NiO - hole doping and bandstructure of charge transfer insulator

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Outline

- NiO - charge transfer insulator
- Theory so far
- Single particle spectra (PES, BIS)
- Hole doping \( \text{Li}_x\text{Ni}_{1-x}\text{O} \)
- Bandstructure \( A(k, \omega) \) (ARPES)
- Conclusions
- Single out an atom from the lattice
- Replace the rest of the lattice by an effective medium
- Time resolved treatment of local electronic interactions
NiO - so far
NiO - Bunsenite

- rock-salt structure (\(T_m = 2261\) K)
  bulk modulus: 209 GPa
  (CoO 194, MnO 148, diamond 462, Li 11)
- type II AFM (\(T_N = 532\) K)
- charge gap: 3.7 eV
- Formal valency: \(\text{Ni}^{2+}: d^8s^0\)  \(\text{O}^{2-}: p^6\)
- \(U \sim 9\) eV
Transition metal oxides: ZSA scheme

Mott-Hubbard type (Ti-O, V-O)

charge-transfer type (Ni-O, Cu-O)

O - 2p

Transition metal - 3d

Δ

∪

Δ

∪

Δ

∪

Δ

∪
NiO - photoemission

Eastman & Freeouf, PRL 34, 395 (1974):

- 1253 eV: d-states
- 78 eV: multielectron satellite
- 40 eV: p-states
- 30 eV: resonant d-peak at the top of valence band
- 20 eV: distribution of spectral weight between LHB and resonant peak
- p-band between LHB and resonant peak
NiO - LDA+U

Anisimov et al., PRB 44, 943 (1991)

- LDA + orbitally dependent potential
  -> mean-field solution of Hubbard model

- long-range magnetic order
- $m_s \sim 2 \mu_B (2 E_g \text{ holes})$
- gap $\sim 4 \text{ eV}$
- all d-spectral weight in LHB
NiO - Cluster results

Fujimori et al. PRB 29, 5225 (1984)

Exact diagonalization on $[\text{NiO}_6]^{10-}$ molecule with local Coulomb interaction

- model ($\sim 10$ parameters)
- correct groundstate $m_s$, gap
- correct d-weight distribution
- no dispersion (ARPES)
- not applicable to metals (doping, metal-insulator transition)
DMFT (QMC) - full p-d hybridization

Part I: Photoemission
**NiO - DMFT (QMC)**

Converged LDA Hamiltonian used as input for DMFT

QMC impurity solver

$T = 1160 \, K$

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NiO - DMFT (QMC)

Converged LDA Hamiltonian used as input for DMFT

QMC impurity solver

\[ T = 1160 \, \text{K} \]

Orbital resolved spectral densities - DMFT

![Graph showing spectral densities with bands labeled p, t\textsubscript{2g}, and e\textsubscript{g}.]
More experiment: XES/XAS

courtesy of Prof. Ernst Kurmaev:
DMFT (QMC) - full p-d hybridization
Part II: Hole doping
Hole doping of NiO

Orbital occupations:

<table>
<thead>
<tr>
<th>$n_h$</th>
<th>$n_{eg}$</th>
<th>$n_{t2g}$</th>
<th>$n_p$</th>
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</tr>
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Hole doping of NiO

\[ n_h = 0.6 \]

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**Holes reside on O-sites!**
Experimental realization $\text{Li}_x\text{Ni}_{1-x}\text{O}$

van Elp et al. PRB 45, 1612 (1992)

$\text{Li}_{0.4}\text{Ni}_{0.6}\text{O}$:

$n_h = x/1-x$
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$n_h = x/(1-x)$

Spectral weight transfer
DMFT (QMC) - full p-d hybridization
Part III: ARPES
NiO: k-resolved spectral functions

\[ \text{O-p} \]

\[ \text{Ni-E}_g \]

\[ \text{Ni-T}_{2g} \]
NiO: angle-resolved photoemission

Shen et al. PRB 44, 3604 (1991)
NiO: angle-resolved photoemission

Shen et al. PRB 44, 3604 (1991)
NiO: k-resolved spectral functions

$O-p$

$Ni-E_g$

$Ni-T_{2g}$
NiO: Zhang-Rice bands

- localized (k-independent) $d$-contribution
- strongly k-dependent $p$-contribution
Conclusions

Anonymous referee: ‘…, all the DMFT community (excluding Kunes and co-authors) are realizing this fact and simply do not encroach upon charge-transfer systems.’

LDA+DMFT can treat charge-transfer systems and does a very good job for NiO.

- combination of dynamic correlations and $p$-$d$ hybridization is crucial -> Zhang-Rice bands at the top of the valence manifold and distribution of spectral weight between ZR and LH bands

- ARPES is characterized by non-trivial combination of dispersive and incoherent features, the ZR bands exhibit strong $k$-dependence of the $p$-spectral weight (extensively discussed on models)

- NiO is charge-transfer system <- doped holes sit on O sites
Lessons/questions:

- Filled unhybridized bands may exhibit pronounced correlation effects.
- Bandstructure intuition fails when it comes to doping correlated systems (NiO: $p$-holes vs $d$-peak at $\mu$, closing of the gap by doping - different from the single-band Hubbard model).
- Ergodicity of QMC sampling is an issue in multi-orbital insulators.

- How do we recognize a local moment system? Do we have to calculate $\chi(0)$ vs $T$?

Future: Massive application to charge-transfer systems. Full Coulomb interaction perturbative expansions (CTQMC). Lower temperatures temperature dependent local moment transitions.
NiO: k-resolved spectral functions
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NiO: k-resolved spectral functions
NiO: local moment dynamics

\[ <m_z(\tau) m_z(0)> (\mu_B^2) \]

- \( n_h = 0 \)
- \( n_h = 0.6 \)
- \( n_h = 1.2 \)
Simple p-d molecule

**Initial state**

- $\varepsilon_d + U$
- $\varepsilon_p$
- $\varepsilon_d$

**Final state**

- Electron transfer

Graphical representation of electron transitions and energy levels.