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Theoretical Material Science: Electronic structure theory at  
the computer

Dilute magnetic semiconductors

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# 1 Important Note

If any problems occur please do not hesitate to contact me.  
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## 2 Background

### 2.1 Dilute magnetic semiconductors

For a few years, there have been sketches of electronic devices (for instance, transistors) based on the electrons' spin instead of just their charge. The associated field is known as "spintronics" and producing workable devices along these lines would be really good indeed.

Now, nature seems to dictate that for semiconductor devices, semiconductor materials are a plus, and for spin-polarized electrons, ferromagnetic materials are not a bad idea either. It would be good if we had a material that is semiconducting and ferromagnetic at the same time, at room temperature, and that can be grown by conventional semiconductor technology. Then we could realize "spintronics".

One of the most popular candidate materials is  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , with  $x \approx 2\%$ - $10\%$  in most experiments. This material can be understood as a solid solution. The basic lattice is GaAs (zincblende), but with a fraction of the Ga atoms replaced by Mn.

### 2.2 Spin models

What we can explore for this exercise are two degrees of freedom:

1. Configurational
2. Spin

"Configurational" means that we get to choose where we place the Mn atoms in the crystal. We always use periodic supercells, but there are different possible Mn arrangements. We can try to suggest the one with the highest  $T_C$ . (Growing that exact structure in experiment is then a task for someone else.)

"Spin" means that we can legislate which spin sits on which Mn atom – "up" or "down". It is important to note that in spin-polarized density functional theory as we use it here, there are really only two spin directions, up or down. We can thus calculate configurations that are purely "ferromagnetic" (all spins point up), purely "antiferromagnetic" (equally many up or down spins on the Mn atoms), or anything inbetween.

As a result, for a particular placement of Mn atoms on the lattice, we can compute different total energies  $E_{\text{FM}}$ ,  $E_{\text{AFM}}(\{S_i\})$ , or anything inbetween. Note that there can be different ways to distribute spins on a lattice to give an overall antiferromagnetic state.

Since there are only up- and down-spins, the appropriate model to represent our energetics is not a Heisenberg model but an Ising-type model. We can postulate:

$$E(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i \cdot S_j \quad , \quad (1)$$

where we can formally choose  $S_i = \pm 1$ , and then move on to determine the parameter  $J$  from total energy calculations for different spin arrangements.

If we let the sum in Eq. (1) run over all possible inequivalent types of pairs, triplets, quadruplets etc. formed by the Mn atoms on the lattice, with different interaction parameters  $J_f$  for each such inequivalent "figure"  $f$ , this mapping on an Ising Hamiltonian would even be exact, known as a cluster expansion. The nearest-neighbour form above is just a common truncated interaction Hamiltonian used in the literature.

Note that the spin on the Mn atoms is due to the spin splitting of the  $d$  levels on Mn, which is much larger than typical experimental temperatures. The moments located on each Mn atom themselves thus do not vanish with temperature, only their orientations can change. Our simple Ising model above will thus remain valid even at finite  $T$ .

### 2.3 Vegard's law

The change of the lattice parameter with the solute concentration  $x$  is often approximated by Vegard's law. It relates the lattice parameter of a solid solution to the concentration of the solute by a linear approximation. For example, consider the semiconductor compound  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ . The relation between the constituent elements and their associated lattice parameters,  $a$ , is such that:

$$a_{\text{GaMnAs}} = x \cdot a_{\text{MnAs}} + (1 - x) \cdot a_{\text{GaAs}} \quad (2)$$

where  $x$  is the atomic concentration of manganese.

Often, Vegard's law is not a great approximation, but in this case and for small concentrations, experiments seem to indicate that it holds – see figure.

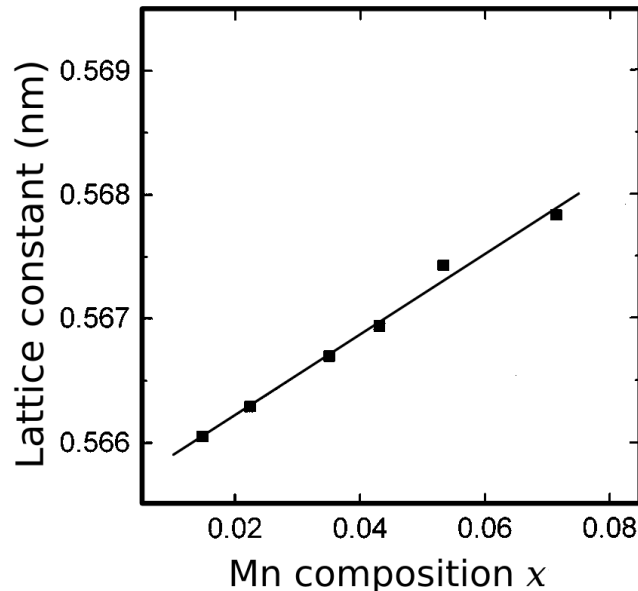


Figure 1: Vegard's law for  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ : The lattice constant  $a$  is plotted versus Mn composition  $x$  in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  at room temperature. Plot taken from Ohno et al., APL 69, 363 (1996)

### 3 Reminder: FHI-aims in the Virtual Machine

As a quick reminder, here is (again) an overview of the most important pieces needed for FHI-aims:

- To run the code, create the necessary input files (`control.in` and `geometry.in`) in a working directory of your choice.
- The calling sequence for FHI-aims is:

```
mpirun -np 1 aims.VERSION.mpi.x | tee calculation.out
```

As before, although you should not need it, there is a complete manual (pdf) for the FHI-aims code located in `/home/theory/fhi-aims.160328 3/FHI-aims.pdf`.

For this exercise we will require some pre-computed results. Those can be found under the link <https://thcloud.rz-berlin.mpg.de/s/sUukGO44aljs9Wk>

Alternatively, you can just re-download and re-install the updated virtual machine instance that already contains these files from <https://thcloud.rz-berlin.mpg.de/s/kElVkeik4aSfMEQ>. Please note that deleting the old virtual machine will also delete the data that you created with it during the previous exercises.

#### 3.1 Exercise 25a

This exercise is not yet computational.

The idea is to find out how many  $d$  levels there are in Mn, how many  $d$  electrons are left in a  $\text{Mn}^{3+}$  ion, and then use Hund's rules to see how these electrons are distributed if there were no field whatsoever.

Next, this Mn ion lives in a real GaAs crystal, and thus in a tetrahedral environment. Remember that there is such a thing as crystal field splitting of the  $d$  levels, go to Wikipedia or elsewhere, and deduce what the appropriate splitting is for a tetrahedral environment. Then, assume that the spin splitting is much larger than the crystal field splitting (it is!) and draw a schematic level diagram.

In real GaMnAs, some of the  $d$  levels you have just drawn will hybridize with the As  $sp$  levels that surround them (someone has to do the bonding!), others will not (providing the spin).

#### 3.2 Exercise 25b

In real life, we would now predict equilibrium geometries (lattice parameters, local atomic positions etc.) directly from first principles. Since we have no time, we will instead take lattice parameters from experiment, and keep all atoms fixed at their *ideal* lattice positions.

The idea of this exercise is to estimate how the lattice parameter should vary for GaMnAs alloys of varying composition (we will need those as input later).

#### 3.3 Exercise 25c

The goal is to find out what the electronic level occupations of Mn even look like in this system, in DFT-LDA.

We do so by a "supercell" calculation, i.e. we assume a particular (and simple) supercell geometry with Ga and Mn atoms distributed on a lattice. To create a manageable structure, we choose the *conventional* (!) fcc cell formed by four Ga atoms and four As atoms which is given by

```

lattice_vector a 0.0 0.0
lattice_vector 0.0 a 0.0
lattice_vector 0.0 0.0 a

atom_frac 0.0 0.0 0.0 Ga
atom_frac 0.25 0.25 0.25 As
atom_frac 0.5 0.5 0.0 Ga
atom_frac 0.75 0.75 0.25 As
atom_frac 0.5 0.0 0.5 Ga
atom_frac 0.75 0.25 0.75 As
atom_frac 0.0 0.5 0.5 Ga
atom_frac 0.25 0.75 0.75 As

```

and replace one of them (e.g., the corner) by Mn. This gives us a total composition  $\text{Ga}_3\text{Mn}_1\text{As}_4$ , eight atoms. A schematic picture of the structure is included.

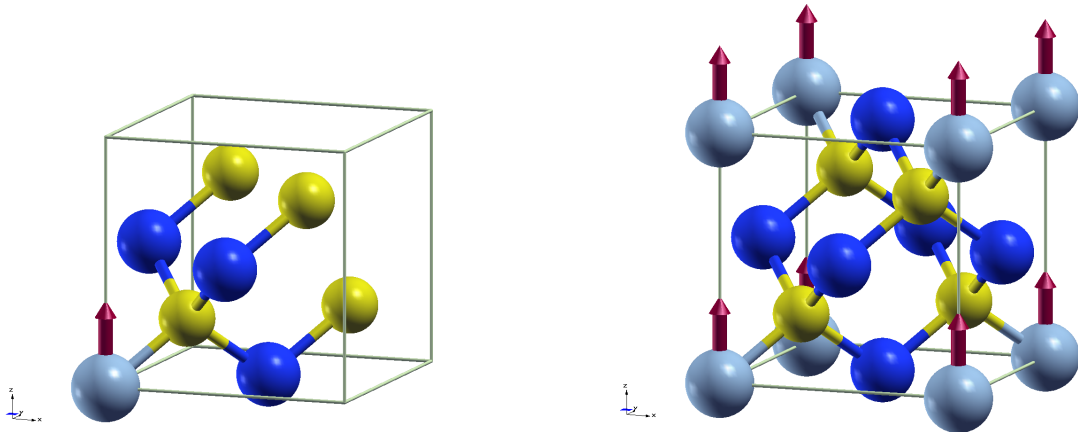


Figure 2: The cubic  $(\text{Ga}_3\text{Mn}_1)\text{As}_4$  cell with 8 atoms. One Ga atom is replaced by an Mn. The left figure shows only the 8 atoms that are unique to the cubic cell. The right figure adds the other atoms on the corners and faces only for illustration.

- Create a `geometry.in` file for this structure as you did before, with the appropriate lattice parameter.
  - Remember that you could use the `atom_frac` keyword to specify atomic positions in units of the lattice vectors.
  - The single Mn atom in the structure needs to be equipped with an initial guess for the magnetic moment. Specifying:

```
initial_moment 4
```

immediately after that atom will do the trick.
- Create a `control.in` file for Ga, Mn, As with “light” species defaults, LDA as the exchange-correlation functional, and spin (the `spin collinear` keyword).
  - Use a dense enough  $k$ -grid -  $4 \times 4 \times 4$  is on the low end.
  - Set the value of the gaussian broadening to `occupation_type gaussian 0.1`
  - Set the convergence settings to `sc_accuracy_rho 1e-4`, `sc_accuracy_eev 1e-2`, and `sc_accuracy_etot 1e-5`
  - The *total* DOS can be plotted as usual by:

```
output dos -30 0 1000 0.1
```

```
dos_kgrid_factors 5 5 5
```

- You also want the “projected density of states,” i.e., the fraction that is attributable to the atomic orbitals of any given atom. Use:

```
output species_proj_dos -30 0 1000 0.1
```

That should suffice to give you the required results. Two things:

The “projected density of states” onto a given atom is not a uniquely defined thing. We here require a concept called “atoms in molecules”, and if there is more than one atom, there *is no unique way* to decide whether a given part of the electron density came from the angular momentum channels of one atom or of another.

We here use a concept called a “Mulliken analysis” which simply takes the Kohn-Sham levels and distributes the electrons in each state (at single-particle energy  $\epsilon$ ) into the atoms and angular momentum channels where the associated basis functions came from – a projection. Since basis functions overlap between different atoms, electrons are “evenly assigned” between them. This way of classifying is anything but unique and gives increasingly bad results as the basis set increases in size (because then, electrons on one atom can easily be represented by the basis functions coming from another atom).

With our settings and basis size the concept still works well on a qualitative level, but again, different schemes could be found.

In any event, based on the keywords above, the code produces files called

- KS\_DOS\_total.dat
- Mn.l\_proj\_dos\_spin\_up.dat
- Mn.l\_proj\_dos\_spin\_down.dat

The total DOS contains information for *both* spin channels. For the Mn files, this is the occupation of angular momentum channels on the atom for the up and down channels, separately. You are interested in the *d* channels ( $l=2$ ), which is the fifth column. Read the header of either file if you are unsure.

All these densities of states can be plotted together using `xmgrace` (directly), do not try to use a pre-built script. If you plot the total spin up DOS, the total spin down DOS, the Mn spin up *d* DOS and the Mn spin down *d* DOS together as a function of energy, you will see which part of the Kohn-Sham density of states is derived from which atomic levels, approximately.

We also note that the `output species_proj_dos [...]` keywords already sums up all the contributions from every atom of a given element, so there is only one file for Ga instead of 3, etc. This is ok, as we do not need to see 3 Ga atoms separately here, anyway.

**(continued on next page for clarity)**

There is some more information in the FHI-aims standard output if all went well. Look for the following section:

Performing Mulliken charge analysis on all atoms.  
 Full analysis (per state, per k-point, etc.) will NOT be written to separate file 'Mulliken.out'.  
 This file can be requested by stating 'output mulliken' explicitly.  
 Summary of the per-atom charge analysis:

atom	electrons	charge	l=0	l=1	l=2
1	24.822252	0.177748	6.665034	12.486492	5.661639
2	33.311139	-0.311139	7.772708	15.407925	10.130506
3	30.644398	0.355602	7.137535	13.344343	10.162520
4	33.311139	-0.311139	7.772708	15.407925	10.130506
5	30.644398	0.355602	7.137535	13.344343	10.162520
6	33.311139	-0.311139	7.772708	15.407925	10.130506
7	30.644398	0.355602	7.137535	13.344343	10.162520
8	33.311139	-0.311139	7.772708	15.407925	10.130506
Total	250.000000	0.000000			

Summary of the per-atom spin analysis:

atom	spin	l=0	l=1	l=2	l=3
1	4.018188	0.105790	0.102621	3.810078	-0.000302
2	-0.049338	0.000128	-0.070500	0.021035	
3	0.059064	0.024862	0.034323	-0.000122	
4	-0.049338	0.000128	-0.070500	0.021035	
5	0.059064	0.024862	0.034323	-0.000122	
6	-0.049338	0.000128	-0.070500	0.021035	
7	0.059064	0.024862	0.034323	-0.000122	
8	-0.049338	0.000128	-0.070500	0.021035	
Total	3.998030				

This gives you integrated values for the spin and angular momentum occupations of each atom. How many *d* states are filled on Mn (total)? Given the residual spin per atom (given as  $N_{\text{up}} - N_{\text{down}}$ ), how many spin down electrons are there?

**Compare this count of *d* electrons to what was expected for  $\text{Mn}^{3+}$  ion! You will find a difference.**



### 3.4 Exercise 25d

An 8-atom cell is not really dilute. We have therefore doubled the unit cell size in all directions and computed the properties of a more isolated Mn atom in a 64 atom cell. Since the computation would be too time-consuming, just look at the results and plot the various densities of states as in the previous exercise.

The results can be found under the link

<https://thcloud.rz-berlin.mpg.de/s/sUukGO44aljs9Wk>

### 3.5 Exercise 25e

For this part you may utilize the Hamiltonian from Eq. 1. Remember that the interaction is between the Mn atoms only. Which kind of lattice do they form?

### 3.6 Exercise 25f

For this exercise use the pre-calculated results that contain this antiferromagnetic and ferromagnetic case. You can find them under the link

<https://thcloud.rz-berlin.mpg.de/s/sUukGO44aljs9Wk>

If you subtract the total energies of both calculations from one another, you will get a very small value. You can calculate the  $J$  parameter of an Ising model (but make sure you count the right number of Mn neighbour pairs per cell!) and then calculate  $T_c$ . What do you get?