“Fundamentals of Thermodynamic Modelling of Materials”

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PROFESSOR & TOPIC

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Magnetic Models for CT

[05001]

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Magnetic models

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Degrees of freedom to be taken into account in solids

- Atomic defects (non-stoichiometry, high temperature)
- Vibrational (harmonic and anharmonic)
- Magnetic excitations
- Electronic excitations

Time scale

- $> 10^{-6}$ s
- $\sim 10^{-13}$ s
- $\sim 10^{-14}$ s
- $\sim 10^{-15}$ s
Schrödinger equation

\[ \hat{H} \Psi(r, R) = \left[ \hat{H}_r + \hat{H}_R + \hat{H}_{rR} \right] \Psi(r, R) = E \Psi(r, R) \]

Depends on the coordinates of all the electrons \((r_i)\) and nuclei \((R_I)\) in the system

\[ \Psi(r, R) \equiv \Psi(r_1, r_2, ..., r_N, R_1, R_2, ..., R_M) = \psi(r_1, r_2, ..., r_N) \cdot \varphi(R_1, R_2, ..., R_M) \equiv \psi(r) \cdot \varphi(R) \]

Adiabatic (Born-Oppenheimer) approximation makes use of the fact that nuclei are much heavier (and, therefore, slower) than electrons. Therefore, electronic wave function can be determined first, while the nuclei are considered as static point-charges.

Self-consistent field approach: reduce the many body problem to a one-particle problem. Each electron moves in the effective potential created by the nuclei and all the other electrons. The problem is to be solved iteratively (self-consistently).

Classical molecular dynamics (MD)

MD simulation of solidification of Ni.

Potential energy for a system of \(N\) particles:

From now on: \(r_i\) denote coordinates of the nuclei.

\[ U = U(r_1, r_2, ..., r_N) = U_0 + \sum_i U_i(r_i) + \sum_{i<j} V^{(2)}(r_i, r_j) + \sum_{i<j<k} V^{(3)}(r_i, r_j, r_k) + \cdots + \sum_{i<j<...<n} V^{(N)}(r_i, r_j, ..., r_n) \]


See also: http://cms.northwestern.edu/Intro.html
Classical and quantum description of ionic motion

**Classical mechanics:**

\[ C_V = 3N_A k_B \]

**Classical (Dulong-Petit) law**

\[ \frac{C_V}{3k_B} \]

\[ T/T_D \]

Thermodynamics and magnetism of iron

**Components of the Thermodynamic Functions of Iron**

R. J. Weiss and E. J. Thomas

Ordnance Materials Research Office, Watertown Arsenal, Watertown, Massachusetts

(Received January 23, 1956)

**Magnetic energy, α-Fe:**

\[ E_{\text{magn}} = \int_0^\infty C_{\text{magn}} dT \approx 1103 \text{ K} \]

**Magnetic entropy, α-Fe:**

\[ S_{\text{magn}} = \int_0^\infty \frac{C_{\text{magn}}}{T} dT \approx R \ln(2s + 1) \approx 1.169 \cdot k_B \]

**Figure 1.** Specific heat of α (b.c.c.) Fe. Curve A is the calculated lattice specific heat for a Debye \( \theta = 420^\circ \text{K} \). Curve B includes the electronic specific heat.
Localized vs. itinerant electron magnetism

Heisenberg picture

Paramagnetism:

Stoner picture

Curie-Weiss

Pauli

T

T

Fermi-surface nesting and spin density wave in pure Cr

Antiferromagnetic spin density wave due to Fermi surface nesting in chromium and its influence on the transport coefficients.

Co-Fe phase diagram

Fe-Ni phase diagram
Magnetic effects in the thermodynamics of iron and steel

Impact of Magnetism Upon Metallurgy


A MODEL FOR ALLOYING EFFECTS IN FERROMAGNETIC METALS

Matt Hillert and Magnus Jarl
Division of Physical Metallurgy
Royal Institute of Technology
S-100 44 STOCKHOLM 70
Sweden


\[
\begin{align*}
\alpha_{\text{OY}}^{\text{Fe}} - \alpha_{\text{O}}^{\text{Fe}} &= -5188.3 + 45.79T - 6.3711T + 0.0024T^2 \\
&\quad + 6597[T^{4/10} + T^{14/10}]^{1/2} / 1500T^{2/3} \quad \text{J/mol}
\end{align*}
\]

Below the Curie temperature we obtain

\[
\begin{align*}
\alpha_{\text{OY}}^{\text{Fe}} - \alpha_{\text{O}}^{\text{Fe}} &= 3589.4 + 36.07T - 6.3711T + 0.0024T^2 \\
&\quad + 9309[T^{4/10} + T^{10}]^{1/2} / 135[T^{10} + T^{14} / 600T^{16}] \quad \text{J/mol}
\end{align*}
\]
Magnetic heat capacity model for pure elements


Workshop on

THERMODYNAMIC MODELS AND DATA FOR PURE ELEMENTS AND OTHER ENDMEMBERS OF SOLUTIONS

Schloß Ringberg, Febr. 26, to March 3, 1995

Group 4: \( \lambda \)-Transitions

Group members:

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Shuang-Lin Chen
Dept. Mater. Sci. & Engg. Univ. of Wisconsin, Madison, USA

Thermodynamics and magnetism of iron

Magnetic heat capacity, \( \alpha \)-Fe:

\[
C_{\text{magn}} = \begin{cases} 
2K_\alpha \left( \tau^3 + \tau^9/3 + \tau^{15}/5 \right), & \tau < 1; \\
2K_\beta \left( \tau^{-5} + \tau^{-15}/3 + \tau^{-25}/5 \right), & \tau > 1.
\end{cases}
\]

\[
\tau = \frac{T}{T_c},
\]

\[
K_\alpha = 0.6417 \ln(\beta + 1), \quad K_\beta = 0.918 \ln(\beta + 1).
\]

Magnetic energy, \( \alpha \)-Fe:

\[
E_{\text{magn}} = \int_0^\infty C_{\text{magn}} dT \approx 1103 \text{ K}
\]

Magnetic entropy, \( \alpha \)-Fe:

\[
S_{\text{magn}} = \int_0^\infty \frac{C_{\text{magn}}}{T} dT \approx k_B \ln(\beta + 1)
\]

\[
\approx 1.169 \cdot k_B
\]
Random alloys: Coherent potential approximation (CPA)

Disordered local moment (DLM) model of paramagnetic state

"Equivalence" theorem:

Magnetic entropy:
$$S_{\text{magn}} = k_B \ln(M_s + 1)$$

Fe(DLM) = 50% Fe↑ + 50% Fe↓
First-principles approach to iron and steel

Exact Muffin-Tin Orbitals theory

Coherent Potential Approximation
-chemical and magnetic disorder

EMTO-CPA method
L. Vitos, I.A. Abrikosov, B. Johansson, Phys.

Application to austenitic steels
(paramagnetic, DLM)


Applications to Fe-Cr alloys: Magnetic moments in bcc and σ phases

BCC Fe-Cr
FM – ferromagnetic
DLM – paramagnetic

Local magnetic moments on Fe atoms on different sites in σ-FeCr

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Magnetic models
11/19 2010

Applications to magnetic excitations in metals

Calculated magnetic moments of planar spin-spirals
Schallcross et al. PHYSICAL REVIEW B 72, 104437 (2005)
Effective interatomic interactions (ECI), “chemical” and “magnetic”

**Configurational Hamiltonian**

\[ H_{\text{conf}} = \frac{1}{2} \sum_{i \neq j} V_{ij}^{(2)} c_i c_j + \frac{1}{3!} \sum_{i \neq j \neq k} V_{ijk}^{(3)} c_i c_j c_k + \ldots \]

**Heisenberg (classical) Hamiltonian**

\[ H_{\text{magn}} = -\sum_{i \neq j} J_{ij}^{(2)} \hat{\sigma}_i \hat{\sigma}_j + \sum_{i \neq j} V_{ij}^{(2b)} (\hat{\sigma}_i \hat{\sigma}_j)^2 + \ldots \]

\[ c_i = \begin{cases} 1 & \text{if site } i \text{ is occupied by A} \\ 0 & \text{if site } i \text{ is occupied by B} \end{cases} \]

\[ \hat{\sigma}_i \] spin direction on site \( i \), here treated as a vector, but may be a QM operator, or Ising pseudospin \( \pm 1 \), etc.

**Mixed-type Hamiltonian**

\[ H_{\text{mixed}} = \frac{1}{2} \sum_{i \neq j} \left[ (V_{ij}^{AA} - 2J_{ij}^{AA} \hat{\sigma}_i \hat{\sigma}_j) c_j - 2(V_{ij}^{AB} - 2J_{ij}^{AB} \hat{\sigma}_i \hat{\sigma}_j) c_i (1 - c_j) \right] + 2(V_{ij}^{BB} - 2J_{ij}^{BB} \hat{\sigma}_i \hat{\sigma}_j)(1 - c_i)(1 - c_j) \]

**Generalized perturbation method (GPM)**

**Original formulation:** F. Ducastelle and F. Gautier, 1976.

**Consistent extension to the ab initio methods:** Ruban et al, 2002.


The reference state is a random \( \text{A}_n \text{B}_{1-n} \) alloy. Its electronic structure is given by the coherent potential approximation (CPA). Then interactions of an Ising-like Hamiltonian are just the energies of the following exchange of atoms:

\[ (V_{ij}^{(2)} = V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB} ) \]

\[ V_s^{(n)} = \frac{1}{2^{n-1}} (E_{A\text{-even}} - E_{A\text{-odd}}) \]
Effective pair interactions (EPI) in Fe-Cr


Effect of magnetic transformation in iron on the solubility of impurities


For an impurity X whose effect on Curie temperature of the host is

$$\Delta T_X = d T_c(x)/dx$$

where $x$ is the concentration, one gets

$$\Delta E_{\text{sol}} \propto \Delta T_X$$
Cu precipitation in Fe: a serious issue for nuclear reactor safety

- Nano-sized precipitates of bcc Cu form under irradiation of reactor pressure vessel (RPV) steels
- Cu particles impede dislocation motion by pinning the dislocation lines – strengthening effect
- Increase in yield strength correlates with the increase of brittle-to-ductile transition temperature – embrittlement


Excercise: A toy model of Fe-Cu alloy

Consider Fe-Cu alloy as a ternary alloy of the following species: Fe↑, Fe↓, and Cu, with concentrations \( x_{Fe↑} \), \( x_{Fe↓} \), and \( x_{Cu} \), respectively, in the mean-field approximation:

\[
E = \varepsilon_c x_{Cu} \left( x_{Fe↑} + x_{Fe↓} \right) + 4\varepsilon_m x_{Fe↑} x_{Fe↓}
\]

\[
S = -k_B \left( x_{Cu} \ln x_{Cu} + x_{Fe↑} \ln x_{Fe↑} + x_{Fe↓} \ln x_{Fe↓} \right)
\]

Introduce new variables: \( c \equiv x_{Cu} \) and \( \mu \equiv x_{Fe↑} - x_{Fe↓} \).

Minimize free energy, \( F(c,\mu) = E - TS \), to find the Curie temperature \( T_C(c) \).

Find the solution energy of Cu in Fe in the following limiting cases:

1) \( T \to 0 \), \( \mu \to (1-c) \); Answer: \( E_{sol} = (1/2) d^2E/dc^2 = \varepsilon_c \)

2) \( T > T_C \), \( \mu = 0 \). Answer: \( E_{sol} = \varepsilon_c - \varepsilon_m \)

\( E^{PM}_{sol} = E^{FM}_{sol} - E^{magn} \)
Mixing energy in Fe-Cu alloys

Inversion of chemical short-range order in the ferromagnetic state of Fe-Cr alloys

Materials needs for fusion

P. Olsson, I. A. Abrikosov, and J. Wallenius
Ordering and decomposition in Fe-Cr

Magnetic energy in bcc Fe-Cr
Magnetic energy (pure Fe)

Magnetic energy, $\alpha$-Fe:

$$E_{\text{magn}} = \int_0^\infty C_{\text{magn}} \, dT \cong 1103 \, \text{K}$$

Monte Carlo modeling vs. Calphad/experiment

TABLE III. The energy of magnetic ordering in bcc Fe, in units of the experimental Curie temperature $T_C = 1043 \, \text{K}$. The theoretical results obtained using the GGA and LDA are compared with the Calphad representation of experimental information.

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta E_{\text{magn}} / T_C$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calphad</td>
<td>1.06</td>
<td>Calphad, from $C_{\text{magn}}$</td>
</tr>
<tr>
<td>This work</td>
<td>2.60</td>
<td>LDA, from $J_{\text{pp}}$ DLM state</td>
</tr>
<tr>
<td>This work</td>
<td>1.82</td>
<td>LDA, as $E_{\text{DLM}} - E_{\text{FM}}$</td>
</tr>
<tr>
<td>This work</td>
<td>2.03</td>
<td>GGA, as $E_{\text{DLM}} - E_{\text{FM}}$</td>
</tr>
</tbody>
</table>

We need more theory!
Conclusions

- Magnetic state in steels affects strongly all the properties
- Main problem for theory is how to model the magnetic $C_p$ contribution in steels, as a function of temperature and composition
- Accurate first-principles description of the magnetism and bonding in steels at high temperature requires the use of advanced theoretical techniques