Lattice dynamics of Co-deficient and Fe-doped CoO

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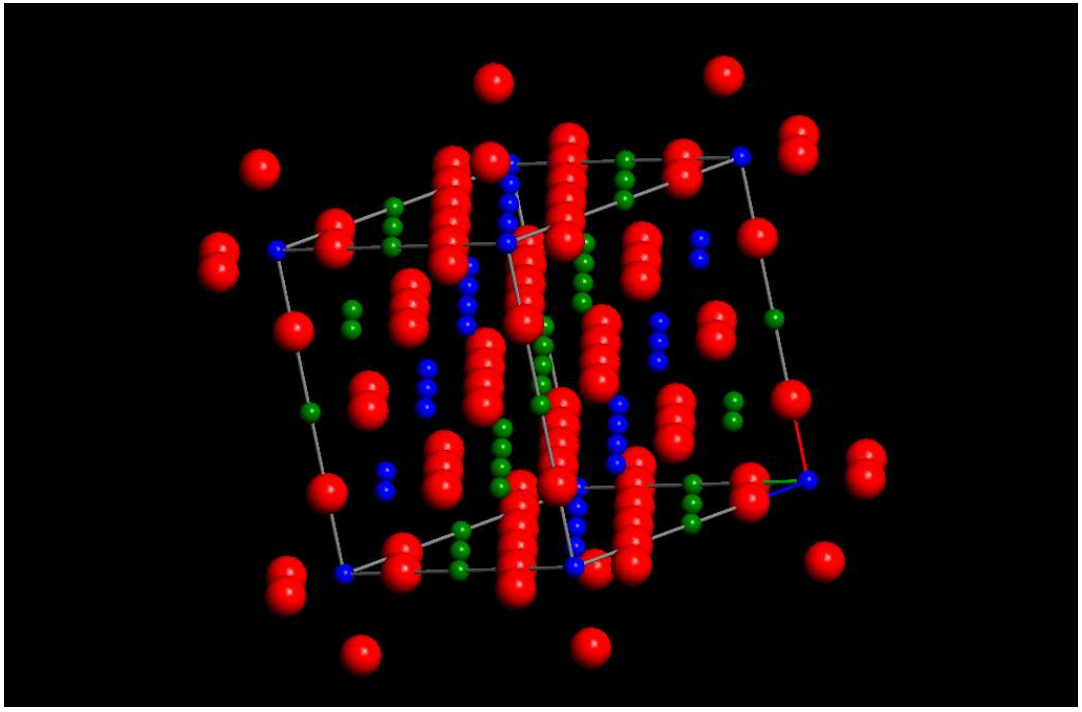
Perfect CoO



- HT - paramagnetic ($Fm\bar{3}m$) $a_{exp} = 4.26$ Å, $E_g = 2.5 - 2.8$ eV
- LT - small trigonal distortion along <111> below $T_N = 293$ K
  2^{nd} kind of AF ordering, AFII structure

Calculations with DFT+U

- Charge-transfer insulator
- DFT+U formalism required (strongly correlated electron system)
- Interactions between correlated states - U & J

VASP code

- spin-polarized DFT, PAW PP
- AFII structure (64-atom sc.)
- Exchange-interactions: GGA+U

U = 7.1 eV, J = 1 eV

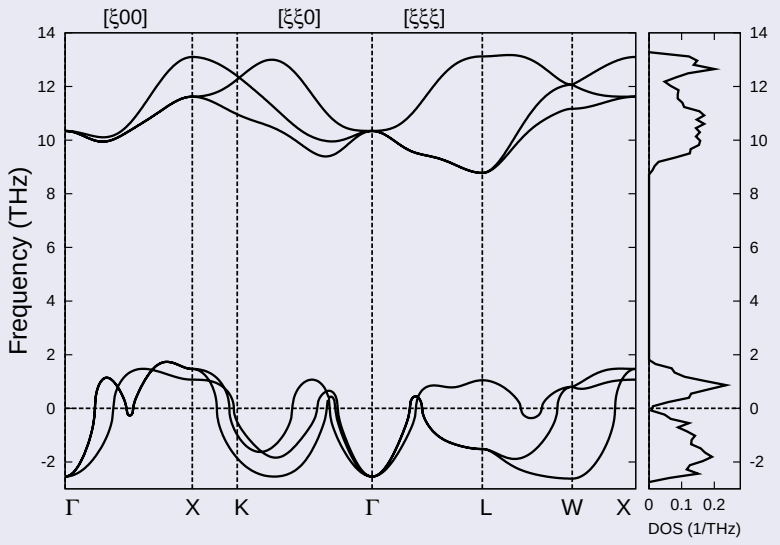
- Trigonal distortion of 0.3^o ($R\bar{3}m$)
- a = 4.27 Å, $E_g = 2.77$ eV

Phonons

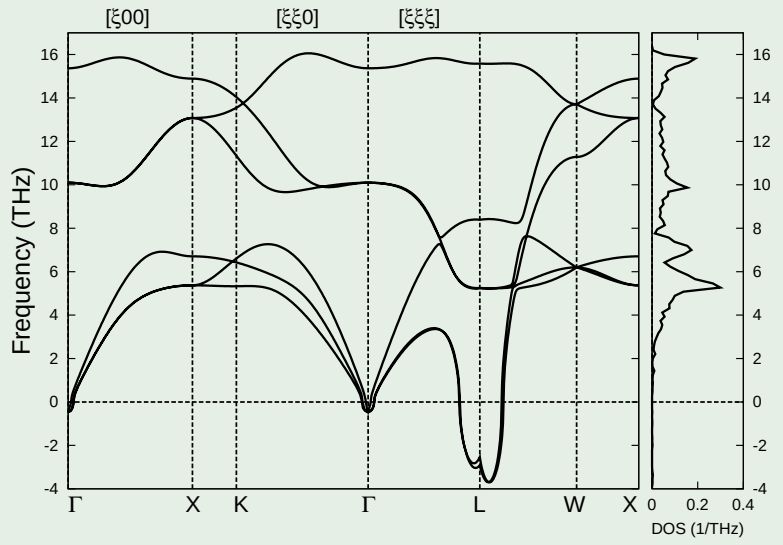
- Direct method - **PHONON** software by K. Parlinski
- Harmonic approximation

Phonon dispersion relations for U = 0 eV and U = 3 eV

U_{eff} = 0 eV



U_{eff} = 2 eV



- imaginary frequencies of acoustic modes ⇒ instability of CoO
- significant underestimation of HF forces ⇒ artificial mode softening
- small U_{eff} ⇒ too low repulsion in Co-3d shell

CoO with point defects

Cationic vacancies - native defects in CoO

- Co deficiency in 'almost stoichiometric' samples: 0.1-3%
- uncharged, singly and doubly charged vacancies
- nonstoichiometry depends on temperature and oxygen partial pressure

Simulation of point defects (vacancies, impurities)

- supercell approach
- remove atoms $\Rightarrow$ vacancies
- replace host atoms by different kind of atoms $\Rightarrow$ impurities

CoO with 3% vacancies/impurities

- Co @ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ removed from 64-atom supercell $\Rightarrow$ $Co_{0.97}O$
- Co @ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ replaced by Fe atom $\Rightarrow$ CoO + 3% Fe

Description of phonons within supercell

CoO

- primitive unit cell
  N = 2 $\Rightarrow$ 6 branches

CoO as 64-atom supercell

- N_S = 64 $\Rightarrow$ 192 branches ?

$Co_{0.97}O$

- supercell - already primitive unit cell
  N_S = 63 $\Rightarrow$ 189 branches

- dimensions of **D**(**k**) increase to $3N_S$
- number of phonon dispersion curves increases to $3N_S$
- size of BZ conjugated with supercell shrinks
- selection of a different kind of unit cell
  $\Downarrow$
  number of phonon dispersion curves is blown up

Phonon form factor and *filter*

Phonon form factor

$$F^{(p)}(\mathbf{k},j) = \frac{1}{\mathbf{k}^2}\left|\sum_\mu \frac{\mathbf{k}\cdot\mathbf{e}(\mathbf{k},j;\mu)}{\sqrt{M_\mu}}\right|^2$$

$$\int_\Omega d\Omega\, F^{(p)}(\mathbf{k},j) = \frac{1}{3}F^{(s)}(\mathbf{k},j)$$

Filter

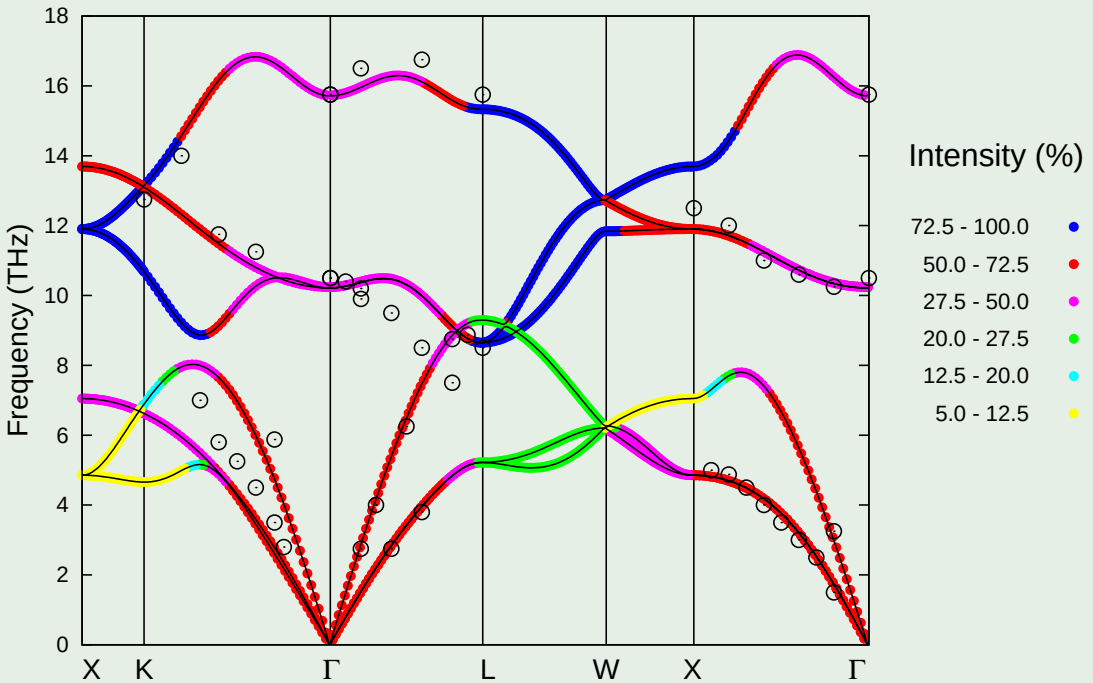
$$F^{(s)}(\mathbf{k},j) = \left|\sum_\mu \frac{\mathbf{e}(\mathbf{k},j;\mu)}{\sqrt{M_\mu}}\right|^2$$

Fake phonon modes

$$F^{(p)}(\mathbf{k},j) = 0$$

Application of filter to stoichiometric CoO

Intensities of modes for CoO



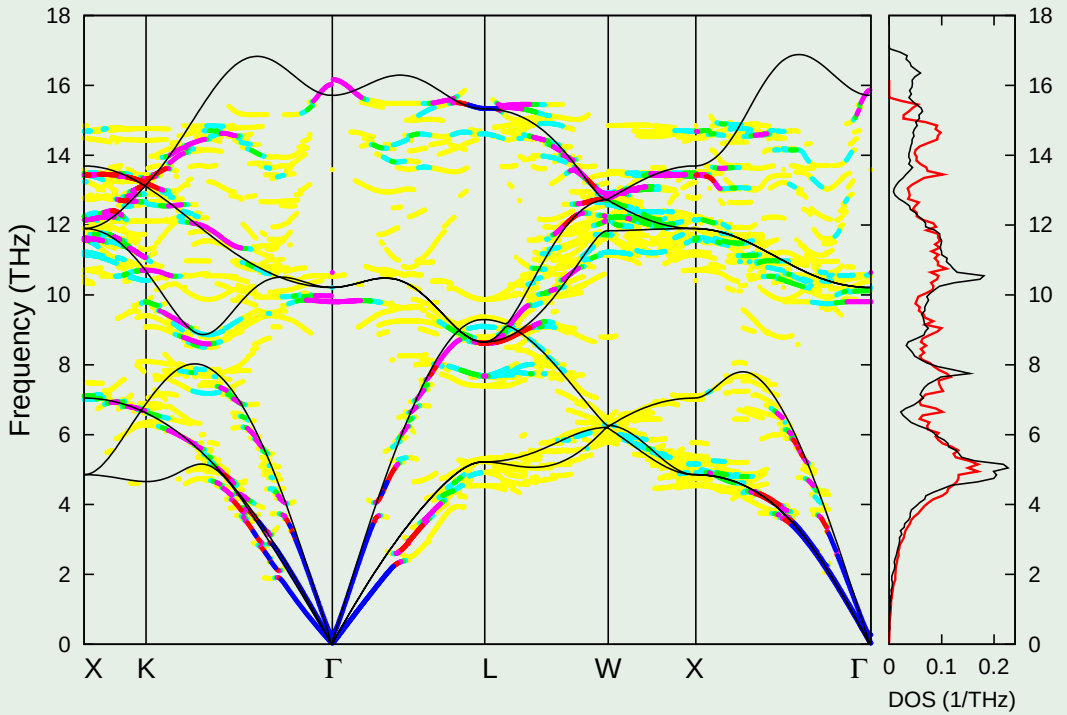
experimental data close to branches with intensities higher than 30%

Inelastic neutron scattering experiments

J. Sakurai, W.J.L. Buyers, R.A. Cowley, and G. Dolling, Phys. Rev. 167, 510 (1968)

Application of filter to non-stoichiometric CoO

$Co_{0.97}O$



acoustic branches at small **k** not affected by vacancies

⇓

long wavelength phonons insensitive to point defects

missing Co

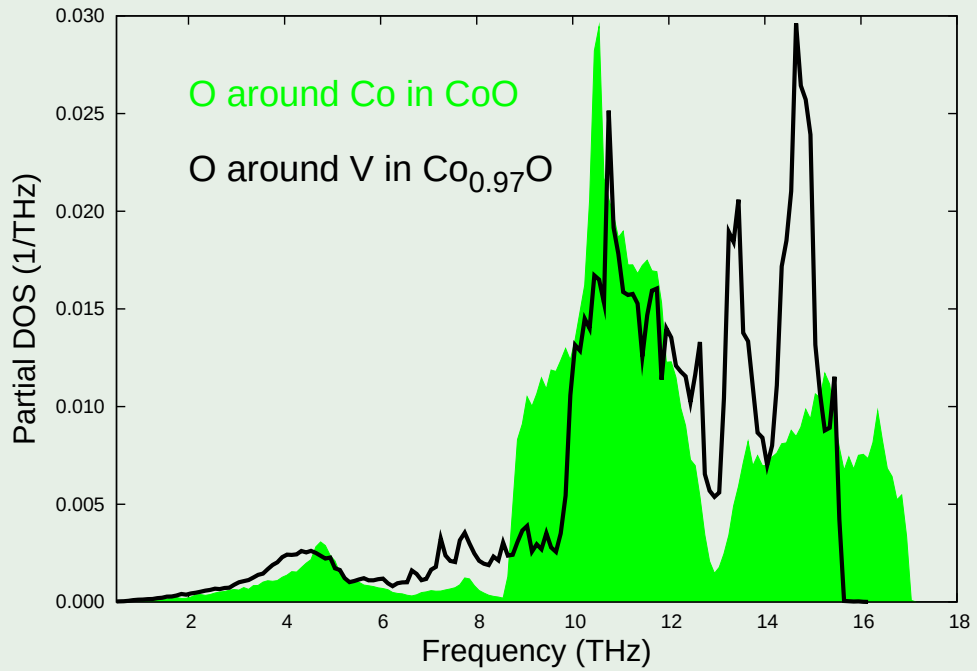
⇓

additional O vibrations (new modes)

perturbed phonons with wavelength $\sim$ size of region disturbed by vacancy

Oxygens surrounding vacancies

Partial phonon DOS



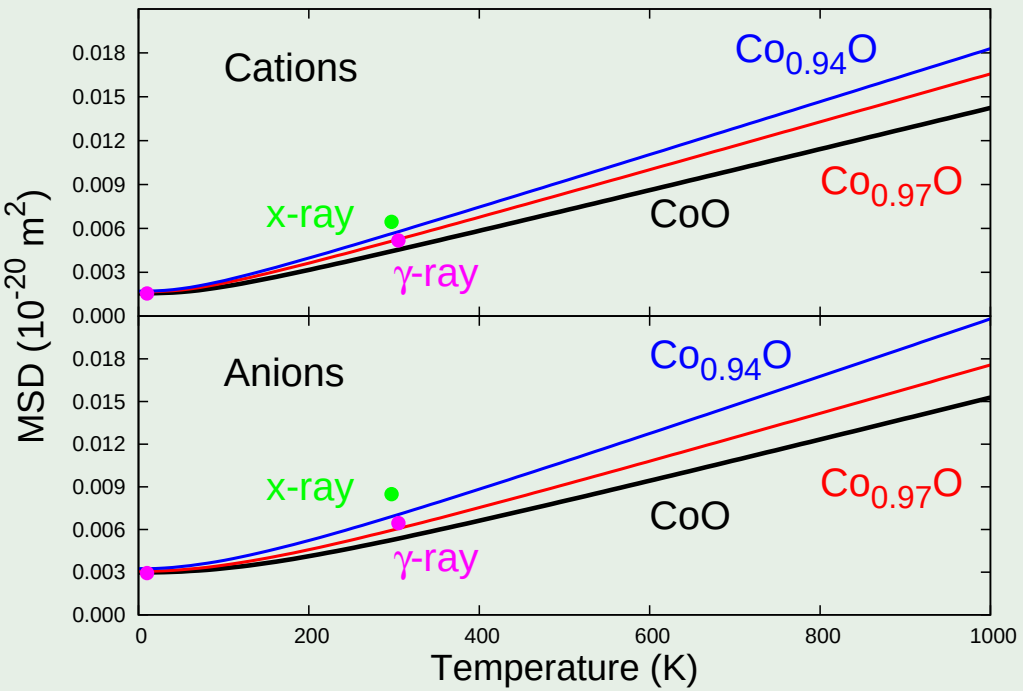
Γ-point frequencies (THz)

	ω_{TO}	ω_{LO}
CoO	10.25	15.73
$Co_{0.97}O$	9.81	15.87
$Co_{0.94}O$	9.61	16.08
Neutron	10.50	15.75
Infrared	10.50	16.40

- vacancies affect the highest frequency LO modes
- no change in low-frequency acoustic region

Mean-squared displacements vs temperature

Thermal vibrations of Co and O



Co and O at low T

- 5% larger MSD than in stoichiometric CoO
- negligible difference between $Co_{0.97}O$ and $Co_{0.94}O$

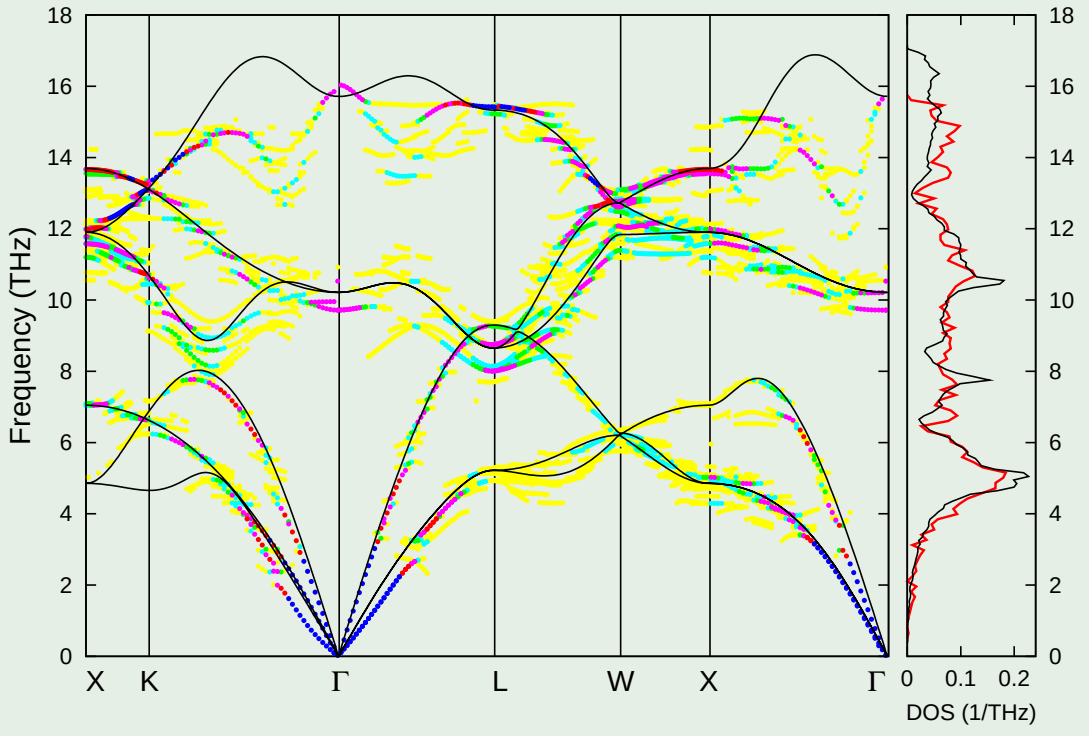
Co and O above RT

	Co	O
$Co_{0.97}O$	13%	19%
$Co_{0.94}O$	22%	23%

Experiment: W. Jauch *et al.* , PRB 65, 125111 (2002); S. Sasaki *et al.*, Proc. Jpn. Acad. B 55, 43 (1979)

Lattice dynamics of Fe-doped CoO

Dispersion curves $U_{Fe} = U_{Co} = 7.1$ eV



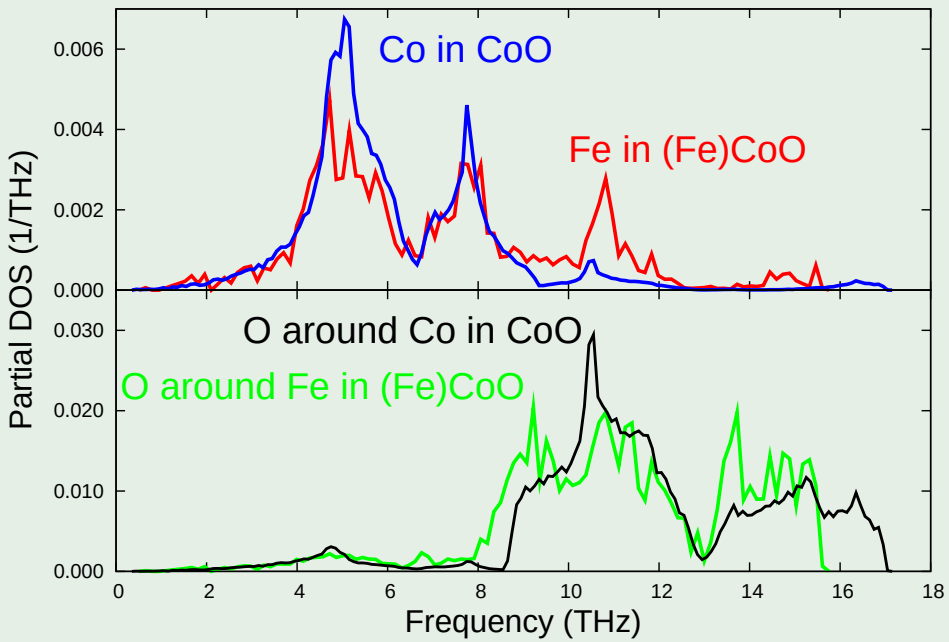
- additional modes
- mass defect negligible
- change in Φ_{ij} at Fe site
- Φ_{ij}(Co) = 160.4 N/m const. vs U_{Fe}

Force constant at Fe site

U_{Fe} (eV)	Φ_{ij} (N/m)
5.1	196.5
6.1	204.9
7.1	213.3

Dynamics of Fe impurity

Partial phonon DOS $U_{Fe} = U_{Co} = 7.1$ eV



Oxygens neighboring Fe

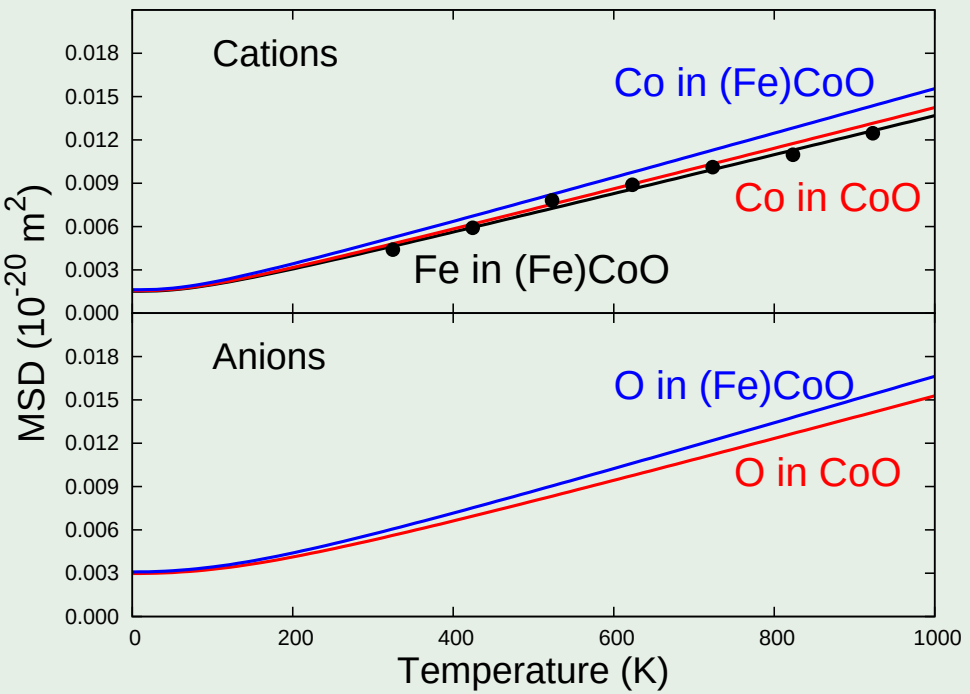
U_{Fe} (eV)	ω_{TO} (THz)
5.1	9.67
6.1	9.68
7.1	9.72

Splitting of ω_{TO} into modes corresponding to:

- oxygens vibrating around Co ω_{TO} = 10.51 THz (const. vs U_{Fe})
- oxygens vibrating around Fe ω_{TO} = 9.72 THz

Debye-Waller factors in Fe-doped CoO

Thermal vibrations of Co, Fe and O



Mőssbauer exp.: K. Ruebenbauer and U.D. Wdowik, J. Phys. Chem. Solids 65, 1785 (2004)

- U_{ij}(Fe) < U_{ij}(Co) < U_{ij}(O)
- 5% increase in U_{ij}(Fe) with decreasing U_{Fe}

Low T (10 K)

- U_{ij}(Co) > U_{ij}(Fe) by 7% mass + force const. defect
- U_{ij}(Co), U_{ij}(O) in (Fe)CoO 4% higher than U_{ij} in CoO

Above RT (U_{Fe} = 7.1 eV)

- exp. slope = calc. slope
- Θ_D (K)

(^{57}Fe)CoO	(Fe)CoO	CoO
440	440	500

Summary and conclusions

1. Filter allows to present phonon-dispersion curves to be more close to dispersion relations of a real defected sample
2. Point defects influence mainly optical phonon region. Long-wavelength acoustic phonons are practically not affected by defects, i.e., small concentration of defects does not disturb those crystal properties which are due to the low-frequency acoustic phonons
3. Average U_{ij} of ions increase with increasing vacancy concentration (decreased intensity of scattered radiation)
4. Differences in the vibrational dynamics of a dopant and host atoms arise from the difference in their force constants
5. Details can be found in:
   PRB 75, 104306 (2007)
   PRB 78, 224114 (2008)
   J.Phys.:Condens. Matter 21, 125601 (2009)