

SEGREGATION AND ORDERING OF IMPURITIES IN DMS

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SPATIAL DISTRIBUTION OF IMPURITIES

two-step approach:

I. Ising-type alloy Hamiltonian

$$H^{\text{Ising}} = E_0 + \sum_{i,Q} V_i^Q \eta_i^Q + \frac{1}{2} \sum_{i,j,Q,Q'} V_{ij}^{QQ'} \eta_i^Q \eta_j^{Q'} + \dots$$

occupation indices

$$\eta_i^Q = \begin{cases} 1 & \text{if site } i \text{ is occupied by atom } Q \\ 0 & \text{otherwise} \end{cases}$$

effective interatomic interactions $V_{ij}^{QQ'}$ are calculated ab initio

II. find equilibrium structure by methods of statistical mechanics

it corresponds to a minimum of free energy $F = E - TS$

ISING TYPE HAMILTONIAN 1

- occupation indices $\eta_i^A = \eta_i$, $\eta_i^B = 1 - \eta_i$

$$H^{\text{Ising}} = E'_0 + \sum_i V_i \eta_i + \frac{1}{2} \sum_{i,j} V_{ij} \eta_i \eta_j + \dots$$

$$V_i = V_i^A - V_i^B + \sum_j (V_{ij}^{AB} - V_{ij}^{BB}) + \dots$$

$$V_{ij} = V_{ij}^{AA} + V_{ij}^{BB} - V_{ij}^{AB} - V_{ij}^{BA}, \quad V_{ijl} = \dots$$

- occupation indices vs. spin variables

$$\eta_i = (\sigma_i + 1)/2, \quad \sigma_i = 2\eta_i - 1$$

- homogeneous systems: on-site term $\sum_{i,Q} V_i^Q \eta_i^Q$ not important, because it is independent of alloy configuration

- convergence of H^{Ising} ?

ISING TYPE HAMILTONIAN 2

effective interatomic interactions:

on-site terms V_i^Q

pair interactions $V_{ij}^{QQ'}$,

triplet interactions $V_{ijk}^{QQ'Q''}$, etc.

parameters of the Ising Hamiltonian can be determined by:

- Connolly-Williams inversion (CWI)
- Generalized Perturbation Method (GPM)

CONNOLLY-WILLIAMS INVERSION 1

J.W.D. Connolly and A.R. Williams, PRB **27** 5169 (1983)

$$E[\Gamma] = \sum_n v_n \xi_n[\Gamma]$$

$$\xi_n = \frac{1}{N_n} \sum_{\{p_k\}}^{\text{clusters}} \sigma_{p_1} \sigma_{p_2} \cdots \sigma_{p_n}$$

Γ ... ordered structures

ab initio $E[\Gamma]$

full potential methods

system of linear equations for
unknown cluster interactions v_n 's

linear independent

well-conditioned

simplest version:

TABLE I. Cluster correlation functions for five structures on an fcc lattice. ξ_0 represents the structure-independent term, $\xi_1 = x_A - x_B$ is the "point" correlation function, and ξ_2 , ξ_3 , and ξ_4 correspond to NN pairs, NN triangles, and NN tetrahedra, respectively, where NN means nearest neighbor.

Formula	Structure	Correlation functions				
		ξ_0	ξ_1	ξ_2	ξ_3	ξ_4
<i>A</i>	fcc	1	1	1	1	1
<i>A₃B</i>	<i>L1₂</i>	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1
<i>AB</i>	<i>L1₀</i>	1	0	$-\frac{1}{3}$	0	1
<i>AB₃</i>	<i>L1₂</i>	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	-1
<i>B</i>	fcc	1	-1	1	-1	1

CONNOLLY-WILLIAMS INVERSION 2

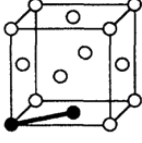
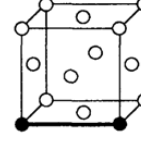
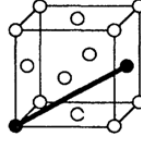
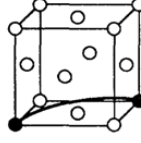
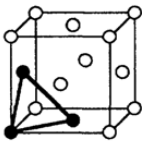
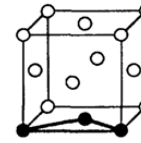
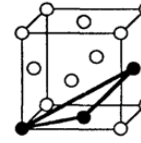
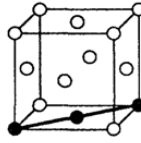
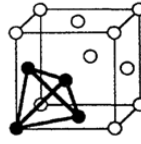
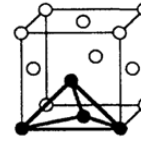
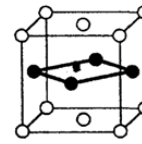
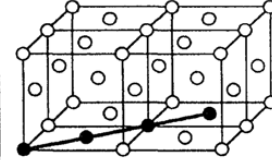
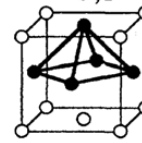
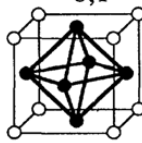
ordered structures:

- supercells
- special quasirandom structures

Z.W. Lu, S.-H. Wei, A. Zunger, S. Frota-Pesoa, and L.G. Ferreira, PRB **44** 512 (1991).

effective interatomic interactions
are concentration independent

TABLE I. Effective cluster interactions for fcc lattice.

$V_{2,1}$  NN PAIR	$V_{2,2}$  2NN PAIR	$V_{2,3}$  3NN PAIR	$V_{2,4}$  4NN PAIR
$V_{3,1}$  NN TRIPLET	$V_{3,2}$  2NN TRI.	$V_{3,3}$  3NN TRI.	$V_{3,4}$  4NN TRI.
$V_{4,1}$  NN QUAD	$V_{4,2}$  IRR. QUAD.	$V_{4,3}$  SQUARE	$V_{4,4}$  LINEAR QUAD.
$V_{5,1}$  PYRAMID		$V_{6,1}$  OCTAHEDRON	

GENERALIZED PERTURBATION METHOD (GPM)

F. Ducastelle: J. Phys. F: Metal Phys. **8** 1437 (1978).

F. Ducastelle: *Order and Phase Stability in Alloys*, North Holland, 1991

- total energy of a random alloy is mapped onto Ising alloy Hamiltonian
- based on the coherent potential approximation (CPA)

total energy for one configuration of the alloy

$$E_{tot}^{\Gamma} = E_{band}^{\Gamma} + E_{core}^{\Gamma} + E_{dc}^{\Gamma} + E_{Mad}^{\Gamma}$$

$$E_{band}^{\Gamma} = \int_{-\infty}^{E_F} E n^{\Gamma}(E) dE$$

$$E_{core}^{\Gamma} = \sum_i \sum_{\alpha}^{occ} \varepsilon_{i\alpha}^{core}$$

GPM 2

$$E_{dc}^{\Gamma} = \sum_i \Phi_{dc}[\rho_i]$$

$$\Phi_{dc}[\rho_i] = \int_{s_i} d^3r \rho_i(r) \left[\epsilon_{xc}(\rho_i(r)) - \mu_{xc}(\rho_i(r)) - \int_{s_i} d^3r' \frac{\rho_i(r')}{|\mathbf{r} - \mathbf{r}'|} \right]$$

$$E_{Mad}^{\Gamma} = \sum_{i,j} \sum_{L,L'} q_i^L \mathcal{M}_{ij}^{L,L'} q_j^{L'}$$

- on-site terms: band, core, dc, Mad
- pair interactions: band, Mad (neutral spheres in TB-LMTO)
- higher interactions: band only

GPM 3

$$V_i^{Q,\text{band}} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{tr} \ln \left[1 - v_i^Q(z) \bar{g}_{ii}(z) \right]$$

$$V_{ij}^{QQ',\text{band}} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{tr} \ln \left[1 - t_i^Q(z) \bar{g}_{ij}(z) t_j^{Q'}(z) \bar{g}_{ji}(z) \right]$$

$$V_{ij}^{QQ',\text{band}} \approx \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{tr} \left[t_i^Q(z) \bar{g}_{ij}(z) t_j^{Q'}(z) \bar{g}_{ji}(z) \right]$$

$$V_{ij}^{\text{Mad}} = V_{ij}^{\text{AA}} + V_{ij}^{\text{BB}} - V_{ij}^{\text{AB}} - V_{ij}^{\text{BA}} = M_{ij}^{\text{scr}} (q_i^{\text{A}} - q_i^{\text{B}}) (q_j^{\text{A}} - q_j^{\text{B}})$$

$V_{ij} > 0$... ordering

$V_{ij} < 0$... segregation

STATISTICAL MECHANICS 1

- Bragg-Williams (single-site approximation)

$$S_{\text{config}} = -k_B \sum_{iQ} c_i^Q \ln(c_i^Q), \quad c_i^Q = \langle \eta_i^Q \rangle$$

- concentration-wave method $c_i^Q = c_0^Q + \delta c_i^Q$

$$F = \frac{1}{2} \sum_{ij} \sum_{QQ'} V_{ij}^{QQ'} c_i^Q c_j^{Q'} + k_B T \sum_i \sum_Q c_i^Q \ln(c_i^Q)$$

$$F \approx F_0 + \frac{1}{2} \sum_{\mathbf{k}} \sum_{QQ'}^{\text{BZ}} \left[V^{QQ'}(\mathbf{k}) + \frac{k_B T}{c^Q} \delta_{QQ'} \right] [\delta c^Q(\mathbf{k})]^* \delta c^{Q'}(\mathbf{k})$$

- gives critical temperature and LRO

A.G. Khachatryan, *Theory of Structural Transformations in Solids*, Wiley, New York (1983).

STATISTICAL MECHANICS 2

- cluster variation method
- Monte Carlo
- Warren-Cowley short-range order parameters (above critical temperature)

$$\alpha_{ij}^{QQ'} = -\frac{\langle \eta_i^Q \eta_j^{Q'} \rangle - \langle \eta_i^Q \rangle \langle \eta_j^{Q'} \rangle}{\langle \eta_i^Q \rangle \langle \eta_j^{Q'} \rangle} = 1 - \frac{\langle \eta_i^Q \eta_j^{Q'} \rangle}{c^Q c^{Q'}}$$

Krivoglaz-Clapp-Moss (KCM) formula (\approx RPA)

$$\alpha(\mathbf{k}) = -D[M + \beta \tilde{V}(\mathbf{k})]^{-1} D^T, \quad [M]_{QQ'} = \frac{1}{c^0} + \delta_{Q,Q'} \frac{1}{c^Q}$$

- effective cluster interactions can be used in CALPHAD

DILUTED MAGNETIC SEMICONDUCTORS 1

- zincblende GaAs: substitutional $3d$ impurities at Ga sublattice
- reference state: disordered local moment (DLM) or ferromagnetic
- details of formalism, SRO, impurity formation energy and thermodynamic stability of (Ga,Mn)As

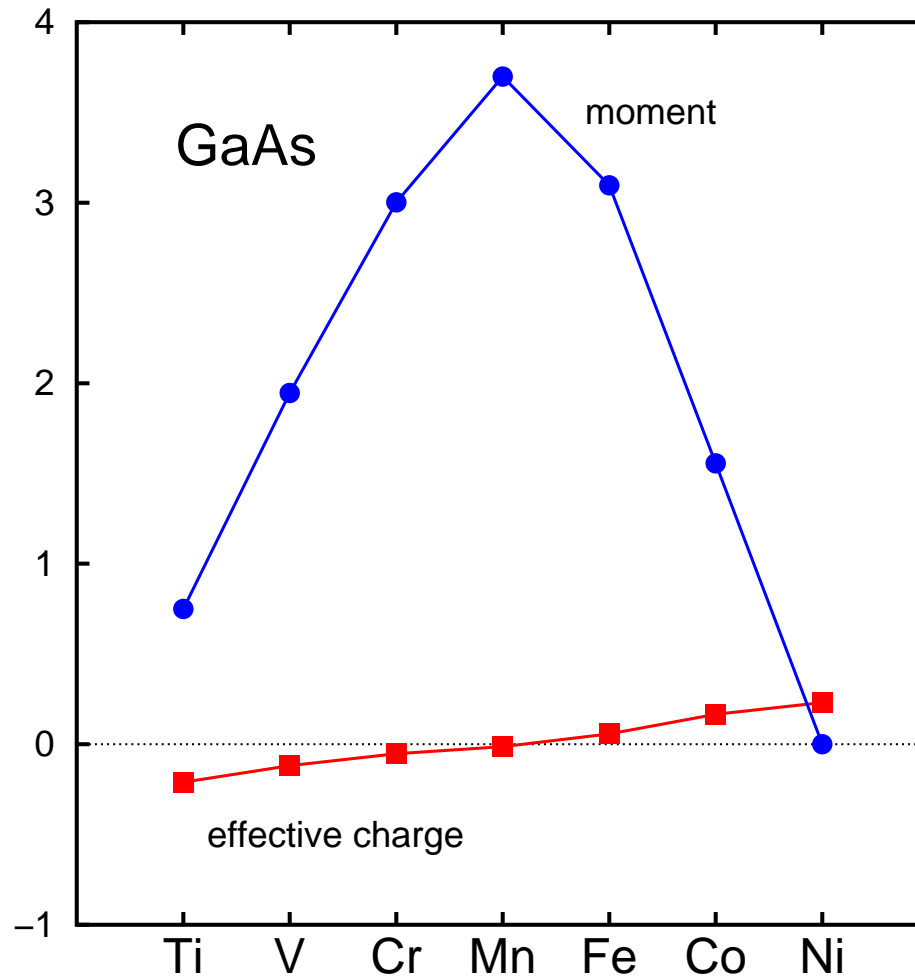
V. Drchal, J. Kudrnovský, I. Turek, F. Máca, and P. Weinberger: *Phil. Mag.* **84** (2004), 1889.

- Coulomb interaction are partially screened

V. Drchal, R. Hammerling, and P. Weinberger: *PRB* **74** (2006), 214202.

DILUTED MAGNETIC SEMICONDUCTORS 2

effective charge ... $q^{\text{eff}} = q^{\text{imp}} - q^{\text{at}}$



Results for 3d impurities (5 at. %) in GaAs

impurity	without Madelung		with Madelung	
	T^* [K]	\mathbf{k}	T^* [K]	\mathbf{k}
Ti	870	(0,0,0)	509	$2\pi(1,0,0)$
V	259	(0,0,0)	259	(0,0,0)
Cr	1489	(0,0,0)	1489	(0,0,0)
Mn	1182	(0,0,0)	1182	(0,0,0)
Fe	1028	(0,0,0)	477	(1.77,0,0)
Co	1084	(0.46,0,0)	373	2.74 (1,1,1)
Ni	1854	(0.34,0,0)	758	2.97 (1,1,-1)

- disordered reference state (disordered local moments)
- $\mathbf{k} = (0,0,0)$ corresponds to segregation
- non-zero critical vector \mathbf{k} represents its star (point group T_d)
- mean-field approximation overestimates critical temperatures

Results for 3d impurities (5 at. %) in GaAs

impurity	without Madelung		with Madelung	
	T^* [K]	\mathbf{k}	T^* [K]	\mathbf{k}
Ti	664	(0,0,0)	391	$2\pi(1,0,0)$
V	181	(1.49,0,0)	81	$\pi(1,1,-1)$
Cr	1259	(0,0,0)	805	(1.82,0,0)
Mn	748	(0.63,0,0)	683	(1.08,0,0)
Fe	460	(0,0,0)	72	$2\pi(1,0,0)$
Co	734	(0.86,0,0)	340	2.86 (1,1,1)

- ferromagnetic reference state
- lower critical temperatures, more complex structures than for DLM

Comparison of III-V and II-VI materials

system	q^{eff}	m [μ_B]	T^* [K]	\mathbf{k}
$\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$	-0.010	3.68	1182	$\pi(0,0,0)$
$\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$	-0.109	4.17	185	$\pi(0,1,2)$
$\text{Zn}_{0.75}\text{Mn}_{0.25}\text{Se}$	-0.110	4.14	845	$\pi(0,1,2)$
$\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te}$	0.040	4.44	62	$\pi(0,1,2)$
$\text{Cd}_{0.50}\text{Mn}_{0.50}\text{Te}$	0.055	4.39	656	$\pi(0,1,2)$

- DLM reference state
- effective charges close to 0
- ordering vector $\mathbf{k} = \pi(0,1,2)$

CONCLUSIONS

- two-step approach:
 - total energy is mapped onto effective alloy Ising Hamiltonian
 - methods of classical statistical mechanics are used
- predict atomic structure in thermodynamic equilibrium
- concentration-wave method as a mean-field approximation overestimates critical temperature
- screening of Coulomb interactions important
- dynamics unavailable (barriers are not accessible)
- can be applied to 3-dim bulk systems, surfaces, overlayers, multilayers, etc.