Influence of Electronic Correlations on the Structural Stability of Solids

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Workshop on Correlated Electronic Structure and Spin Dynamics
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Influence of Electronic Correlations on the Structural Stability of Solids

Outline

- *Ab initio* approach to correlated electron materials: LDA+DMFT
- Fe: Why are there two bcc phases?
- FeSe: Will the Fermi surface change upon lattice expansion?
- V$_2$O$_3$: Is the Mott transition accompanied by a lattice distortion?
- Perspectives
Properties of real materials?

DFT approximations

Model approaches

Held (2004)
Computational scheme for correlated electron materials:

**Material specific electronic structure**
(Density functional theory: LDA, GGA, ...) or GW

**Local electronic correlations**
(Many-body theory: DMFT)

Metzner, DV (1989)
Georges, Kotliar (1992)

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)

Lichtenstein, Katsnelson: LDA++ (1997/98)
Computational scheme for correlated electron materials:

**Material specific electronic structure**
(Density functional theory: LDA, GGA, ...) or GW

+ 

**Local electronic correlations**
(Many-body theory: DMFT)

\[ \Sigma(k, \omega) \]

Metzner, DV (1989)
Georges, Kotliar (1992)

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)

Lichtenstein, Katsnelson: LDA++ (1997/98)
LDA+DMFT (simplest version)

1) Calculate LDA band structure: \( \varepsilon_{lml'm'}(k) \) → \( \hat{H}_{LDA} \)

2) Supplement LDA by local Coulomb interaction (only for correlated bands)

\[
\hat{H} = \sum_{kll'm'm'\sigma} \varepsilon_{lml'm'}(k) \hat{c}_{klm\sigma}^\dagger \hat{c}_{kl'm'\sigma} - \sum_{i=i_d, m\sigma} \sum_{l=l_d} \Delta \varepsilon_d \hat{n}_{i\ell m\sigma} \\
\hat{H}_{LDA}
\]

\[
+ \sum_{i=i_d, m\sigma, m'\sigma'} \sum_{l=l_d} \frac{U^{\sigma\sigma'}_{mm'}}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'}
\]

local Coulomb interaction

\[
- \sum_{i=i_d, m\sigma, m'\sigma'} \sum_{l=l_d} J_{mm'} \hat{c}_{ilm\sigma}^\dagger \hat{c}_{ilm'\sigma'}^\dagger \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma'}
\]

Hund’s rule coupling

“double counting correction“
3) Solve within DMFT
→ effective multi-orbital Anderson impurity model with self-consistency condition

(i) Effective single impurity problem

\[ G = -\frac{1}{Z} \int D[\psi \psi^*] \psi \psi^* e^{\psi^*} \left[ G^{-1} + \Sigma \right] \psi - U \psi^* \psi \psi^* \psi + J \psi^* \psi \psi^* \psi \]

(ii) \( k \)-integrated Dyson equ.

\[ G_{mm'}^{\sigma}(\omega) = \frac{1}{V_B} \int d^3k \left[ (\omega - \Sigma^{\sigma}(\omega)) \delta_{m,m'} - \left( H_{LDA}(k) \right)_{m,m'} \right]^{-1} \]

Employ an impurity solver, e.g., QMC

Jarrell (1992)
Werner et al., (2006)
Goal: Dynamical mean-field approach with predictive power for strongly correlated materials
Application of LDA+DMFT to Fe

- Ferromagnetism: Longest known quantum many-body phenomenon
- Iron: Most abundant element by mass on Earth
- Most widely used metal in modern day industry
Narrow d,f-orbitals/bands → electronic correlations important
Exceptional:
- Abundance of allotropes: $\alpha$, $\gamma$, $\delta$, $\varepsilon$, ... phases
- bcc-phase stable for $P,T \rightarrow 0$
- Very high Curie temperature ($T_C \sim 1043$ K)
Mikhaylushkin, Simak, Dubrovinsky, Dubrovinskaia, Johansson, Abrikosov (2007)
Finite-Temperature Magnetism of Transition Metals: An \textit{ab initio} Dynamical Mean-Field Theory

A. I. Lichtenstein and M. I. Katsnelson*

\textit{University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands}

G. Kotliar

\textit{Serin Physics Laboratory, Rutgers University, Piscataway, New Jersey 08855}
Until recently:
LDA+DMFT investigations of correlated materials for given lattice structure

- How do electrons + ions influence each other?
- Which lattice structure is stabilized?
Investigation of the structural stability of Fe

Collaborators: Ivan Leonov (Augsburg)
Vladimir Anisimov (Ekaterinburg)
Alexander Poteryaev (Ekaterinburg)

Leonov, Poteryaev, Anisimov, DV; PRL 106, 106405 (2011)
DFT(GGA): finds paramagnetic $bcc$ phase to be unstable

- What stabilizes the paramagnetic $\alpha$-phase?
- What causes the $bcc$-$fcc$ structural phase transition?
**bcc-fcc structural transition in paramagnetic Fe**

Total energies calculated along *bcc-fcc* Bain transformation path:

- continuous transformation path from *bcc-phase to fcc-phase*
- volume per atom fixed at exp. value of α-Fe

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**bcc (c/a=1)**

![bcc structure](image1)

\[Z = 8\]

**fcc (c/a = \sqrt{2})**

![fcc structure](image2)

\[Z = 12\]

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Bain and Dunkirk (1924)
**bcc-fcc structural transition in paramagnetic Fe**

Goal: Demonstrate structural stability of paramagnetic *bcc* phase

Construct Wannier functions for partially filled Fe *sd* orbitals

First-principles multi-band Hamiltonian including local interactions

\[
\hat{H} = \hat{H}_{\text{GGA}} + \frac{1}{2} \sum_{mm',\sigma\sigma'} U_{mm'}^{\sigma\sigma'} \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} - \hat{H}_{\text{DC}}
\]

Coulomb interaction between Fe 3d electrons: $U=1.8$ eV, $J=0.9$ eV
**bcc-fcc structural transition in paramagnetic Fe**

**Goal:** Demonstrate structural stability of paramagnetic *bcc* phase

Construct Wannier functions for partially filled Fe *sd* orbitals

**GGA:**
Only paramagnetic *fcc* structure stable

**GGA+DMFT:**
*bcc-fcc* structural transition at $T_{\text{struct}} \approx 1.3 \ T_C$

What determines the temperature dependence of the total energy?
**bcc-fcc** structural transition in paramagnetic Fe

Contributions to the GGA+DMFT total energy:

\[ E_{\text{tot}} = E_{\text{kin}} + E_{\text{int}} \]

- kinetic energy favors *fcc* structure
- correlation energy indifferent as in GGA \( \rightarrow fcc \) structure stable

![GGA+DMFT total energy graph](image)
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{tot} = E_{kin} + E_{int} \]

- kinetic energy favors *fcc* structure
- correlation energy increases

\[ \rightarrow fcc \text{ structure still stable} \]
$bcc$-$fcc$ structural transition in paramagnetic Fe

Contributions to the GGA+DMFT total energy:

$$E_{tot} = E_{kin} + E_{int}$$

GGA+DMFT:

$bcc$-$fcc$ structural transition at $T_{struct} \approx 1.3 \, T_C$

- kinetic energy favors $fcc$ structure
- correlation energy increases

$\implies bcc$ structure becomes stable
bcc-fcc structural transition in paramagnetic Fe

Contributions to the GGA+DMFT total energy:

\[ E_{\text{tot}} = E_{\text{kin}} + E_{\text{int}} \]

GGA+DMFT: bcc-fcc structural transition at \( T_{\text{struct}} \approx 1.3 \, T_C \)

- kinetic energy favors fcc structure
- correlation energy increases

\[ \rightarrow \text{bcc structure remains stable} \]
Electronic correlations responsible for $T_{\text{struct}} > T_C$
$\textit{bcc-fcc structural transition in paramagnetic Fe}$

Equilibrium volume $V$

**GGA+DMFT**

- $V \sim 161.5/158.5 \text{ au}^3$ in $\text{bcc/fcc}$ phase
- Increased by electronic repulsion

**Non-magnetic GGA:**
- $V \sim 141/138 \text{ au}^3$ in $\text{bcc/fcc}$ phase
  - too small $\rightarrow$ density too high

**GGA+DMFT:**
- $V \sim 161.5/158.5 \text{ au}^3$ in $\text{bcc/fcc}$ phase
- Agrees well with exp. data:
  - $V_{\text{exp}} \sim 165 / 158 \text{ au}^3$
**bcc-fcc structural transition in paramagnetic Fe**

**Equilibrium volume V and bulk modulus**

**GGA+DMFT**

- **bcc Fe**
- **fcc Fe**

\[
\text{Volume (au}^3\text{)}
\]

\[
\text{T/T}_C
\]

- **Bulk modulus (Mbar)**
  - **Non-magnetic GGA:**
    - Bulk modulus \(\sim 2.66/2.82\) Mbar in \(bcc/fcc\) phase too large
  - **GGA+DMFT:**
    - Bulk modulus \(\sim 1.48/1.61\) Mbar reduced by electronic repulsion

Agrees well with exp. data: \(B_{exp} \sim 1.62 - 1.76\) Mbar

**Conclusion:**

Structural transformation caused by electronic correlations
Lattice dynamics and phonon spectra of Fe

Leonov, Poteryaev, Anisimov, DV; Phys. Rev. B 85, 020401(R) (2012)
Lattice dynamics of paramagnetic bcc iron

Non-magnetic GGA phonon dispersion

1. Brillouin zone

Exp.: Neuhaus, Petry, Krimmel (1997)

Dynamically unstable + elastically unstable ($C_{11}, C' < 0$)
Lattice dynamics of paramagnetic \textit{bcc} iron

- phonon frequencies calculated with frozen-phonon method
  
  Stokes, Hatch, Campbell (2007)

- harmonic approximation

GGA+DMFT phonon dispersion at 1.2 $T_c$

Calculated:
- equilibrium lattice constant $a \sim 2.883$ Å \hspace{1cm} ($a_{exp} \sim 2.897$ Å)
- Debye temperature $\Theta \sim 458$ K

Exp.: Neuhaus, Petry, Krimmel (1997)
Closer look: Phonon dispersion of \textit{bcc} iron at higher $T$

GGA+DMFT phonon dispersion

Above \textit{bcc-fcc} phase transition ($\sim 1.3 \ T_C$):
Instability of \textit{bcc} phase due to soft transverse $T_1$ acoustic mode near $N$-point

Leonov, Poteryaev, Gornostyrev, Lichtenstein, Katsnelson, Anisimov, DV (2014)

Anharmonic effects stronger
Lattice dynamics of paramagnetic \textit{fcc} iron

Non-magnetic GGA phonon dispersion

1. Brillouin zone

Elastic constants much too large

Exp.: Zarestky, Stassis (1987)
Lattice dynamics of paramagnetic fcc iron

GGA+DMFT phonon dispersion at 1.4 $T_C$

Calculated:
- equilibrium lattice constant $a \sim 3.605 \, \text{Å}$ ($a_{\text{exp}} \sim 3.662 \, \text{Å}$)
- Debye temperature $\Theta \sim 349 \, \text{K}$

Exp.: Zarestky, Stassis (1987)
What stabilizes the high temperature \textit{bcc} (\(\delta\)) phase of iron?

\(T_1\) mode becomes strongly anharmonic \(\rightarrow\) high lattice entropy
\(\rightarrow\) lowers free energy \(F = E - TS\)

\textbf{Quantitative estimate:} \textit{bcc} (\(\delta\)) phase of iron stabilized by electronic correlations + lattice entropy

Leonov, Poteryaev, Anisimov, DV (2012)
Investigation of the structural stability of FeSe

Leonov, Skornyakov, Anisimov, DV; arXiv:1411.0604
FeSe: Crystal structure and properties

- Simplest structure of/parent compound for Fe-based superconductors
- tetragonal crystal structure
- $T_c \sim 8$ K ($\sim 37$ K under hydrostatic pressure)
- isovalent substitution Se $\rightarrow$ Te:
  - lattice expansion
  - $T_c$ increases up to $\sim 14$ K

<table>
<thead>
<tr>
<th>FeSe</th>
<th>FeSe$_{1-x}$Te$_x$, $x&lt;0.7$</th>
<th>FeTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>no static magnetic order, short-range fluctuations with $Q_m=\left(\pi, \pi\right)$</td>
<td>$T_N \sim 70$ K $; Q_m=\left(\pi, 0\right)$</td>
<td></td>
</tr>
<tr>
<td>$T_c \sim 8$ K</td>
<td>$T_c \sim 14$ K</td>
<td>-</td>
</tr>
</tbody>
</table>

How does the electronic and magnetic structure of FeSe change with lattice expansion?
FeSe: Phase stability and local magnetism

GGA+DMFT total energy

$U = 3.5 \text{ eV}$, $J = 0.85 \text{ eV}$

- isostructural transformation upon $\sim 10\%$ expansion of the lattice ($p_c \sim -6.4 \text{ GPa}$)
- strong increase of the fluctuating magnetic moment

FeTe:
- tetragonal to collapsed-tetragonal phase transformation under pressure
- suppression of magnetism $> 4-6 \text{ GPa}$

Exp: Zhang et al. (2009)
FeSe: Spectral function

Low-volume phase

High-volume phase

Van Hove singularity shifts to $E_F$ due to correlations

Exp.: Yokoya et al. (2012)

Spectral weight suppressed with Te substitution ( = lattice expansion)

Exp.: Yokoya et al. (2012)
Shift of Van Hove singularity to $E_F$ correlates with increase of $T_c$ in FeSe$_{1-x}$Te$_x$

**Conjecture:**
Superconductivity in FeSe$_{1-x}$Te$_x$ sensitively depends on Van Hove singularity
Correlation-induced change of magnetic structure upon expansion of lattice

In accord with experiments on FeSe$_{1-x}$Te$_x$
Xia et al. (2009), Tamai et al. (2010), Maletz et al. (2014), Nakayama et al. (2014)

Leonov et al., arXiv:1411.0604

Low-volume phase:
• Correlations do not change FS
• In-plane nesting with $Q_m = (\pi, \pi)$

High-volume phase:
• Correlations induce topological change of FS → Lifshitz transition
• Electron pocket at M point vanishes
• In-plane nesting with $Q_m = (\pi, 0)$
Investigation of the structural stability of $V_2O_3$ at the Mott metal-insulator transition

Leonov, Anisimov, DV (PRB, 2015, in press)
Phase diagram and electronic structure of $\text{V}_2\text{O}_3$

Electronic structure - $\text{V}^{3+}$ (3d$^2$)

$S = 1$

McWhan et al. (1973)
Metal-Insulator Transition vs. Structural Transition in $V_2O_3$

- implementation with plane-wave pseudo-potentials: $U = 5.0 \text{ eV}, J = 0.93 \text{ eV}, T = 390 \text{ K}$

LDA+DMFT total energy

Strong $a_{1g} - e_{g}^{\pi}$ crystal-field splitting

Structural transition at $\Delta V / V \sim -7\%$, critical pressure $p_c \sim 186 \text{ kbar}$

$(V_{0.96}Cr_{0.04})_2O_3$ (PI phase $\square$) stable at ambient pressure:

$\rightarrow$ inconsistent with experiment

Mo et al. (2003), Keller et al. (2004); Poteryaev et al. (2007)
Metal-Insulator Transition vs. Structural Transition in V$_2$O$_3$

- implementation with plane-wave pseudo-potentials $U = 5.0$ eV, $J = 0.93$ eV
- fully charge-self-consistent LDA+DMFT scheme $T = 390$ K

V$_2$O$_3$ (PM phase ○) stable at ambient pressure: → agreement with exp.

- structural transition at $\Delta V / V \sim 1.5\%$; critical pressure $p_c \sim -28$ kbar
- structural transformation decoupled from metal-insulator transition

Exp: Pfalzer et al. (2006); Kondel et al. (2013)
Conclusion:
Electronic correlations have strong effect on lattice stability
Perspectives
Explain and predict properties of complex correlated materials using DFT+DMFT

Phase diagram of light actinide series

Phase diagram connecting individual binary alloy diagrams
Black: two-phase regions; Brown: details unknown

Boring and Smith (2000)
Time-dependent processes in correlated materials

Goal: DFT/GW+noneqDMFT

Goal: Prediction of non-equilibrium properties of correlated materials

http://qc-md.mpsd.mpg.de/
Happy Birthday, Sasha!