Struktura elektronowa i dynamika sieci czystego i zdefektowanego CoO

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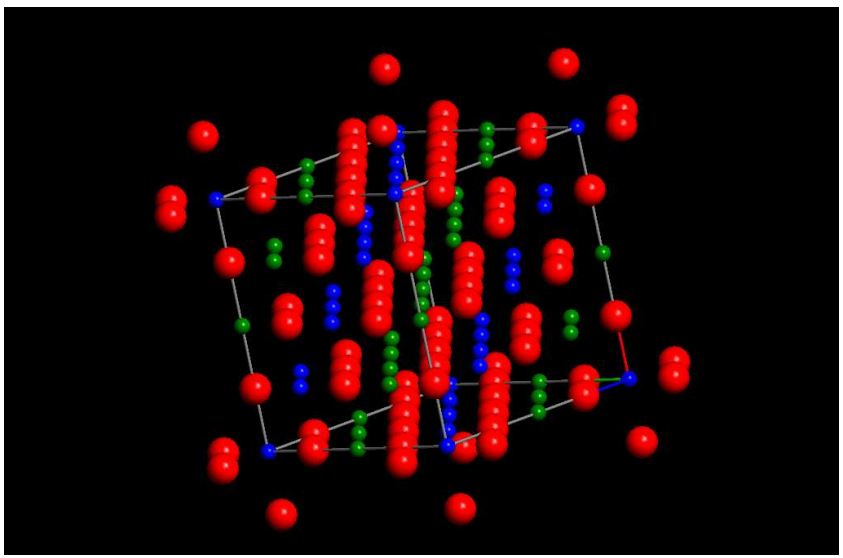
Outline

1. Introduction
   - structure, electronic and magnetic properties of CoO
2. Methodology
3. Results for defect-free CoO
4. Phonons (direct method)
5. Cobalt-deficient CoO
   - electronic structure
   - lattice dynamics
6. Fe-doped CoO
   - lattice dynamics
   - charge and spin states of Fe in CoO and vacancy-defected CoO
   - electronic structure

CoO structure



High temperature structure

- Paramagnetic ($Fm\bar{3}m$)
- $a_{exp} = 4.26$ Å

Low temperature structure

- distorted NaCl structure ($R\bar{3}m$) below $T_N = 293$ K
- rhombohedral distortion along <111>, $0.2 - 0.3^{\circ}$
- 2^{nd} kind of antiferromagnetic ordering, AFII structure

Electronic and magnetic properties of CoO

Experiment

- Insulator, $E_g = 2.5 - 2.8$ eV (experiment)
- $M_{total} = 3.8 - 3.98 \mu_B$

Theory (DFT)

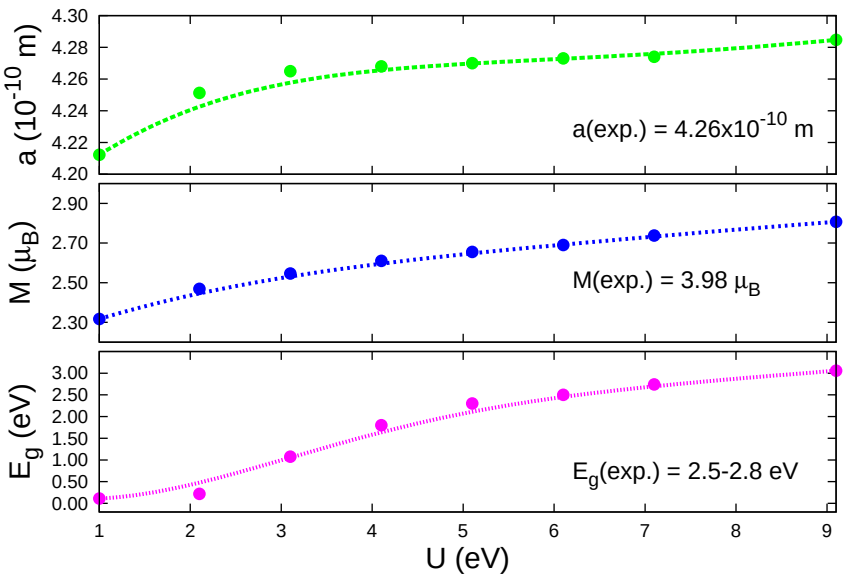
- Charge-transfer insulator
- Strong on-site Coulomb interactions in 3d shell cannot be neglected (strongly correlated electron system)
- DFT+U formalism required
- Interactions between correlated states - Hubbard potential U and the exchange interaction J

Calculations with +U formalism

Pseudopotential plane-wave method - VASP code

- spin-polarized DFT for AFII structure (64-atom supercell)
- Projector-augmented wave pseudopotentials (PAWs)
- Exchange-interaction: GGA+U
- Full relaxations of AFII structure
- U = ?, J = ?

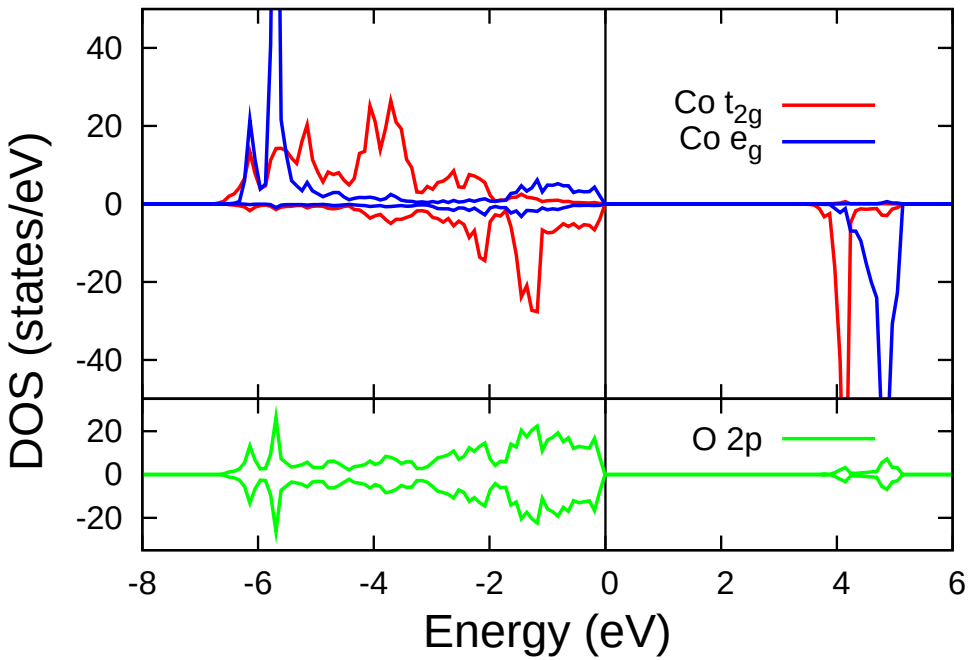
Energy gap, spin magnetic moment, lattice constant vs U



Results

- a - weak dependence upon U
- M_S changes by ca. 17%
- Underestimation of E_g for U < 5 eV
- E_g vanishes for U = 1 eV (GGA limit)

Defect-free CoO. Results for U = 7.1 eV, J = 1 eV



U = 7.1 eV, J = 1 eV

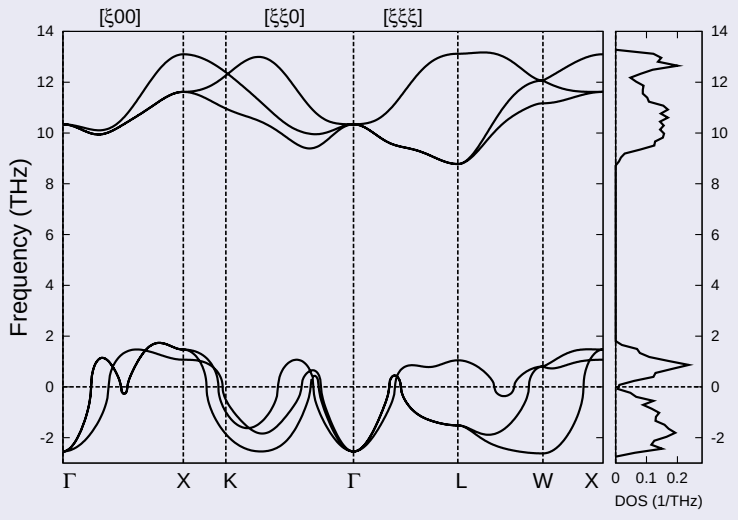
- a = 4.27Å
- Rhombohedral distortion along <111> (0.3^o)
  space group D^5_{3d} ($R\bar{3}m$)
- $E_g = 2.77$ eV
- $M_s = 2.74\mu_B$

Method to calculate phonons

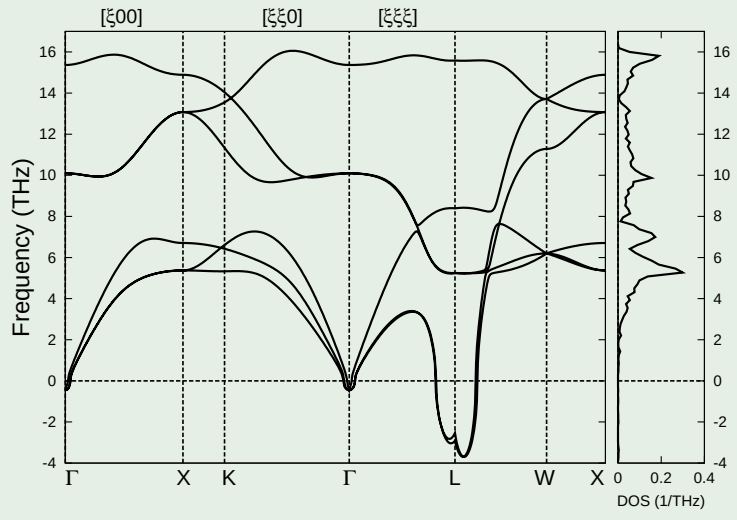
- Harmonic approximation
- Direct method - **PHONON** software by K. Parlinski
  - displace crystallographically nonequivalent atoms from their equilibrium positions
  - calculate Hellmann-Feynman forces $\mathbf{F}(\mathbf{n},\mu) = \frac{-\delta E}{\delta \mathbf{R}(\mathbf{n},\mu)}$
    $F_i(\mathbf{n},\mu) = -\sum_{\mathbf{m},\nu,j} \Phi_{ij}(\mathbf{n},\mu,\mathbf{m},\nu) U_j(\mathbf{m},\nu)$
  - solve dynamical matrix $\mathbf{D}(\mathbf{k})$
    $\omega^2(\mathbf{k},j)\mathbf{e}(\mathbf{k},j) = \mathbf{D}(\mathbf{k})\mathbf{e}(\mathbf{k},j)$
    $\Downarrow$
    - $\omega(\mathbf{k},j)$ - phonon frequencies
    - $\mathbf{e}(\mathbf{k},j)$ - polarization vectors of phonons

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

$U_{eff} = 0$ eV



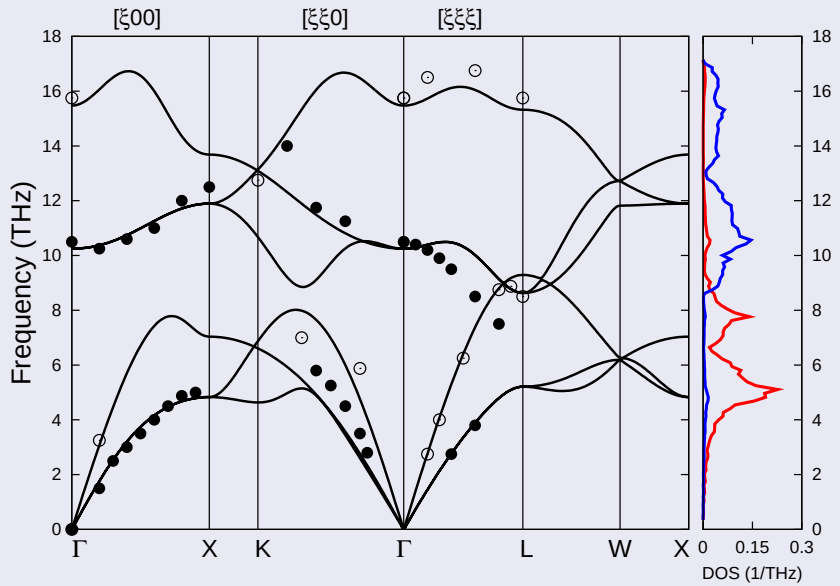
$U_{eff} = 2$ eV



- imaginary frequencies of acoustic modes $\Rightarrow$ instability of such CoO structure
- significantly underestimated HF forces $\Rightarrow$ artificial mode softening
- small $U_{eff} \Rightarrow$ too low repulsion in 3d shell

Dispersion relations and phonon DOS for U = 7 eV

U = 7.1 eV, J = 1 eV



Data for LO-TO splitting

- $\mathbf{D}(\mathbf{k}) = \mathbf{D_0}(\mathbf{k}) + D_N(\epsilon_\infty, \mathbf{Z}^*, \dots)$
- high-frequency dielectric constant $\epsilon_\infty = 5.3$[1]
- Born effective charges $|Z^*| = 2.06$

Experimental data from neutron scattering (T = 110 K)

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

Comparison with experiment

Experiment vs theory

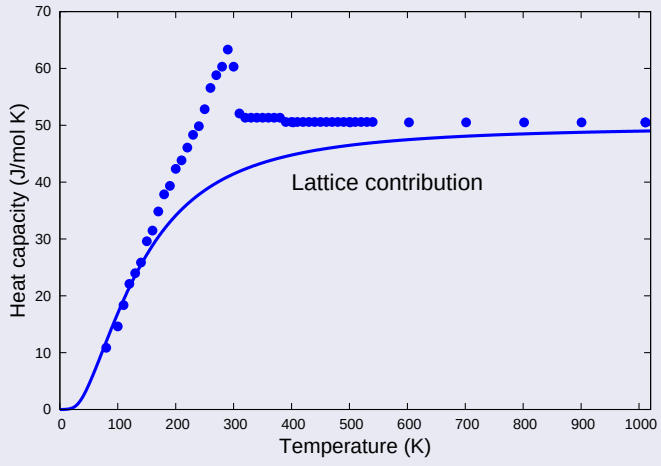
Γ-point frequencies (THz)	Neutron scattering[1]	Infrared spectroscopy[2]	Theory
ω_{TO}	10.50	10.40-10.50	10.25
ω_{LO}	15.75	16.30-16.40	15.73

Experimental data

[1] J. Sakurai, W.J.L. Buyers, R.A. Cowley, and G. Dolling, Phys. Rev. 167, 510 (1968)
[2] J.P. Gielisse, J.N. Plendl, L.C. Mansur, R. Marshall, S.S. Mitra, R. Mikolajewicz, and A. Smakula, J. Appl. Phys. 36 2426 (1965)

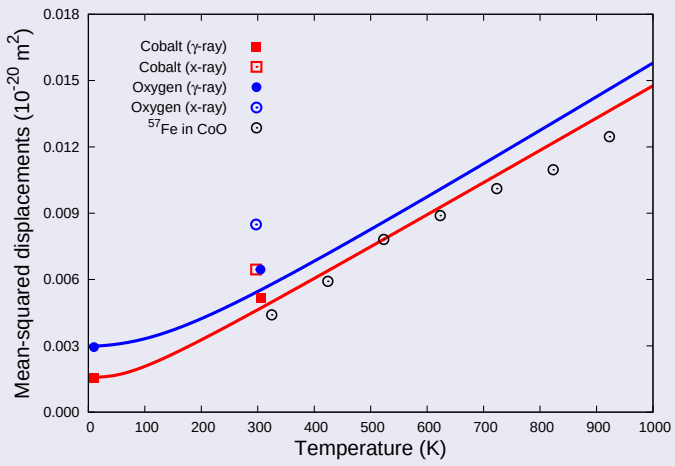
Heat capacity and Debye-Waller factors

Heat capacity



- magnetic contribution below T_N
- Dulong-Petit law @ HT

Debye-Waller factors



- calculated $\Theta_D = 500$ K
- Mössbauer $\Rightarrow \Theta_D = 440$ K

[3] E.G. King nad A.U. Christensen, U.S. Bur.Mines. Tech. Paper 80, 1800 (1956); E.G. King, ibid. 80, 2399 (1956)
[4] W. Jauch and M. Reehuis, PRB 65, 125111 (2002)
[5] S. Sasaki F. Fujino, and K. Takeuchi, Proc. Jpn. Acad. B 55, 43 (1979)
[6] K.Ruebenbauer and U.D. Wdowik, J. Phys. Chem. Solids 65, 1785 (2004)

Is CoO a stoichiometric material?

Native defects in CoO - cationic vacancies

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

How to simulate point defects (vacancies, impurities)

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

Modeling of non-stoichiometric CoO

$Co_{0.97}O$

- Co @ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ removed from 64-atom SC

$\Downarrow$

- CoO with 3% vacancies

$Co_{0.94}O$

- Co @ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ removed from 64-atom SC

$\Downarrow$

- CoO with 6% vacancies

Atomic relaxation in defected systems

- oxygens surrounding vacancies displace outward vacancy site by 0.12 Å
- initial Co-O distance (2.15 Å) changes by ca. 0.01 Å

Trivalent cations in CoO

Pure CoO

- $M_S = 2.74\mu_B$
- valence charges $q_{Co} = +1.33e$, $q_O = -1.33e$
- Co^{2+}-O 2.15 Å

$Co_{0.97}O$

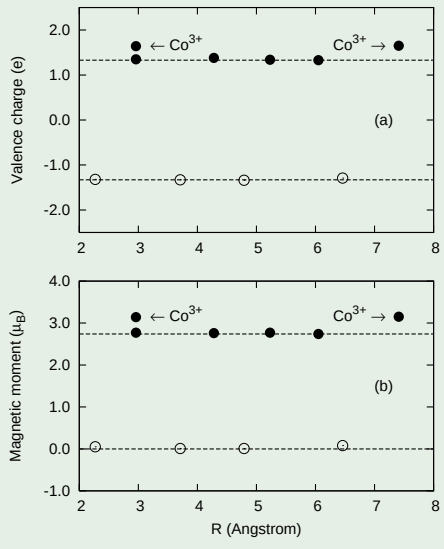
- $M_S = 3.15\mu_B$
- $q_{Co} = +1.65e$
- $Co^{3+} - O$ 2.05 Å
- 2 Co^{3+} in SC

$Co_{0.94}O$

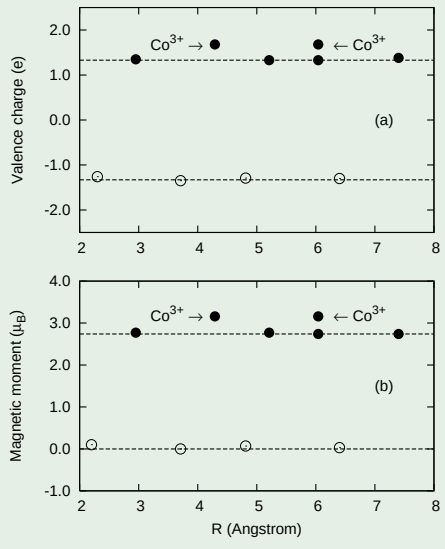
- $M_S = 3.16\mu_B$
- $q_{Co} = +1.68e$
- $Co^{3+} - O$ 2.05 Å
- 4 Co^{3+} in SC

Location of trivalent cations

$Co_{0.97}O$



$Co_{0.94}O$



Co^{3+} distance from vacancy

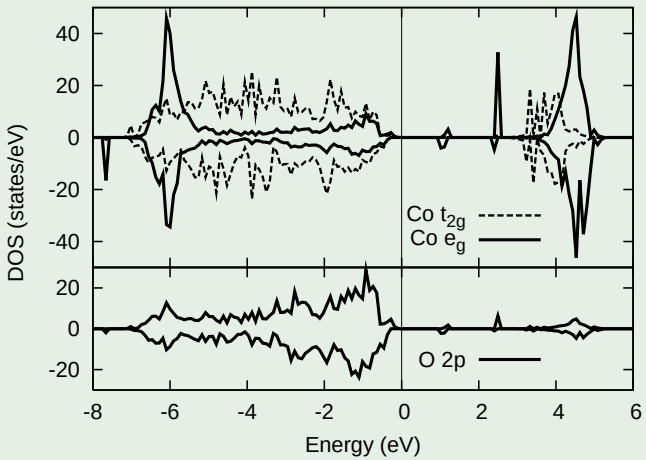
- 2.96 Å 7.41 Å

Co^{3+} distance from vacancy

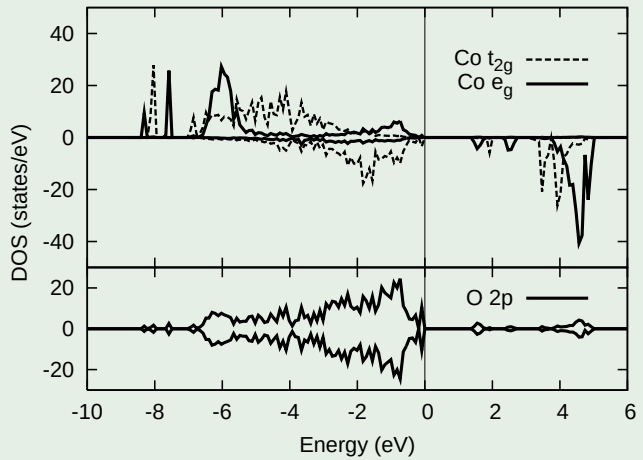
- 4.29 Å 6.04 Å

Electronic structure of vacancy-defected CoO

$Co_{0.97}O$



$Co_{0.94}O$



- charge transfer from Co to O (via s,p states)
- $Co^{2+} \Rightarrow Co^{3+} + e^-$
- 2 holes associated with vacancy are compensated by 2 Co^{3+}

acceptor states in $Co_{0.97}O$

- 1 eV above VBM

acceptor states in $Co_{0.94}O$

- 1.5 eV above VBM

Description of phonons within SC approach

CoO

- primitive UC
  N = 2 $\Rightarrow$ 6 branches

CoO as 64 atom SC

- N_S = 64 $\Rightarrow$ 192 branches ?

$Co_{0.97}O$

- SC - already primitive UC
  N_S = 63 $\Rightarrow$ 189 branches ?

- dimensions of $\mathbf{D}(\mathbf{k})$ increases to $3N_S$
- number of phonon dispersion curves increases to $3N_S$
- size of BZ conjugated with SC 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

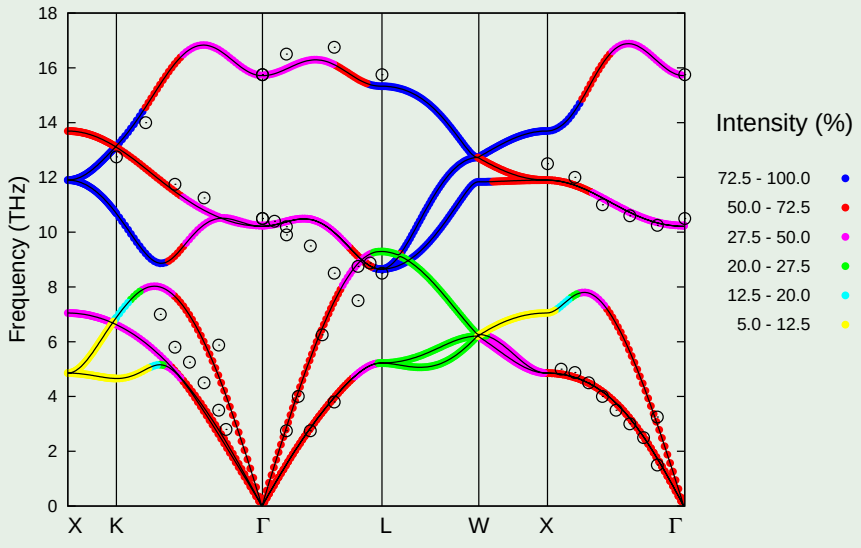
$$F^{(s)}(\mathbf{k},j) = \left|\sum_\mu \frac{\mathbf{e}(\mathbf{k},j;\mu)}{\sqrt{M_\mu}}\right|^2$$

Fake phonon modes

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

Application of filter to stoichiometric CoO

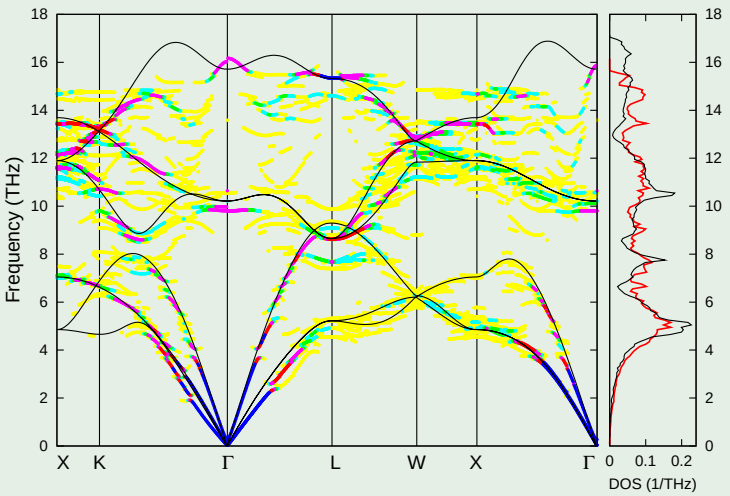
Intensities of modes for CoO



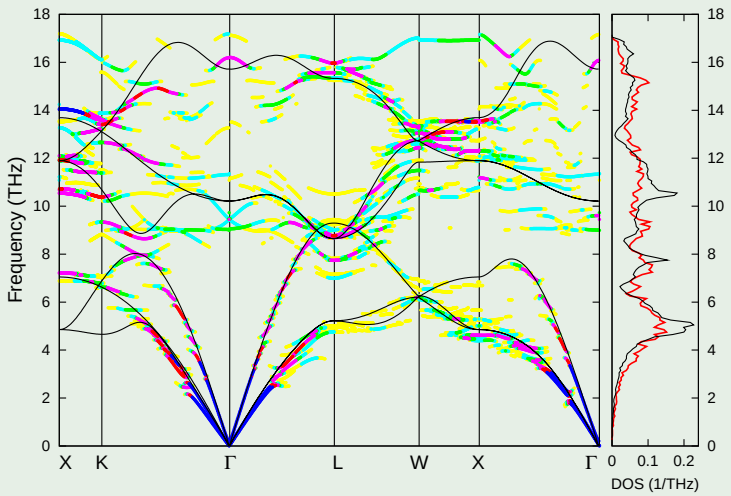
experimental data
close to branches with
intensities > 30%

Application of filter to nonstoichiometric CoO

$Co_{0.97}O$



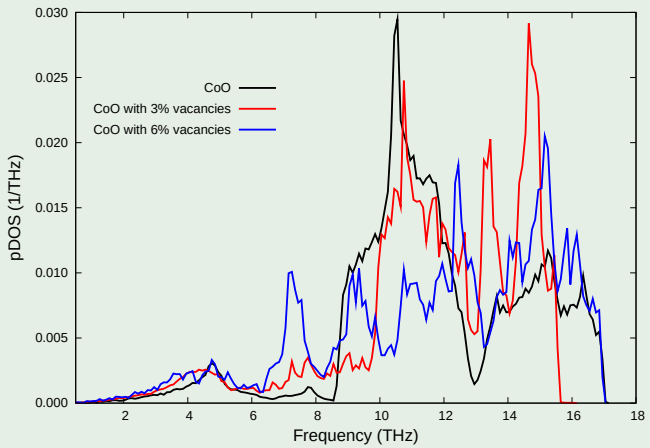
$Co_{0.94}O$



- perturbed phonons with wavelength $\sim$ size of region disturbed by vacancy
- missing Co $\Rightarrow$ additional O vibrations (new modes)
- acoustic branches at small **k** not affected by vacancies
  $\Downarrow$
  long wavelength phonons insensitive to point defects

Oxygens surrounding vacancies

Partial DOS



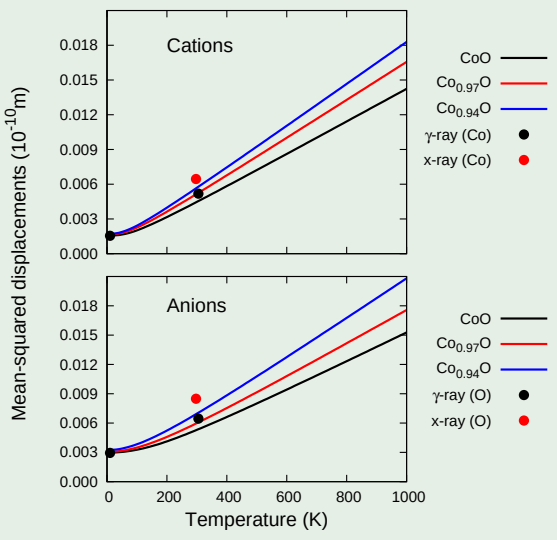
- vacancies affect the highest frequency LO modes
- no change in low-frequency acoustic region

Γ-point frequencies

frequency (THz)	CoO	$Co_{0.97}O$	$Co_{0.94}O$
ω_{TO}	10.25	9.81	9.61
ω_{LO}	15.73	15.87	16.08

Mean-squared displacements vs T

MSD for Co and O



Co and O at low T

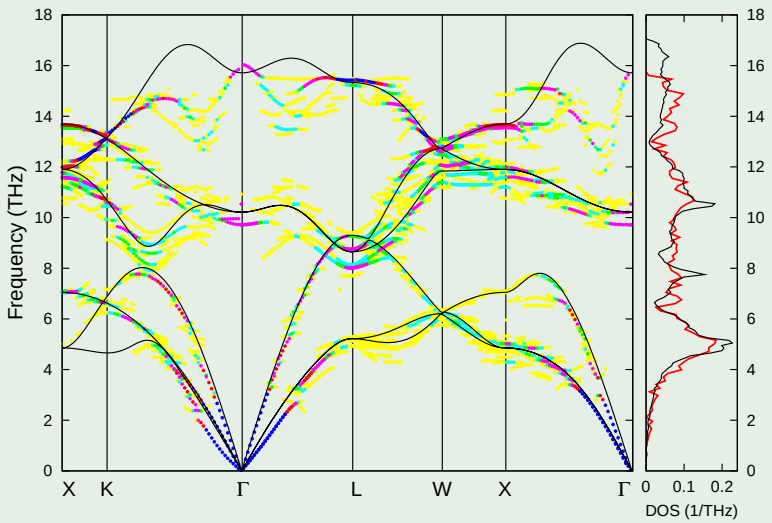
- 5% larger MSD than in stoichiometric CoO
- negligible difference between $Co_{0.97}O$ and $Co_{0.94}O$

Co and O above RT

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

Lattice dynamics of Fe-doped CoO

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



- localized modes
- mass defect negligible
- change in on-site force constant at Fe site
- at Co site Φ = 10.013 (eV/Å^2) const. vs U_{Fe}

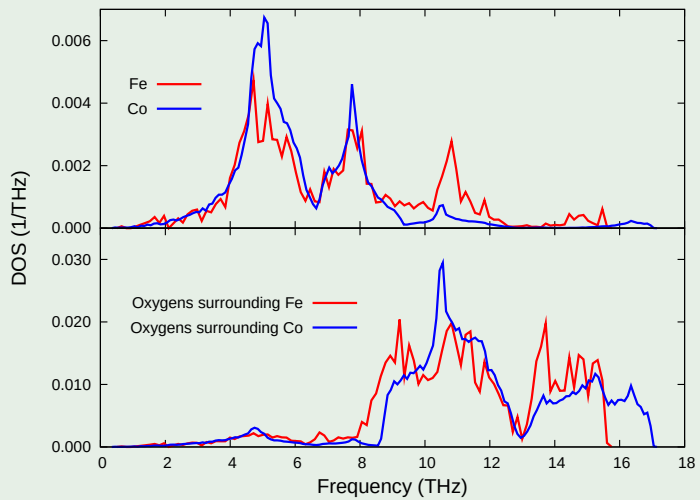
Force constant at Fe site

U_{Fe} (eV)	5.1	6.1	7.1
Φ (eV/Å^2)	12.264	12.787	13.313

Dynamics of Fe impurity

Partial phonon DOS

$U_{Fe} = U_{Co} = 7.1$ **eV**



splitting of ω_{TO}

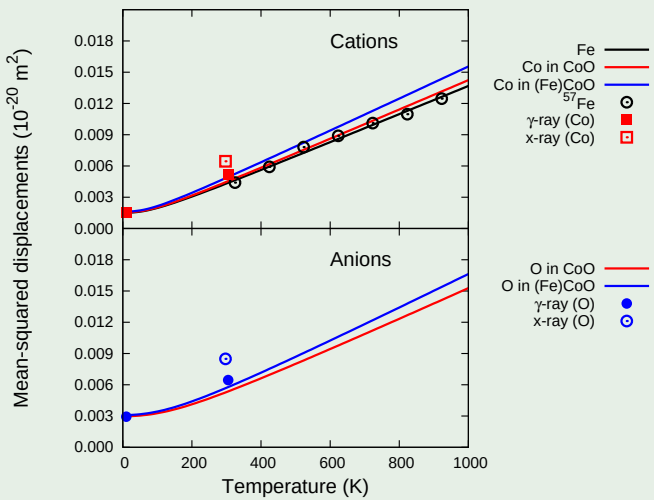
- modes corresponding to:
  - oxygens vibrating around Co
    - ω_{TO} = 10.51 THz
    - const. vs U_{Fe}
  - oxygens vibrating around Fe

oxygens neighboring Fe

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

Debye-Waller factors in Fe-doped CoO

Vibrational amplitudes



- $MSD_{Fe} < MSD_{Co} < MSD_O$
- 5% increase in MSD_{Fe} with decreasing U_{Fe}

Low T (10 K)

- $MSD_{Co} > MSD_{Fe}$ by 7%
  mass + force constant defect
- MSD_{Co}, MSD_O in Co(Fe)O are 4% higher than respective *MSDs* in CoO
  (const. vs U_{Fe})

Above RT (U_{Fe} = 7.1 eV)

- MSD_{Fe} slope
  calc. = exp. Co(^{57}Fe)O

	Co(Fe)O	Co(^{57}Fe)O	CoO
Θ_D (K)	440	440	500

Valence and spin states of Fe in CoO and $CoO_{0.97}O$

Experiment - Mössbauer spectroscopy

- 2 singlets @ RT
  - ferrous line Fe^{2+}
  - ferric line Fe^{3+}
  - vicinity of T_N = 293 K
    magnetically split component due to Fe^{2+}
- T = 78 K magnetically split Fe^{2+} and Fe^{3+}

  G. K. Wertheim, Phys. Rev. 124, 764 (1961)

Method

FP-(L)APW+lo (WIEN2k code)
Full-potential(linearized) augmented plane-wave plus local orbitals
⇓
Isomer shift and EFG on Fe in Co(Fe)O and Co(Fe,V)O

Charge and spin states

- different Fe-V complexes in CoO considered
- negligible changes vs U_{Fe}
- $\alpha = -0.291 \text{a.u.}^3 \text{mms}^{-1}$
  Q = +0.17 b

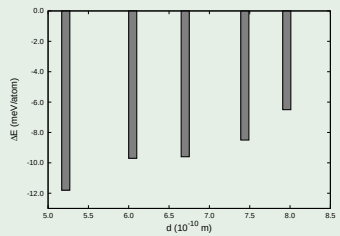
  U.D. Wdowik and K. Ruebenbauer, PRB 76, 155118 (2007)

Results

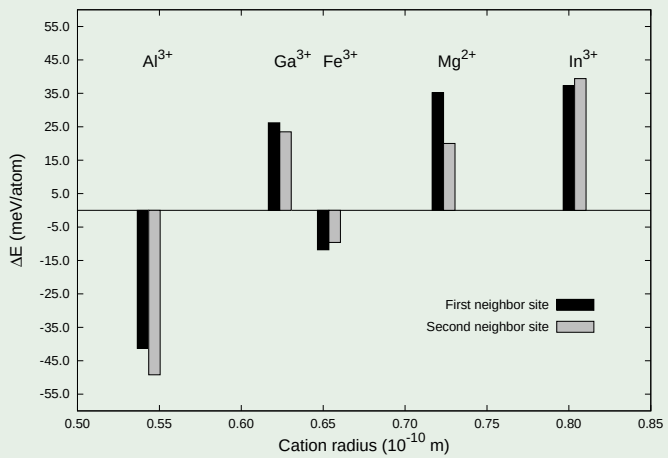
	Co(Fe)O	$Co_{0.97}(Fe)O$	Exp.[6]
M_{Co} (μ_B)	2.74	2.74 Co^{2+} 3.13 Co^{3+}	
M_{Fe} (μ_B)	3.67	4.27	
IS (mm/s)	-1.031	-0.371	-1.1245(8) Fe^{2+} -0.37(5) Fe^{3+}
EFG (mm/s)	0.27	0.28	0 0.3-0.4 mm/s linewidth
η	0.03	0.07	0

Site preferences

Fe-V complex in CoO



Trivalent and divalent impurities in vacancy-defected CoO



magnetic impurities

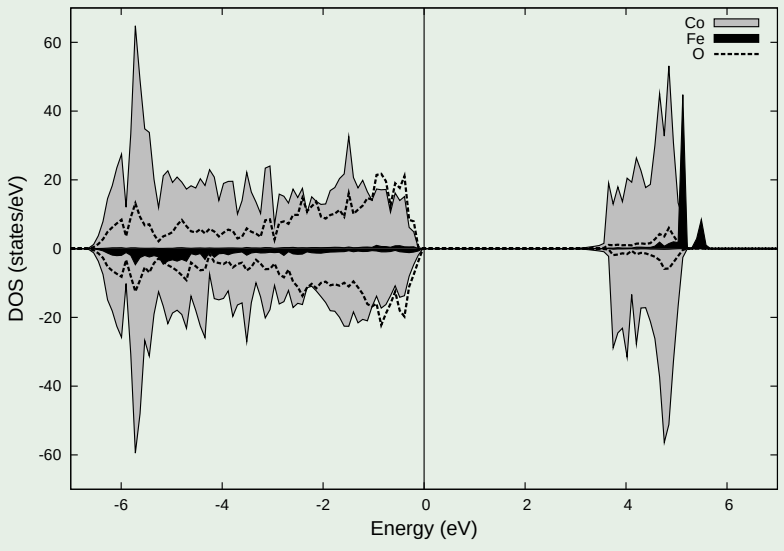
- Fe^{3+} in 1st n.s.
- Co^{3+} in 2nd n.s.
  exception: Fe^{3+} in 2nd n.s.

non-magnetic impurities

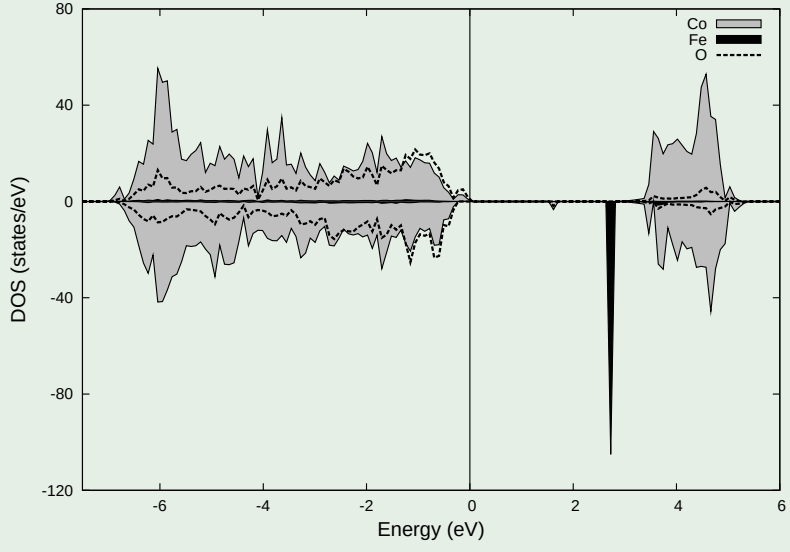
- 'small' trivalent cations in 2nd n.s.
- 'large' trivalent cations in 1st n.s.
- divalent cations in 2nd n.s.

Density od states for Co(Fe)O and $Co_{0.97}(Fe)O$

DOS of Fe-doped CoO



DOS of Fe-doped $Co_{0.97}O$



- Co^{3+} and Fe^{3+} states inside gap

Summary and conclusions

1. DFT+U can predict correct ground states of CoO
2. Trivalent Co are found in vacancy-defected CoO
3. Filter allows to present phonon-dispersion curves to be more close to the dispersion relations of a real defected sample
4. 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
5. Average MSDs of ions increase with increasing vacancy concentration (decreased intensity of scattered radiation)
6. Differences in the vibrational dynamics of a dopant and host atoms arise from the dirrefence in their force constants
7. Divalent Fe is found in the host CoO lattice undisturbed by cobalt vacancies
8. Trivalent Fe is found in the host CoO lattice decorated with cobalt vacancies
9. Details can be found in PRB 75, 104306 (2007); PRB 77, 115110 (2008); PRB 78, 224114; J.Phys.:Condens. Matter 21, 125601 (2009)