Origin of metal-insulator transition in \( \text{NiS}_{2-x} \text{Se}_x \)

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theory

optical spectroscopy

x-ray spectroscopy

CT QMC solver
1-band Hubbard model

\[ D = \infty \]

certainty parameters \( T, \frac{W}{U} \)

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Bulla et al. PRB 64, 045103 (2001)

for review A. Georges et al. RMP 68, 13 (1996)

McWhan et al. PRL 27, 941 (1971)
Motivation

Do the details of non-interacting bandstructure in strongly correlated materials matter?

What is the role of ligand orbitals? (charge-transfer materials)
Dynamical Mean-Field Theory (DMFT)

- Single out an atom from the lattice
- Replace the rest of the lattice by an effective medium
- Time resolved treatment of local electronic interactions
- Reconstruct lattice quantities

A. Georges et al. *RMP* 68, 13 (1996)  
*Physics Today* (March 2004) Kotliar, Vollhardt
Charge-transfer materials

\[ \Delta \]

\[ \Delta \]

\[ U \]

\[ \Delta \]

\[ U \]

\[ O - 2p \]

\[ \text{Transition metal - 3d} \]

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

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

\[ \text{O-p} \]

\[ \text{LHB} \]

\[ \text{UHB} \]
LDA+DMFT for NiO

**Experiment**: 
- 120 eV
- 66 eV

**Theory**: 
- O-p
- Ni-d

**References**:
- *JK et al. PRB 75, 165115 (2007), PRL*
NiS$_{2-x}$Se$_x$ introduction

Crystal structure:

Phase diagram (from Yao et al.)

Metal-insulator transition driven by Se substitution (x), pressure, temperature.
NiS$_{2-x}$Se$_x$ introduction

Crystal structure:

Phase diagram (Takeshita et al.)

Metal-insulator transition driven by Se substitution ($x$), pressure, temperature.
NiS$_2$ / NiSe$_2$

LDA Density of states:

- **Ni-d**
- **$S(Se)$ - p**
- **$S(Se)$ - pp$\sigma$**

Proposed spectral density:

*Matsuura et al. PRB 53, R7586 (1996)*
### Origin of MIT?

**MIT is driven by decreasing U/W**
- Kwizera *et al.* PRB 21, 2328 (1980) \(\exp(\text{transport})\)
- Matsuura *et al.* PRB 53, R7584 (1996) \(\exp(\text{ARPES}) + \text{LDA}\)
- Miyasaka *et al.* JPSJ 69, 3166 (2000) \(\exp(\text{transport})\)
- Takashima *et al.* cond-mat/0704.0591 \(\exp(\text{transport})\)
- Krishnakumar and Sarma, PRB 68, 155110 (2003) \(\exp(\text{XPS}) + \text{cluster ED}\)

**MIT is driven by decrease of CT gap**
- Perucchi *et al.* cond-mat/0811.2154 \(\exp(\text{IR optics}) + \text{LDA}\)
- ? Matsuura *et al.* JPSJ 69, 1503 (2000) \(\exp(\text{transport} + \text{neutron diffr.})\)

**MIT is driven by decrease of U (stronger screening by Se-Se)**
- Folkerts *et al.* JPC: Solid State Phys. 20, 4135 (1985) \(\exp(\text{XPS, BIS}) + \text{LDA}\)
NiS$_2$ / NiSe$_2$

LDA+DMFT spectral density; U=5 eV, J=1 eV, T=580 K
LDA+DMFT spectral density:

\[ d^8 \rightarrow d^9 \]

Initial state: \( d^8 \)

Final state: \( d^9 \)

\( d^8 \) and \( d^9 \) configurations are shown with black and blue circles, respectively.
Where is the dimer band?
NiS$_2$ comparison to experiment

Sugiura & Muramatsu, pss (b) 129, K157 (1985) S K-edge XAS
NiS$_2$ comparison to experiment

Sugiura & Muramatsu, pss (b) 129, K157 (1985)

S K-edge XAS
NiS$_2$ comparison to experiment

Folkerts et al. J. Phys. C 20

X-ray emission and absorption

Energy (eV)

Spectral density (arb. units)

S-p
XES
XAS
NiSe$_2$

NiSe$_2$ (v0, U=4.5, $\beta$=20)

![Graph showing spectral density vs energy for NiSe$_2$ with different U values. The energy scale ranges from $-6$ to $6$ eV, and the spectral density scale ranges from $0$ to $0.4$. The inset shows a close-up view of the spectral density around the Fermi level. The graph indicates that the spectral density changes with varying U values, with distinct peaks at different energies. The inset also highlights a bond distance $d_{Se-Se} = 2.37$ eV.]
Pressure

NiS$_2$

Atomic distance (Å)

Lattice constant (Å)

S-S

Ni-S

Se-Se

0 GPa

~13 GPa

Energy (eV)
NiS$_2$ vs NiSe$_2$ - dimer splitting

controlled by pressure
controlled by alloying

$p_\sigma$ Wannier function
Conclusions

- Details of band structure matter
- The ground state of NiS$_{2-x}$Se$_x$ is controlled by the gap in the p-band
- Pressure and Se-substitution reduce the p-gap by changing the inter-dimer hopping and intra-dimer hybridization splitting