Hydrogen complexes in Mn$_x$Ga$_{1-x}$As dilute magnetic semiconductors: theoretical results

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Dilute Magnetic Semiconductors (DMS)

Semiconductors exhibiting magnetic properties (ideally, room-temperature ferromagnetism) hold promises as new materials for innovative devices based on spin electronics, or *spintronics*

Most studied material: Mn$_x$Ga$_{1-x}$As, with $x$ up to $\sim 5 \div 6\%$

Current picture of Mn$_x$Ga$_{1-x}$As:

- Substitutional Mn provides *both* a localized moment from the half-filled $d$ shell *and* a hole
- The hole is mostly *delocalized* on neighboring As atoms
- The hole is *crucial* for ferromagnetism
- Mn acts as a shallow *acceptor*, with an acceptor level at $E \sim 100$ meV
- Magnetic moment per Mn atom: $\mu \simeq 4\mu_B$
Hydrogenation of semiconductors

H can easily diffuse into semiconductors

General characteristics of hydrogenation:

- H can *saturate* dangling bonds and *passivate* defects (i.e. remove their electrical activity)
- H is an *amphoteric* impurity: it may passivate both donors and acceptors
- H passivation properties *depend* on the occupied site
- H is a structural local probe: it forms *complexes* with impurities, easily detected with IR spectroscopy

Exposure to H is a tool to modify magnetic properties and to achieve selective removal of ferromagnetism
Hydrogenation of DMS: Experiments


formation of H-Mn complexes: H mode observed at 2140 cm⁻¹

dramatic reduction of density of carriers

ferromagnetism disappears, replaced by paramagnetism
Hydrogenation of DMS: current picture

- H removes holes from the band structure
- No holes, no ferromagnetism (which needs hole-mediated exchange)
- H-Mn complex expected to be similar to H-Zn and H-Mg complexes in Mg- and Zn-doped GaAs: H backbonded at As neighbor of Mn

Open questions:

- passivation (i.e. removal of the acceptor level) or compensation (i.e. filling of the level)?
- geometry of Mn-H complexes? is H really backbonded to As or does it prefer a different site?
Theoretical framework: DFT-LSDA

Energy functional under an external potential $V(r)$:

$$ E_{DFT}[n_+(r), n_-(r)] = T_0 + \int n(r)V(r)dr + E_{II} + E_H + E_{xc}[n_+(r), n_-(r)] \quad (1) $$

$n_\sigma(r) = \text{charge density with spin polarization } \sigma$, $n(r) = n_+(r) + n_-(r)$ total charge density
$T_0 = \text{kinetic energy}$, $E_{II} = \text{nuclear interaction energy}$, $E_H = \text{electrostatic (Hartree) energy}$

Minimization of the above functional yields the Kohn-Sham equations:

$$ \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(r) + e^2 \int \frac{n(r')}{|r-r'|}dr' + V_{xc}^\sigma(r) \right] \psi_{k,v}^\sigma(r) = e_{k,v}^\sigma \psi_{k,v}^\sigma(r) \quad (2) $$

Exchange-correlation potential:

$$ V_{xc}^\sigma(r) = \frac{\delta E_{xc}}{\delta n_\sigma(r)} \quad (3) $$

Charge density:

$$ n_\sigma(r) = \sum_{k,v} f_{k,v}^\sigma |\psi_{k,v}^\sigma(r)|^2 \quad (4) $$
Theoretical framework: DFT-LSDA (2)

We use pseudopotentials and a plane-wave basis set in a supercell geometry

- exchange-correlation functional: spin-polarized, gradient-corrected PBE (gradient corrections needed, simple LDA yields bad results for geometry of MnAs)

- Supercell geometry: consider a superset with enlarged period of the original zincblende lattice, replace one Ga with Mn. With a 64-atom supercell, 1 Mn/supercell: \( x = \frac{1}{32} = 0.03125 \)

- \( \mathbf{k} \)-point grid: Monkhorst-Pack 444 grid

- ultrasoft (Vanderbilt) pseudopotentials – very useful for systems containing Mn!

- kinetic-energy cutoff (determines the dimension of the basis set): 25 Ry

All calculations performed using PWscf (http://www.pwscf.org)
**LSDA results**

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“abMn”: E=0 eV

H bound to Mn in antibonding position: 
\[ d_{H-Mn} = 1.60\text{Å}, \quad \nu_H = 1761 \text{ cm}^{-1}, \quad \mu = 3\mu_B \]

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“bcAs”: E=0.33 eV

H off-axis in the Mn-As bond: 
\[ d_{H-Mn}=1.62\text{Å}, \quad d_{H-As}=1.75\text{Å} \]
\[ \nu_H = 1671 \text{ cm}^{-1}, \quad \mu = 5\mu_B \]

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“abAs”: E=0.59 eV

H bound to As in antibonding position: 
\[ d_{H-As}=1.58\text{Å}, \quad \nu_H = 1926 \text{ cm}^{-1}, \quad \mu = 5\mu_B \]

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Results are inconsistent with experiments:

- The preferred configuration has H bound with Mn and Mn in a five-fold coordination
- The value of \( \mu \) indicates pairing of H with one \( d \) state from Mn
- Passivation is not achieved: the acceptor level is still present at \( \sim 120 \text{ meV} \)
- Vibrational frequency is much too low (exp: \( \nu_H = 2143 \text{ cm}^{-1} \))
LSDA results (2)

Other studied sites resulting in higher-energy configurations:

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"bcAsLin": E=0.53 eV
"bcAsGa": E=0.66 eV
"abAsGa": E=1.02 eV
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H in the Mn-As bond (linear):
\[ d_{\text{H-Mn}} = 1.82\text{Å}, \quad d_{\text{H-As}} = 1.56\text{Å} \]
\[ \nu_{\text{H}} = 2119 \text{ cm}^{-1}, \quad \mu = 5\mu_B \]

H in Ga-As bond far from Mn:
\[ d_{\text{H-Ga}} = 1.83\text{Å}, \quad d_{\text{H-As}} = 1.55\text{Å} \]
\[ \nu_{\text{H}} = 2179 \text{ cm}^{-1}, \quad \mu = 5\mu_B \]

H bound to As in antibonding position:
\[ d_{\text{H-As}} = 1.54\text{Å} \]
\[ \nu_{\text{H}} = 2162 \text{ cm}^{-1}, \quad \mu = 5\mu_B \]

Is there formation of di-hydrogen complexes?
LSDA results: H2 complexes

E=0.00 eV

$d_{H-Mn} = 1.59\AA$, $d_{H-As}=1.55\AA$
$
u_{H-Mn}=1829\,cm^{-1}$, $\nu_{H-As}=2261\,cm^{-1}$
No passivation

E=0.37 eV

$d_{H-Mn} = 1.57\AA$, $d_{H-As}=1.54\AA$
$
u_{H-Mn}=1880\,cm^{-1}$, $\nu_{H-As}=2162\,cm^{-1}$
LSDA and highly correlated materials

Simple LSDA approaches can have serious trouble in dealing with highly correlated materials (i.e. atoms with localised, atomic-like electronic states).

Fundamental problem: the inability of LSDA to find the correct occupancy of atomic-like electronic states may lead to qualitatively wrong results – but with the correct occupancy, results are quite good.

Deep reason: the lack of discontinuity in all current approximations to the exchange-correlation functional favors fractionary occupations of localised states.

In Mn$_x$Ga$_{1-x}$As, LSDA yields too shallow Mn 3$d$ bands: $\sim 2.5$eV below the top of the valence band, versus $\sim 4$eV experimentally – corrected by LDA+U calculations (Shick et al, PRB 69, 125207 (2004)).
DFT for highly correlated materials: the LDA+U approach

LDA+U: add a Hubbard-like correlation term to the energy (Anisimov et al, PRB 44, 943 (1991); PRB 48, 16929 (1993)). Simplified form:

\[
E_{LDA+U}[n(r)] = E_{DFT}[n(r)] + E_{U}[n(r)], \quad E_{U}[n(r)] = \frac{U}{2} \sum_{\sigma} \text{Tr}[n^\sigma(1 - n^\sigma)]
\]  

(5)

where \( n^\sigma \) is the matrix of orbital occupancies for a set of atomic-like states \( \phi_m \):

\[
n^\sigma_{mm'} = \sum_{\sigma} \sum_{k,v} f^\sigma_{k,v} \langle \psi^\sigma_{k,v} | P_{mm'} | \psi^\sigma_{k,v} \rangle, \quad P_{mm'} = | \phi_m \rangle \langle \phi_{m'} |
\]  

(6)

Value of Hubbard \( U \) parameter?

- use as empirical, adjustable parameter
- estimate from experiments (i.e. difference between photemission and inverse photoemission)
- calculate from first principles

For Mn, typical value from experiments is \( U \simeq 4 \) eV.
Relative energies of the various sites as a function of $U$:

$U \approx 4$ eV is also the value for which the Mn $3d$ shift towards their correct position!
Geometry of the ground state:
H slightly off-axis in the Mn-As bond
\( d_{\text{H-Mn}} = 1.88 \text{Å}, d_{\text{H-As}} = 1.55 \text{Å} \)
\( \nu_{\text{H}} = 2030 \text{ cm}^{-1} \)

Electronic structure: \( \mu = 5\mu_B \), acceptor level completely removed (passivated)
(Tentative) Conclusions

- Simple LSDA does not account for the properties of H complexes in dilute magnetic semiconductor $\text{Mn}_x \text{Ga}_{1-x} \text{As}$: correlation effects are crucial.

- Simple LDA+U seems to do the job.

- H sits in the center of the bond between Mn and As, somewhat off axis.

- H passivates the Mn impurity.