HIGH-$T_c$ DILUTE MAGNETIC SEMICONDUCTORS AND OXIDES (THEORY)

Materials design for semiconductor spintronics

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OUTLINE

- **Ab initio calculation**
  - Density functional theory and local density approximation
  - Disordered systems
  - Finite temperature magnetism

- **Dilute magnetic semiconductors**
  - Chemical trend
  - Magnetic interactions in DMS
  - Practical and accurate $T_C$ calculation for DMS
  - Inhomogeneity in DMS

- **Oxide-based DMS**
  - LDA error and self interaction correction
  - $(\text{Zn, Co})\text{O}$ and$(\text{Ti, Co})\text{O}_2$
  - MgO-based DMS
AB INITIO CALCULATION

- Based on quantum mechanics, electronic structure of materials is calculated to estimate physical properties of the material.

\[
H \Psi = E \Psi
\]

\[
H = \sum_{i=1}^{N} \left( -\nabla_{i}^{2} + v_{\text{ext}}(r) \right) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{2}{|r_i - r_j|}
\]

\[
\Psi = \Psi(r_1, r_2, r_3, \cdots, r_N)
\]

- No external parameters (experimental values) required → extremely suitable for ‘materials design’

- Many body problem! (N \sim 10^{23}) → impossible to solve
DENSITY FUNCTIONAL THEORY

Hohenberg and Kohn, PR136 (1964) B864
Kohn and Sham, PR 140 (1965) A1133

$\Psi = \Psi(r_1, r_2, r_3, \ldots, r_N)$

$\Psi = \Psi[n(r)]$  \hspace{1cm} \textbf{Hohenberg-Kohn Theorem}

$n(r)$: electron density

- One-electron problem
- Difficult many-body effects

$\rightarrow$ exchange-correlation potential $v_{xc}$
LOCAL DENSITY APPROXIMATION (LDA)

- \( u_{xc} \): calculated from exchange correlation energy of homogeneous electron system

- Successfully predicts
  - Crystal structure
  - Lattice constant
  - Bulk modulus
  - Magnetism
  - ...

- Known shortcomings
  - Overestimation of cohesion
  - Underestimation of band-gap energy
  - Occupied d-states are predicted at too high energy
  - Ground state properties (T=0 K)
  - ...

Akai et al.,
Presented at CMD workshop
APPLICATION TO DMS SYSTEMS

- Crystal:
  - Translation symmetry

- Alloying and doping
  - Magnetic impurities occupy cation sites randomly.
  - p-type or n-type carrier doping

- Magnetic disorder
  - In the paramagnetic state, magnetic moments are randomly oriented.

Coherent potential approximation (CPA)
COHERENT POTENTIAL APPROXIMATION

Soven, PR 156 (1967) 809
Velicky et al., PR 156 (1967) 1017,
Shiba, Prog. Theor. Phys. 46 (1971) 77

Coherent potential approximation
- Electronic structure of substitutional alloy
- Taking configuration average by using multiple scattering technique
EXAMPLE: SLATER-PAULING CURVE

- Magnetic Alloys
- Average magnetic moment behaves regularly
- Theory reproduces experimental curves very well including branches

H. Akai

Figure 1. Calculated [10] and experimental saturation magnetization of Fe-, Ni- and Co-based alloys vs. average electron number. The fcc instead of hcp structure is assumed for Co-based alloys. See ref.[10] for further details.
DISORDERED LOCAL MOMENT STATE

Paramagnetic state (total magnetization = 0)


Electronic structure above $T_C$
- **Fe:** DLM solution exists $\Rightarrow$ local moment picture ($\mu=1.9\mu_B$)
- **Ni:** No DLM solution $\Rightarrow$ Stoner picture ($\mu=0$)

Energy difference between FM and DLM states $\Rightarrow T_C$
MAPPING ON HEISENBERG MODEL

\[ H = - \sum_{i \neq j} J_{ij} e_i \cdot e_j \]

- Finite rotation (Oguchi et al.)
- Infinitesimal rotation (Liechtenstein et al.)
- Frozen magnon approach (Sandratskii et al.)

Curie temperature
- Mean field approximation
  \[ k_B T_C = \frac{2c}{3} \sum_{i \neq 0} J_{0i} \]
- Random phase approximation
  \[ k_B T_C = \frac{2c}{3} \left( \frac{1}{N} \sum_q [J(0) - J(q)]^{-1} \right)^{-1} \]
  \[ J(q) \equiv \sum_{i \neq 0} J_{0i} \exp(iq \cdot R_{0i}) \]
- Monte Carlo simulation (exact)

\[ J_{ij} = \frac{1}{4\pi} \Im \int d\varepsilon \, d\varepsilon' \, \text{Tr} \left[ \Delta_i (\varepsilon) \tau^\dagger_{ij} (\varepsilon) \Delta_j (\varepsilon) \tau^\dagger_{ij} (\varepsilon) \right] \]

\[ \Delta_i (\varepsilon) = t^\dagger_{ij} (\varepsilon) - t_{ij} (\varepsilon) \]

\[ \tau_{ij} (\varepsilon) = \sum_k \left[ t^\dagger (\varepsilon) - g(k, \varepsilon) \right]^{-1} \exp \left[ i \varepsilon \cdot (R_i - R_j) \right] \]

Liechtenstein et al., JMMM 67 (1987) 65
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  - Chemical trend
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Electronically, spin density approximation (LSDA)
- Korringa-Kohn-Rostoker method (KKR)
- Coherent potential approximation (CPA)

→ MACHIKANEYAMA 2002 by Akai

Disordered local moment state

Stability of ferromagnetic state: \( \Delta E = TE(DLM) - TE(FM) \)

Curie temperature in mean field approximation: \( k_B T_C = \frac{2\Delta E}{3c} \)
$T_C^{\text{MFA}}$ OF Mn-DOPED III-V DMS

(Ga, Mn)N; $T_c \sim \sqrt{c}$
(Ga, Mn)Sb; $T_c \sim c$

Electronic structure

- Origin of the ferromagnetism
  - double exchange
  - p-d exchange

ELECTRONIC STRUCTURE OF III-V+Mn DMS

Impurity band in the gap $\rightarrow$ double exchange

Localized d-states below valence band $\rightarrow$ p-d exchange

FERROMAGNETISM IN DMS

Double exchange mechanism $^{1,2}$

Band energy change in impurity d-band

Band energy gain $\sim W \sim c^{1/2}$
(if $E_F$ is in impurity band)

p-d exchange mechanism $^{3,4}$

Hole mediated ferromagnetism
Band energy change in valence band

Half-metallic system

Valence band is polarized: $-1 \mu_B / Mn$

Average polarization (mean field): $-c \mu_B$

Interaction between Mn ions $\sim c$

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CALCULATION OF EXCHANGE INTERACTIONS

Magnetic force theorem
Mapping on effective Heisenberg model

\[
J_{ij} = \frac{1}{4\pi} \text{Im} \int d\varepsilon \text{Tr} \left[ \Delta_i(\varepsilon) \tau_{ij}^\dagger(\varepsilon) \Delta_j(\varepsilon) \tau_{ji}^\dagger(\varepsilon) \right]
\]

\[
\begin{align*}
\Delta_i(\varepsilon) &= t_i^{-1}(\varepsilon) - t_i^{\dagger}(\varepsilon) \\
\tau_{ij}(\varepsilon) &= \left[ t^{-1}(\varepsilon) - \tilde{\tau}^{-1}(\varepsilon) + \tilde{\tau}^{-1}(\varepsilon) \right]_{ij} \\
\tilde{\tau}_{ij}(\varepsilon) &= \sum_k \left[ \tilde{t}^{-1}(\varepsilon) - g(k, \varepsilon) \right]^{-1} \exp\left\{ i k \cdot (\mathbf{R}_i - \mathbf{R}_j) \right\}
\end{align*}
\]

- t: single site t-matrix
- \(\tau\): scattering path operator
- \(\tilde{t}\): cpa single site t-matrix
- \(\tilde{\tau}\): cpa scattering path operator
- \(\mathbf{R}\): lattice vector
- g: KKR structure constant
EXCHANGE INTERACTIONS IN DMS

K. Sato et al., PRB 70 (2004)201202

- double exchange system (Ga, Mn)N → strong, but short-range interactions
- p-d exchange system (Ga, Mn)Sb → weak, but long-range interactions
MAGNETIC PERCOLATION PROBLEM

K. Sato et al., PRB 70 (2004)201202

- 2D square lattice with nearest neighbor interaction.

Percolation threshold (c=0.59)

only clusters → percolated → perfect network

MCS (Reality)

MFA

Table:

<table>
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<tr>
<th>lattice</th>
<th>percolation threshold</th>
</tr>
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<tbody>
<tr>
<td>square</td>
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<tr>
<td>triangle</td>
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</tr>
<tr>
<td>diamond</td>
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<tr>
<td>sc</td>
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<tr>
<td>bcc</td>
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</tr>
<tr>
<td>fcc</td>
<td>0.20</td>
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</tbody>
</table>

D. Stauffer and A. Aharony, ‘Introduction to Percolation Theory’
Taylor & Francis, London, 1994

Short ranged interaction → Ferromagnetism is suppressed below the percolation threshold
Reasonable agreement with experiments.

For low concentration, high-$T_C$ can not be expected. (magnetic percolation)

Origin of high-$T_C$ phases $\rightarrow$ Inhomogeneity
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INHOMOGENEOUS IMPURITY DISTRIBUTION IN DMS

**MBE**

(Al, Cr)N, Cr 7%, Tc>900K

(Ga, Cr)N, Cr 3%, Tc>900K

TEM, EELS

One-dimensional Cr-rich region: Ferromagnetic

Spherical clusters: not FM

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Gu et al., JMMM 290-291(2005)1395.

Singh et al., APL 86 (2005)12504

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Fig. 1. Energy-filtered electron micrographs showing Cr segregation in Al(Cr)N films grown at 700°C: (a) 7% Cr-doped AlN; (b) 2.5% Cr-doped AlN.

Fig. 2. Energy-filtered electron micrographs showing Cr distribution for 4% Cr-doped AlN grown at different substrate temperatures: (a) 700 °C; (b) 800 °C.

SELF-ORGANIZED NANO-COLUMN IN GeMn

- Mn-doped Ge
- MBE crystal growth
- TEM, EELS analysis
- Average: Mn = 6%
- Self-organized nano-column
  - 3nm diameter
  - 10nm interval
  - Mn concentration ~ 35%
- $T_C > 400$ K

T. Devillers et al., PRB 76 (2007) 205306
GENERALIZED PERTURBATION METHOD

Ducastelle and Gautier: ‘Generalized perturbation method’

\[ H = - \sum_{i \neq j} V_{ij} \sigma_i \sigma_j \]

\[ V_{ij} : \text{Effective pair interaction between site } i \text{ and } j \]

\[ \sigma_i : \text{Occupation number} \]

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

\[ X^i_A (\epsilon) - X^i_B (\epsilon) \]

\[ \tau_{ij} (\epsilon) = \sum_k \left[ t^{-1}(\epsilon) - g(k, \epsilon) \right]^{-1} \exp\{i g(k) \cdot (\mathbf{R}_i - \mathbf{R}_j)\} \]


\[ X: \text{single site scattering-matrix} \]
\[ \tau: \text{scattering path operator} \]
\[ \mathbf{R}: \text{lattice vector} \]
\[ g: \text{KKR structure constant} \]
EFFECTIVE PAIR INTERACTIONS IN DMS

- Effective attractive interactions between nearest neighbors
  → phase separation
- Similar results
  - M. van Schilfgaarde et al., PRB 63 (2001) 233205
  - H. Raebiger et al., JMMM 290-291 (2005) 1398
  - J. Osorio-Guillen et al., PRB 74 (2006) 35305

NANO-DECOMPOSITION AND $T_C$ IN (Ga, Mn)N

Spinodal decomposition in DMS
- For low concentrations
  - Independent small clusters $\rightarrow$ super paramagnetism ($T_C=0$)
- For high concentrations
  - Connecting random pattern $\rightarrow$ enhancement of $T_C$

SUPER-PARAMAGNETIC BLOCKING PHENOMENA

Finite relaxation time to flip the magnetization due to the energy barrier caused by the anisotropy
→ Hysteretic behavior

\[ E(\phi, \theta) = KV\sin^2\theta - MV\cos(\phi - \theta) \]

- **K**: Anisotropy
- **V**: volume
- **M**: moment
- **B**: external field

- Hysteresis
- Anisotropy constant \( \varpi \) parameter


D. A. Dimitrov et al., PRB 54 (1996) 9237
Quasi-one dimensional structure due to the spinodal nano-decomposition under the layer-by-layer growth condition

Large clusters for low concentrations

**Layer-by-layer Growth Simulation**

- *Spinodal nano-decomposition in 3D*
  - Small clusters
  - No percolation
  - Super paramagnetism

- **Layer-by-layer condition**
  - One dimensional fragments
  - Large clusters
  - Large blocking temperature

**Materials**

- (Zn, Cr)Te, Cr 5%
- (Ga, Mn)N, Mn 5%

SIMULATION OF BLOCKING PHENOMENA IN DMS


- Homogeneous distribution
  - Above $T_C$ → no hysteresis
- Large cluster → ferromagnetic behavior at high temperature
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MATERIALS DESIGN OF ZnO-BASED DMS

- **ZnO**
  - Wide band gap $E_g = 3.3$ eV (transparent)
  - Environmentally safe

- **High-$T_c$?**
  - (Zn,V)O
    - H. Saeki (SSC 120, 439 (2001)) $T_c > 300K$
    - S. Ramachandran (2005) **Paramagnetic**
  - (Zn,Co)O
    - Ueda (APL 79, 988 (2001)) $T_c > 300K$
    - Schwartz and Gamelin, (Adv. Mater. 23, 2115 (2004)) $T_c > 300K$ (Zn$_i$ n-type defect)
    - Barla (PRB 76, 126201 (2007)) **Paramagnetic**
    - ...

Magnetization curves of (Zn, Co)O. (Schwartz et al.)

AB INITIO WORK ON ZnO-BASED DMS

- LDA, GGA
  - Sato (JJAP 39, L555 (2000))
    (Zn, TM)O, TM=V, Cr, Fe, Co, Ni) ferromagnetism
  - Lee (PRB 69, 85205 (2004))
    (Zn, Co)O, ferromagnetism with high electron doping

- LDA+U (Gopal et al. PRB 74 (2006) 94418)
  - (Zn, TM)O, AFM ordering is more favorable
  - Li doping induces ferromagnetism

- Self interaction correction (Pemmaraju et al. PRB 78 (2008) 54428)
  - (Zn, Co)O, AFM (ab plane), FM (c axis)
  - Co-V\textsubscript{O} pairs, blocked superparamagnetism

- GGA+U, empirical potentials (Lany et al., PRB 77 (2008) 241201R)
  - (Zn, Co)O, (Zn, Cr)O, very small magnetic coupling (para)

LDA error:
1. Occupied d states at too high energy
2. Underestimation of band gap
   → miss-alignment of impurity d states to VB and CB

Raebiger et al., PRB 79 (2009) 165202
SELF-INTERACTION

- Energy functional
  \[ E[n] = U[n] + E_{XC}[n] \]

- Self-interaction
  \[ E[n_i] = U[n_i] + E_{XC}[n_i] = 0 \]

- Correction
  \[ E_{LDA}^{LDA+SIC} = E_{LDA}^{LDA} - \sum_i \delta_i \]

- Formulation and implementation
  A. Filippetti, N. Spaldin, PRB 67 (2003) 125109


ELECTRONIC STRUCTURE OF ZnO

- The position of the Zn-d states is well reproduced by the LDA-SIC.
- Prediction of the Band-gap energy is improved.
(Zn,Co)O

- PES spectra are well reproduced by the SIC.
- No state at the Fermi level
  → double exchange does not work.


EXCHANGE INTERACTION IN (Zn,Co)O

- **LDA:**
  - ferromagnetic interactions due to the double exchange.

- **SIC:**
  - Anti-ferromagnetic superexchange interactions
  - Ferromagnetic interaction is induced by electron doping.

(Lany et al., PRB 77 (2008) 241201R)

- Due to the short ranged nature of the double exchange, high-$T_C$ is not expected.

- $\rightarrow$ Inhomogeneity

TiO$_2$ BASED DMS

- Photoelectrochemical use
  - Honda-Fujishima effect
- Polymorphism
  - Rutile (E$_g$=3.0eV)
  - Anatase (E$_g$=3.2eV)
  - Brookite (E$_g$=3.2eV)

  - Laser-MBE
  - Room temperature FM
  - Anatase, 0.32$\mu_B$/Co, low spin
  - Rutile, $\sim$1$\mu_B$/Co, low spin
- Chambers et al., (APL 79 (2001) 3467)
  - OPA-MBE
  - Room temperature FM
  - Anatase, 1.26$\mu_B$/Co, Co$^{2+}$ low spin
- Quilty et al., PRL 96 (2006) 27202
  - Rutile TiCoO$_2$, XPS, Co$^{2+}$, high spin
- Mamiya et al., APL 89 (2006) 62506
  - Rutile TiCoO$_2$, XMCD, Co$^{2+}$, high spin
ELECTRONIC STRUCTURE OF (Ti, Co)O$_2$

- no oxygen vacancy
- LDA, SIC-LDA $\rightarrow$ fails to reproduce XPS


J. W. Quilty et al., PRL 96 (2006) 27202
ELECTRONIC STRUCTURE OF (Ti, Co)O$_2$ With O VACANCIES

- With Oxygen vacancies (2.5%)
- SIC-LDA reproduces XPS very well (Co$^{2+}$: d$^7$ high spin)

J. W. Quilty et al., PRL 96 (2006) 27202

MGO-BASED DMS

- **TM-doped MgO [1]: TM = Ni, Co**
  - As-grown bulk single crystals exhibit a perfect paramagnetic behavior.
  - By introducing defects by ion irradiation or by thin film deposition, we are able to achieve defect-mediated ferromagnetic ordering.

- **Ferromagnetism induced by Carbon and Nitrogen:**
  - Prediction of half-metallicity and ferromagnetism caused by C and N in alkaline-earth-metal oxides AO (A= Mg, Ca, Sr, Ba) and by N in SiO$_2$ [2].
  - Experiment: Room temperature ferromagnetism in C-doped ZnO [3]

- **Design of MgO-based ferromagnetic materials**
  1. Ni-doped MgO
  2. N-doped MgO

RESULTS (1): NI-DOPED MGO

- In agreement with experiment:
  - Without oxygen vacancies: paramagnetic, homogeneous distribution of Ni
  - Oxygen vacancies: ferromagnetism, nano-scale separation.

- However, $T_c$ is predicted to be lower than 20K (5% Ni) for the homogeneous phase.

$\rightarrow$ Spinodal decomposition?
RESULTS (2): N-DOPED MGO

- The finite DOS appears at the Fermi level of minority spin states → half-metallic

\[ J_{04} \text{ increases} \]
\[ T_c \text{ can exceed 300K at sufficiently high concentrations (x>20%)} \]
RESULTS (3):
PHASE SEPARATION IN N-DOPED MGO

- Chemical pair interaction
  - In MgO and MgS: interaction is attractive → **nano-scale phase separation**
  - In MgSe: at x < 0.15 repulsive interaction → **homogeneous distribution.**

- Nano-scale phase separation:
  100 steps – simulation at 650K

- **MgO$_{0.8}$N$_{0.2}$**
- 1st NN is dominant
- High-$T_B$ ?
SUMMARY

- **Ab initio calculation for materials design**
  - Density functional theory, local density approximation
  - Finite temperature magnetism
    → DLM state, Mapping on Heisenberg model

- **Application to dilute magnetic semiconductors**
  - Mechanism and $T_C$ calculations (double exchange vs. super exchange)
  - Impurity band in the gap
    → **double exchange** → short ranged interaction
  - Localized moment
    → **p-d exchange** → long ranged interaction
  - Low concentration, Low $T_C$ (*Magnetic percolation problem*)
  - Inhomogeneous DMS: **Superparmagnetic blocking temperature can be high**

- **Application to oxide based materials**
  - **LDA can not be justified for oxide systems**
  - **Self-interaction correction** applied to ZnCoO, TiCoO$_2$
    → PES, charge state and spin state well reproduced
  - MgO based DMS
    - Mg$_{1-x}$Ni$_x$O: Oxygen vacancies stabilize ferromagnetism and cause the nano-scale separation.
    - N-doped MgO, MgS, MgAs: All compounds exhibit the **half-metallic ground state and ferromagnetism at high temperatures**