Lattice dynamics of CoO from first principles

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Introduction

CoO: strongly correlated system, charge transfer insulator

- Paramagnetic @ RT : NaCl structure **a = 4.26 Å**
- AFII ordering below **T_N = 293 K**
- Spins aligned along <001>
- Trigonal lattice distortion along <111> below T_N
- Energy gap: 2.5 – 2.8 eV
- Total magnetic moment on Co ion: ~ 3.8 μ_B

Aim

Ab initio phonon calculations of CoO:

- unsuccessful while contributions from strong electron correlations are not taken into account
- DFT+U approach → proper description of phonon dispersion relations of AFII CoO

Methods

Spin-polarized DFT+U implemented in VASP

- Exchange-correlation functional: GGA-PW91
- On-site Coulomb repulsion: Dudarev approach
  - U = 7.1 eV, J = 1 eV
- Ionic cores described by PAW pseudopotentials
- Valence electron configurations:
  - Co ($3d^8 4s^1$)
  - O ($2s^2 2p^4$)
- Supercell: 64 atoms
- Sampling:
  - 2x2x2 *k*-point mesh (Monkhorst-Pack scheme)
- Electronic DOS:
  - 6x6x6 *k*-point mesh (linear tetrahedron method with Blöchl corrections)
- Supercell geometry optimization:
  - combination of conjugate gradient energy minimization and quasi-Newton force minimization

- **Phonon dispersion relations and phonon DOS:**
- Direct method (forces calculated via Hellmann-Feynman theorem) within harmonic approximation
- Forces generated by displacing 4 symmetry inequivalent atoms (2 Co and 2 O)
- Displacement amplitude: 0.03 Å
- Experimental static dielectric constants (Ref. 1):
  - ε_∞ = 5.3
  - ε_0 = 12.9

Results

Crystal geometry optimization

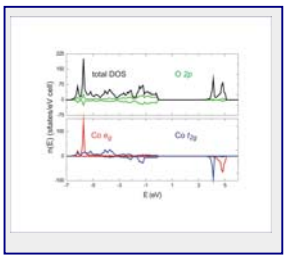
Lattice constant	a = 4.27 Å
Rhombohedral distortion	α = 0.3°

Magnetic moment on Co^{2+}

Spin magnetic moment	S = 2.74 μ_B
Orbital contribution	L = 1.24 μ_B
	L/S = 0.91
Experiment	L/S = 0.95

Electronic structure

Hybridization of Co 3*d* and O 2*p* states

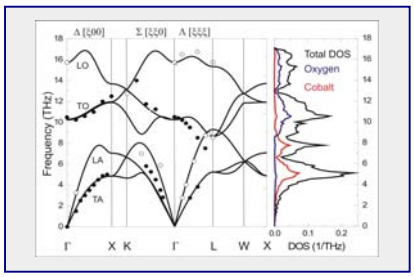


Total and orbital projected DOS for CoO calculated within GGA+U with U = 7.1 eV. Positive (negative) pDOS represent the spin-up (spin-down) component of e_g and t_{2g} projections, respectively.

Lattice dynamics

Γ-point optical frequencies & Born effective charges

	ω_{TO} (THz)	ω_{LO} (THz)	$\|Z^*\|$
Present work	10.25	15.73	2.06
Neutron exp.(1)	10.50	15.75	2.06
Infrared exp.(2)	10.40	16.30	1.78



Phonon dispersion curves and phonon density of states obtained from ab initio calculations and from inelastic neutron scattering experiments (Ref. 1) performed at 110 K.

References

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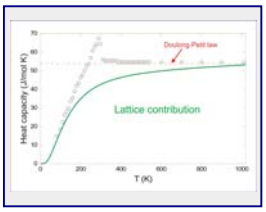
Results

Heat capacity

Contributions to heat capacity of CoO: lattice, magnetic, electronic (Schottky) terms.

Lattice contribution follows the Debye model and approaches the Dulong-Petit law at high temperatures.

Background contribution from disorder of magnetic moments and λ-type behavior in the vicinity of T_N are observed experimentally.

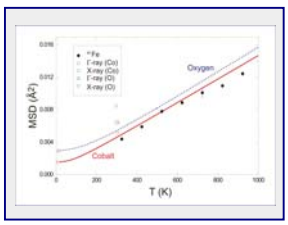


Calculated and experimental specific heat for CoO. Experimental data are taken from Ref. 3.

Debye temp. θ_D = 596 K ← calculated

θ_D = 440(11) K ← experiment (6)

Mean-squared displacements versus temperature for cations and anions in CoO. Experimental data: Γ-ray - Ref. 4 X-ray - Ref. 5 Mössbauer - Ref. 6



Conclusion

- Calculated quantities agree with experiment
- On-site Coulomb interactions between *3d* electrons are crucial for proper description of the band structure and lattice dynamics.
- Hubbard U determines phonon DOS and phonon dispersion curves of CoO
- Small U_{eff} (U_{eff} = U – J)
  - Underestimation of LO and TO modes due to low repulsion in *3d* shell
  - Unphysical mode softening of phonon branches (especially LO modes)
  - U_{eff} < 2 eV ⇒ negative frequencies of acoustic modes (artificial soft modes) due to instability of CoO structure (underestimated Hellmann-Feynman forces)

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