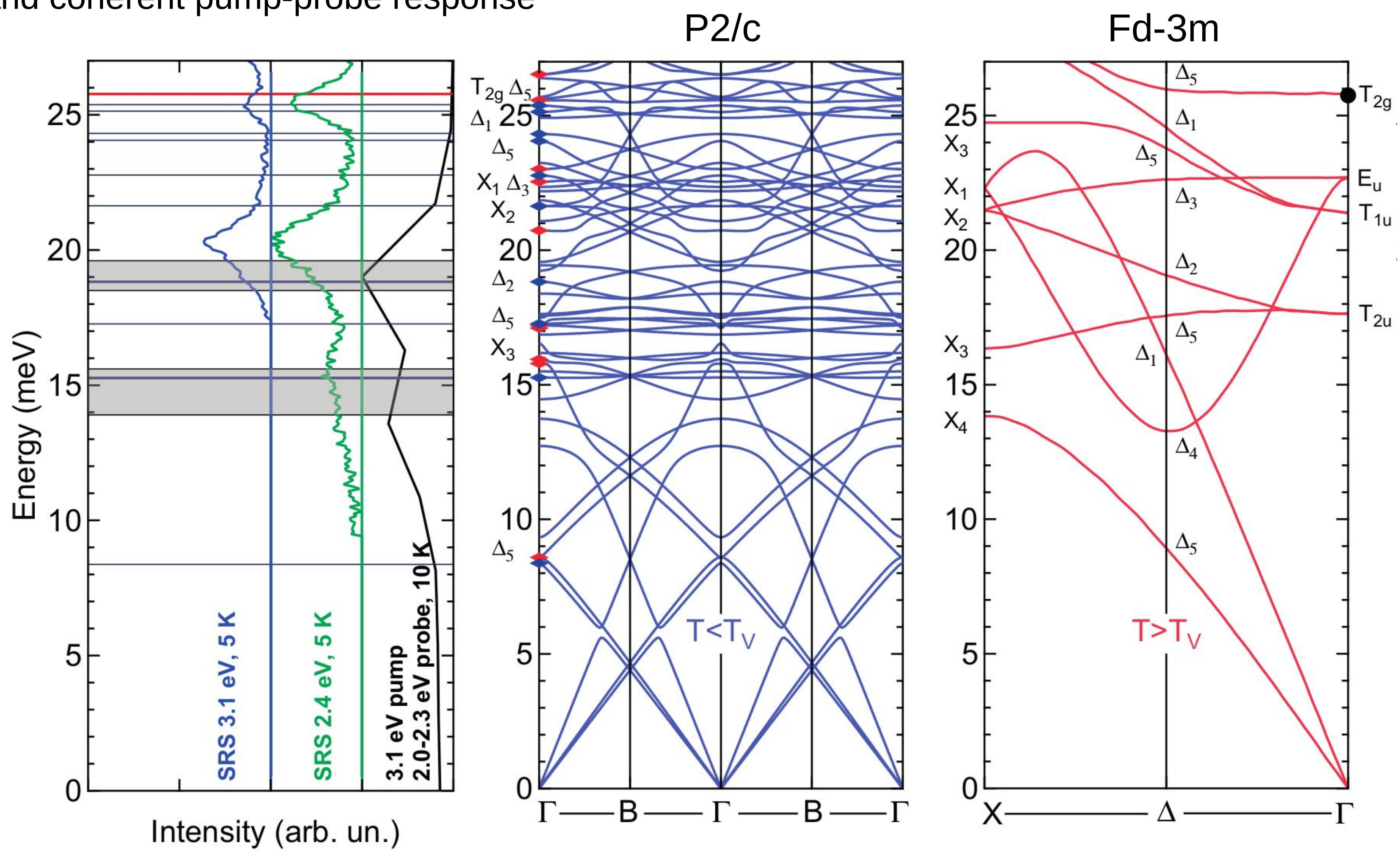
Differential reflectivity as a function of pump-probe delay time and probe photon energy



# Raman modes

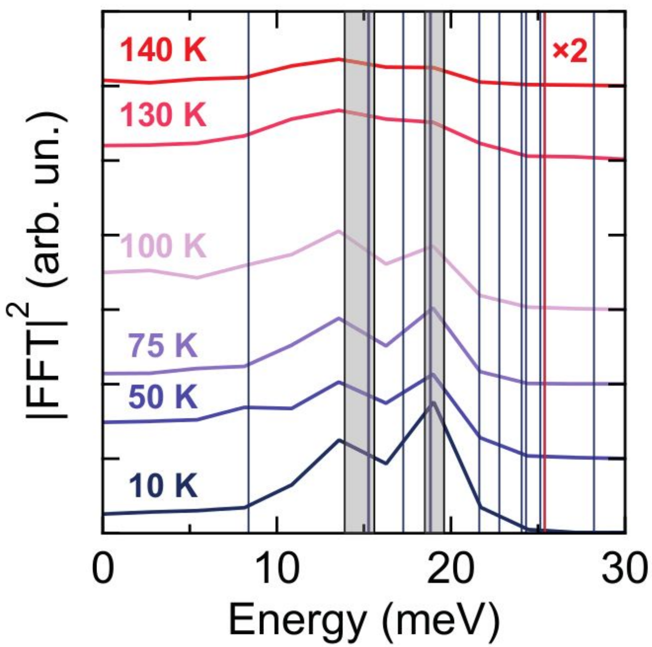
Spontaneous Raman spectra (SRS) and coherent pump-probe response

Ab initio DFT calculations

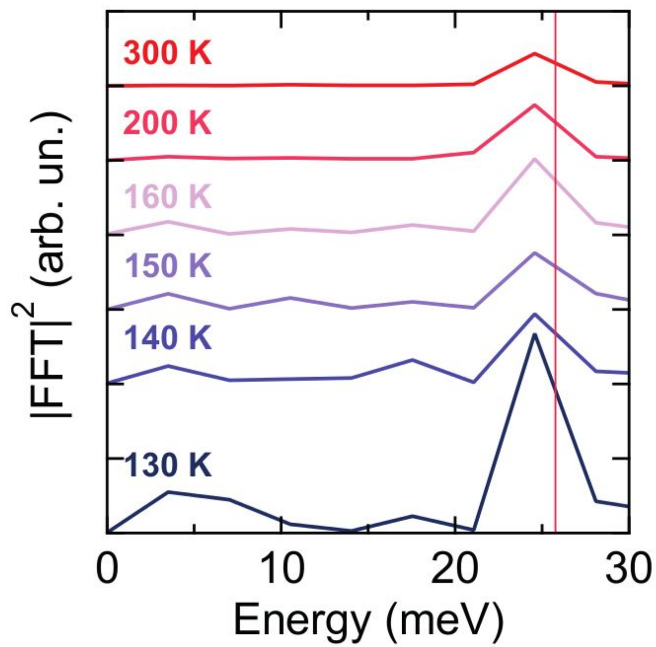


# Raman modes

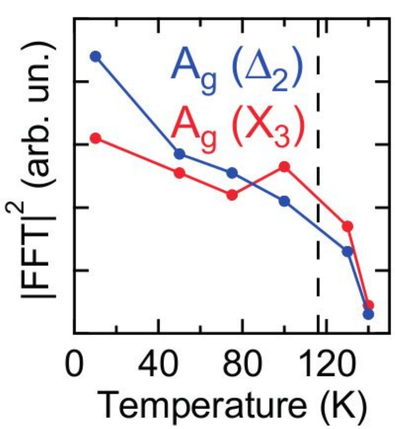
## $A_g$

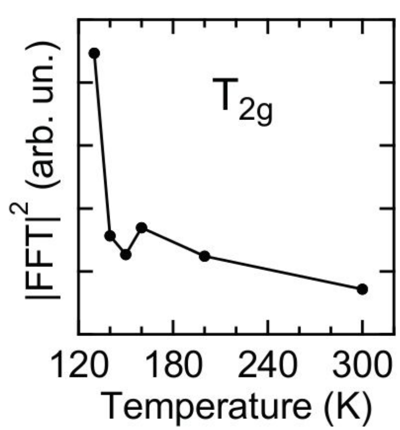



## $T_{2g}$




**Forbidden $A_g$ modes in cubic phase are observed above the Verwey temperature**

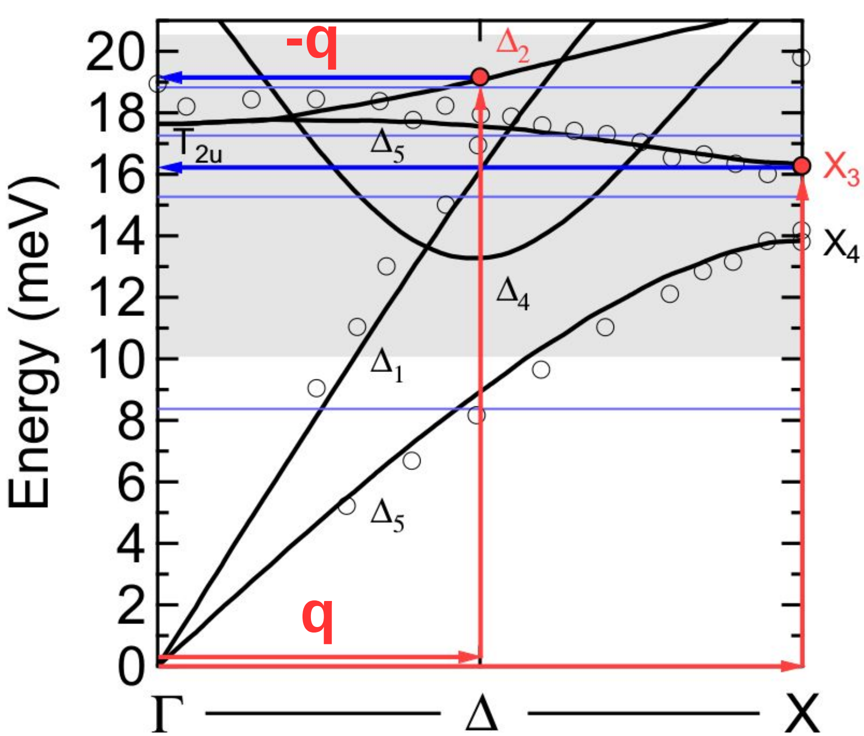


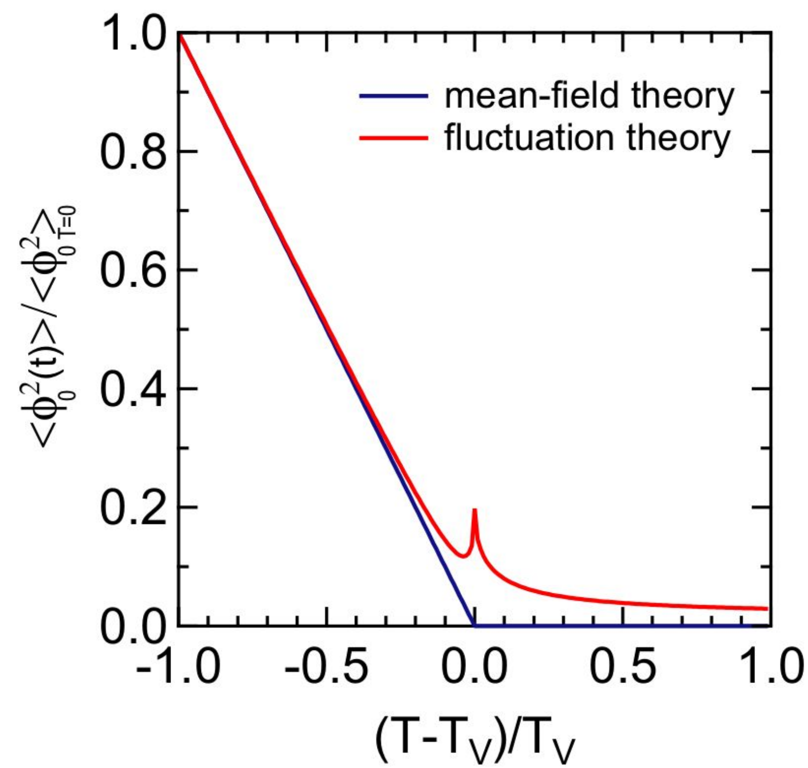




**$T_{2g}$ mode allowed in cubic phase**

A second-order Raman process takes place, in which an electronic mode of wave vector q is excited together with a phonon mode of wave vector −q, so that the total wave vector is conserved

**The coupling between lattice vibrations at finite momentum and fluctuations of the electronic ordering field above the Verwey transition in magnetite**



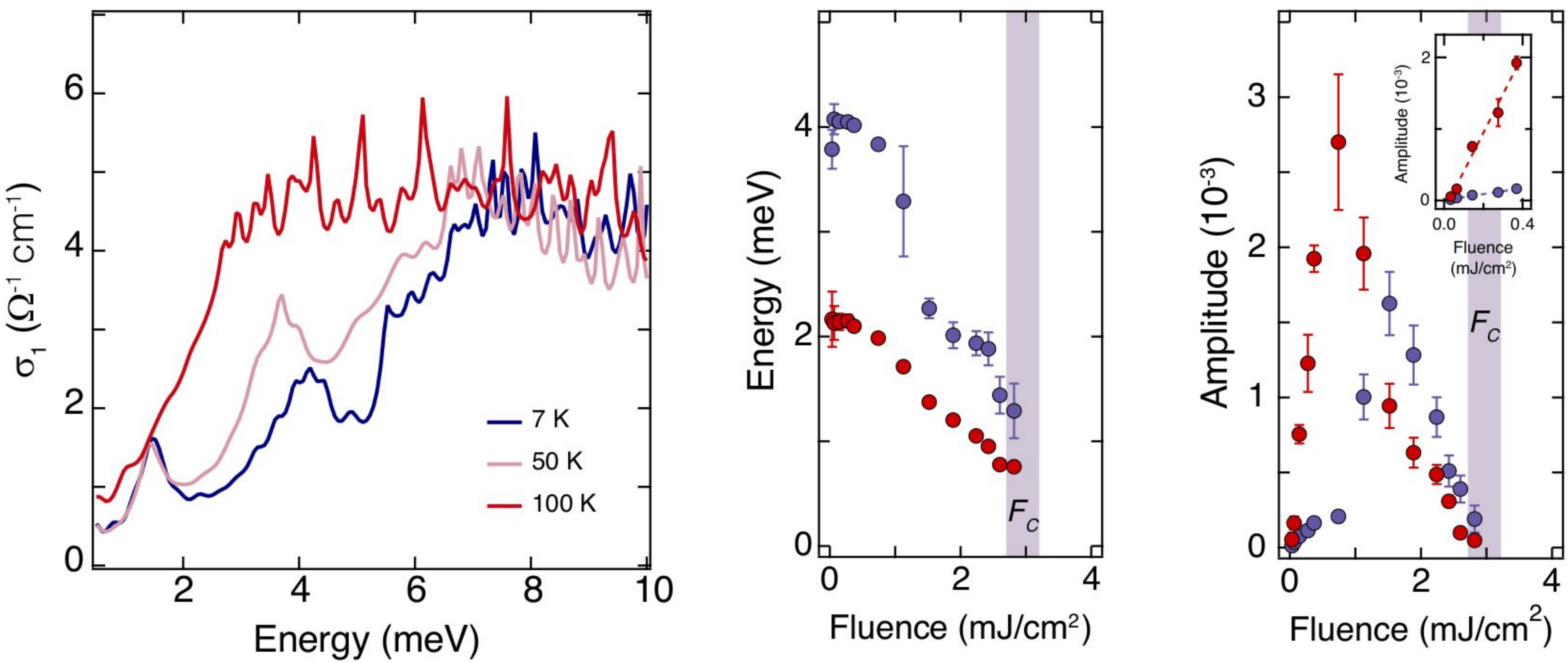




S. Borroni, E. Baldini, V. M. Katukuri, A. Mann, K. Parlinski, D. Legut, C. Arrell, F. van Mourik, J. Teyssier, A. Kozlowski, P. Piekarz, O. V. Yazyev, A. M. Oleś, J. Lorenzana, and F. Carbone, Phys. Rev. B 96, 104308 (2017)

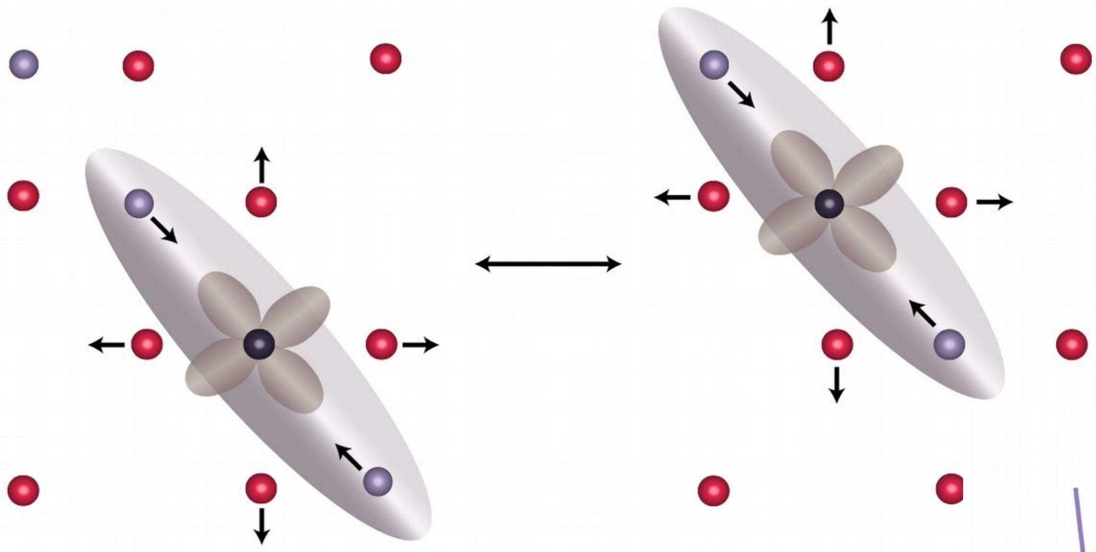
# Low-energy charge fluctuations (MIT)

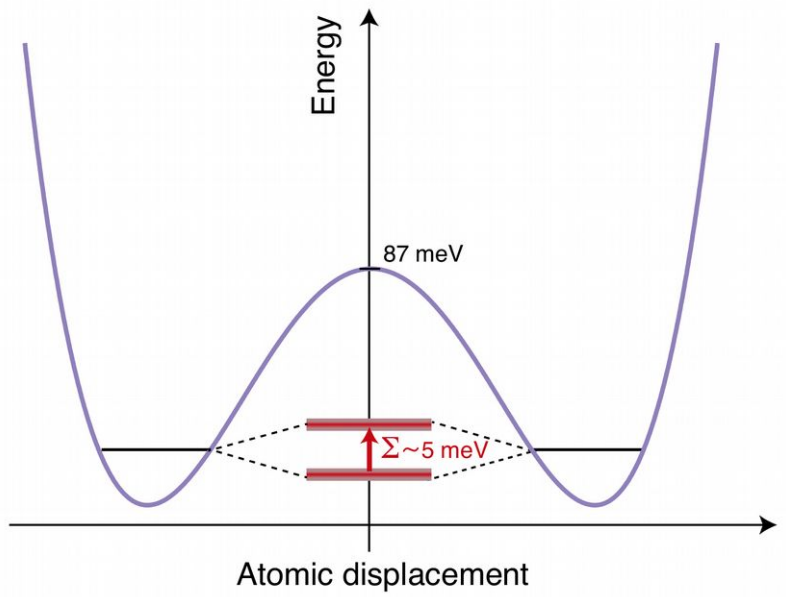
Spectroscopic signatures of the low-energy electronic excitations of the charge-orbital order (trimeron network) using terahertz light. By driving these modes coherently with an ultrashort laser pulse, we reveal their critical softening and hence demonstrate their direct involvement in the Verwey transition

**These findings represent the first observation of soft modes in magnetite and shed new light on the cooperative mechanism at the origin of its exotic ground state**



# Low-energy charge fluctuations (MIT)






$$\Sigma = 2t = 2t_0\, e^{-Ep/Eph} \sim 5\ \text{meV}$$

$t_0$ = 0.2 eV, $E_p$=87 meV, $E_{ph}$~20 meV


E. Baldini, C. A. Belvin, M. Rodriguez-Vega, I. O. Ozel, D. Legut, A. Kozłowski, A. M. Oleś, K. Parlinski, P. Piekarz, J. Lorenzana, G. A. Fiete, and N. Gedik, accepted in Nature Physics arXiv:2001.07815v1

# Conclusions

- DFT studies revealed strong electron-phonon coupling, which opens the gap and induces monoclinic distortion
- Inelastic X-ray scattering found anomalous phonon broadening above $T_V$ indicating anharmonic behaviour due to electron-phonon coupling
- X-ray diffuse scattering revealed new features at incommensurate q-points and short-range order in a wide range of temperatures
- Calculated phonon dispersion curves and phonon density fo states for the Cc structure show very good agreement with the experimental data
- Forbidden phonon modes (below 25 meV) can be induced above $T_V$ due to coupling with the critical fluctuations of the charge order
- New low-energy modes showing critical softening below $T_V$ were discovered by optical conductivity and “pump-probe” experiments

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