First-principles calculations of materials promising for nanoelectronics.

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1. Introduction.

Three types of materials promising for nanoelectronics are considered: diluted magnetic semiconductors (DMS), digital magnetic heterostructures (DMH) and silicon nanoclusters.

DMS and DMH are candidates for spintronics. It is highly desirable to make room temperature ferromagnetic semiconductors, which are compatible with Si technology.

- In many cases DMS and DMH have similar chemical composition and differ only by the spatial distribution of magnetic atoms - random in DMS and planar in DMH.
- The rather high Curie temperatures of DMS and DMH were reported: T_C=188 K (GaAs:Mn) and T_C=170-250 K (Mn δ-doped GaAs/*p*-AlGaAs heterostructure).
- First-principles calculations can provide valuable information about:

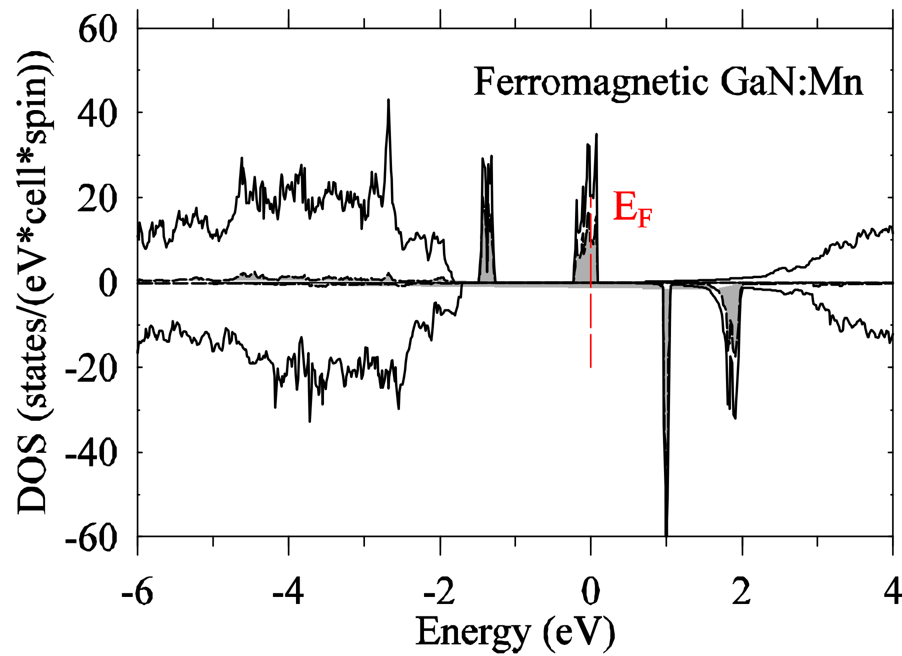
✓ Competition between ferromagnetic (FM) and antiferromagnetic (AFM) spin ordering and the strength of magnetic coupling.

✓ Optical and magneto-optical spectra, which are of interest for the optical excitation of spin polarization.

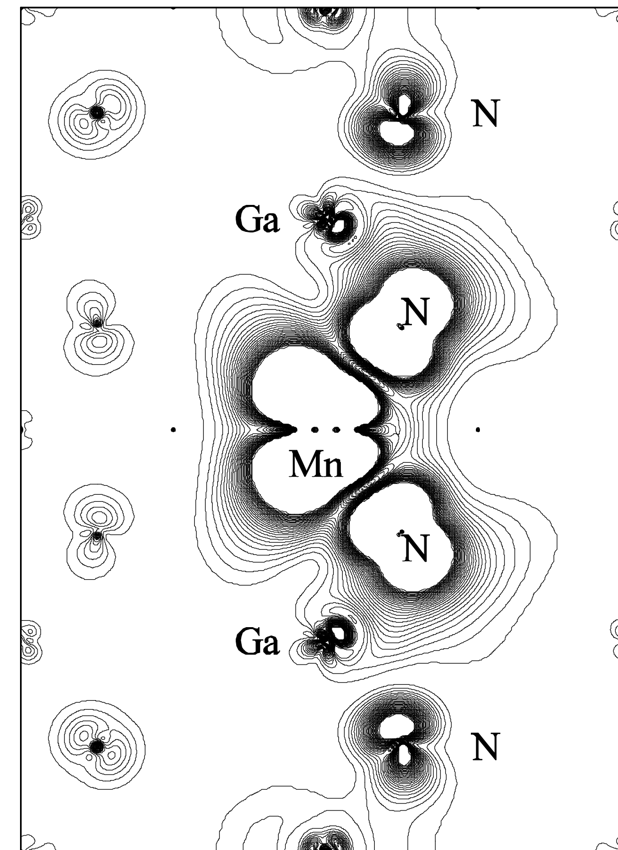
✓ The short-range ordering of magnetic atoms in DMS caused by their high concentration.

Quantum dot structures are widely used in nanoelectroncs. We model a Si quantum dot as a Si nanocluster and study gap narrowing caused by induced carriers.

2. Electronic structure and optical properties of diluted magnetic semiconductors (DMS).

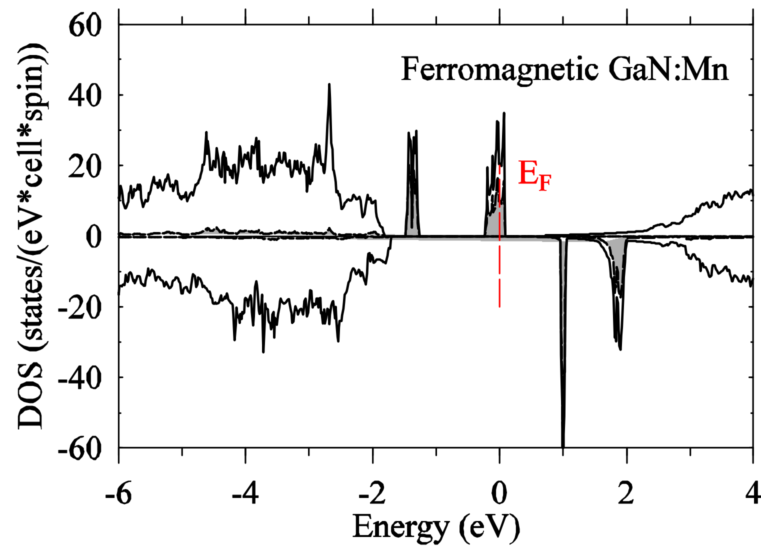


$\rho(r,E_F)$ GaN:Mn 1.56% (a)

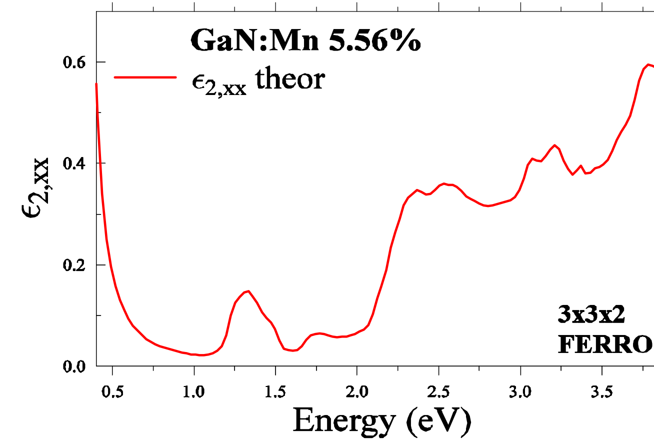


(110) plane

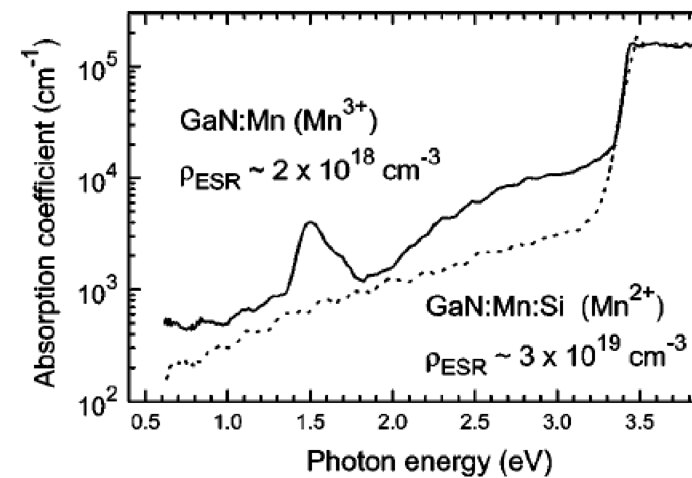
Optical properties of GaN:Mn.



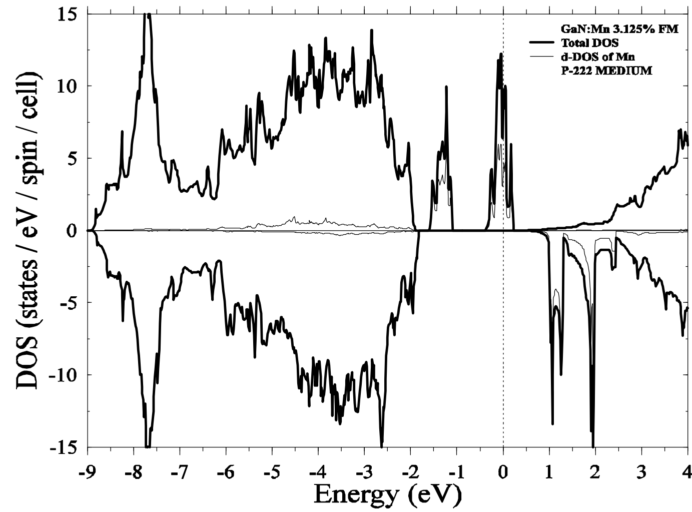
Our calculation



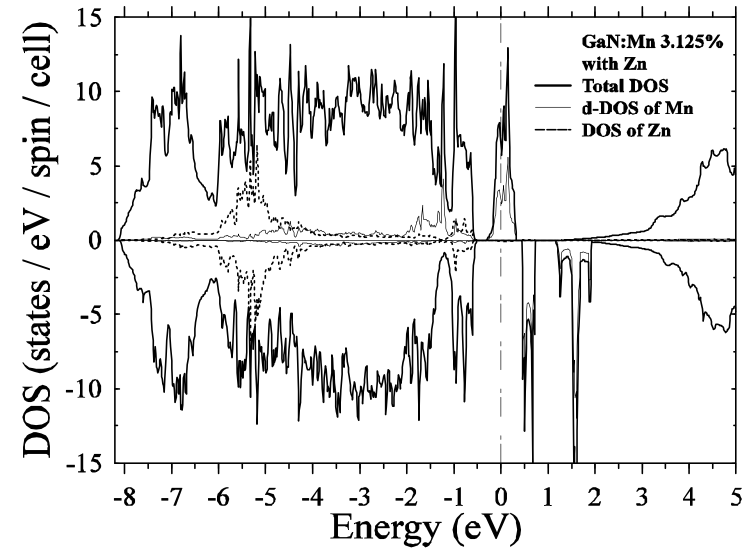
Experiment of Graf et al.



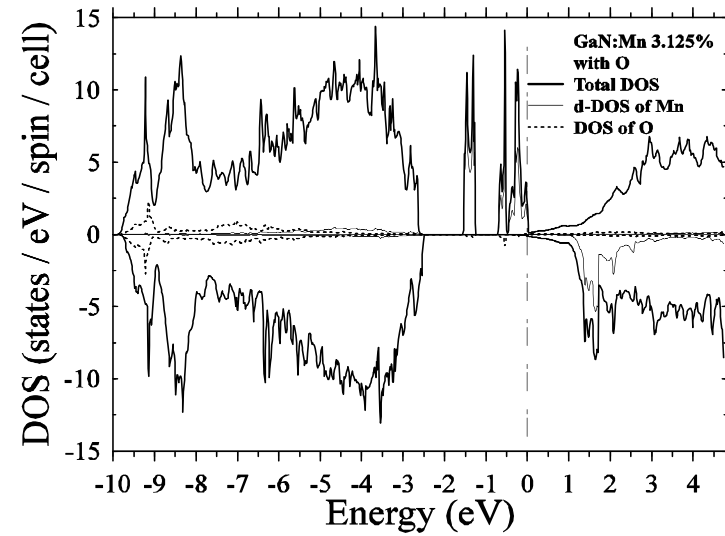
Effect of co-doping on the electronic structure of GaN:Mn



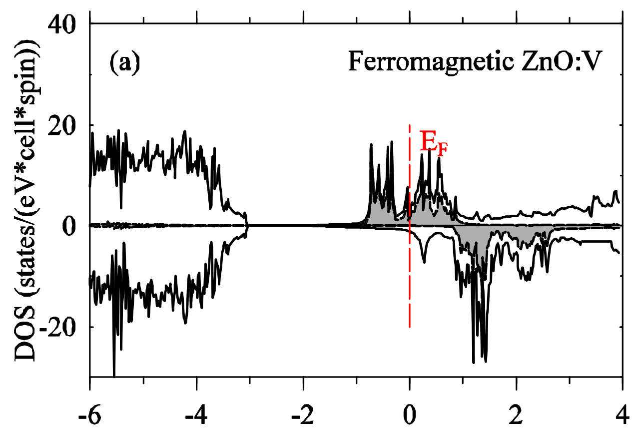
Zn co-doped

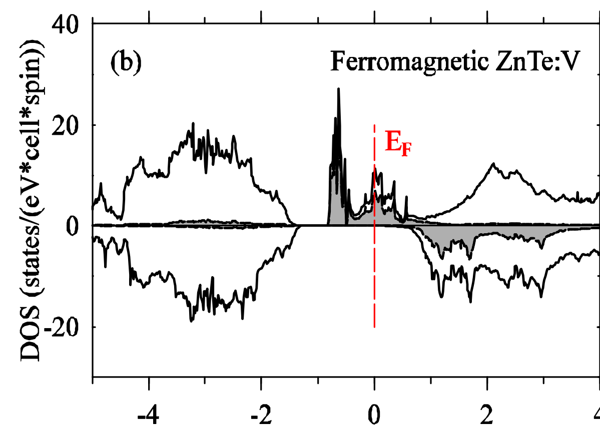


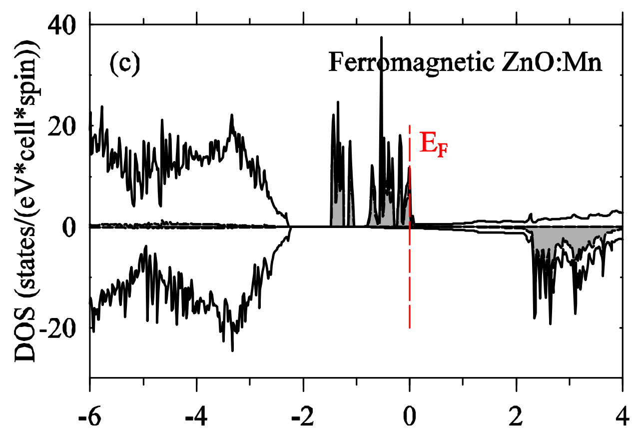
O co-doped

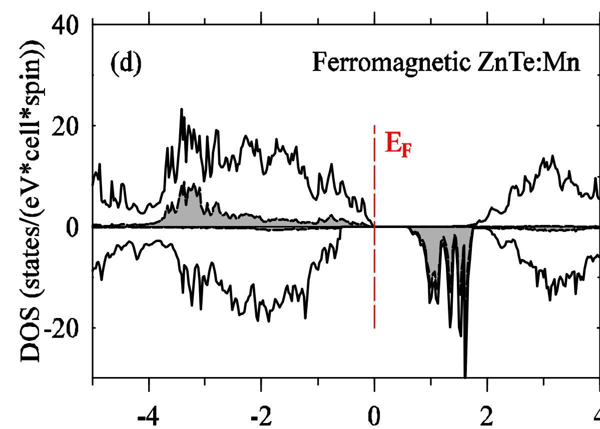


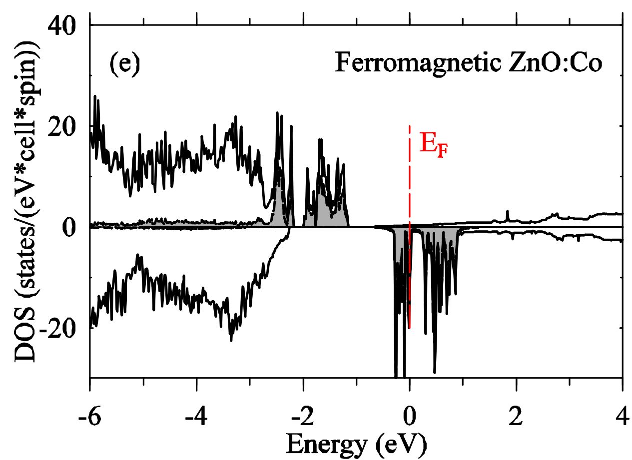
Electron density of states in ZnO:M and ZnTe:M, M=V, Mn, and Co

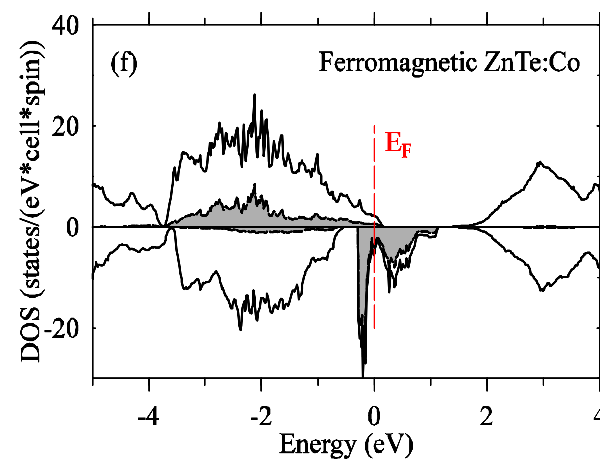




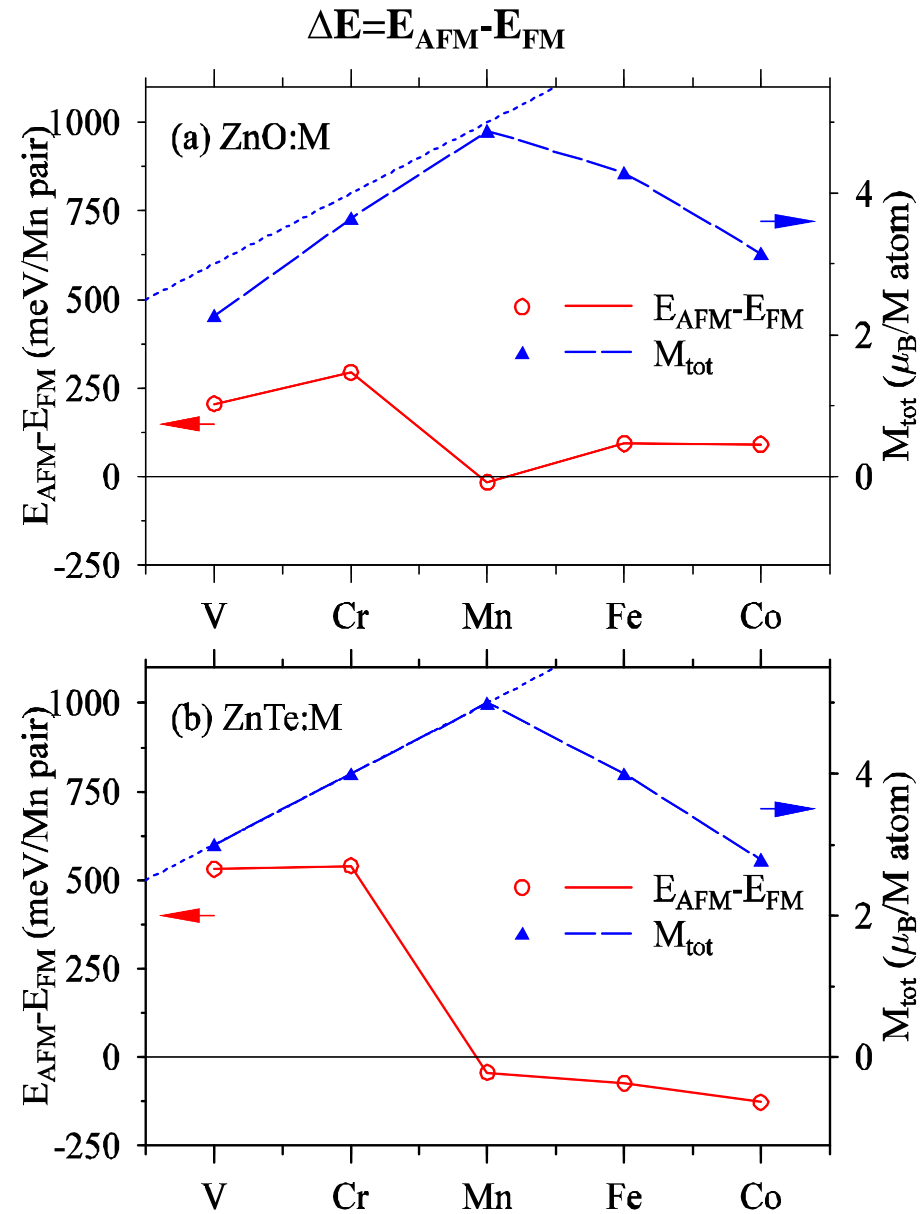








Magnetic ordering in DMS.

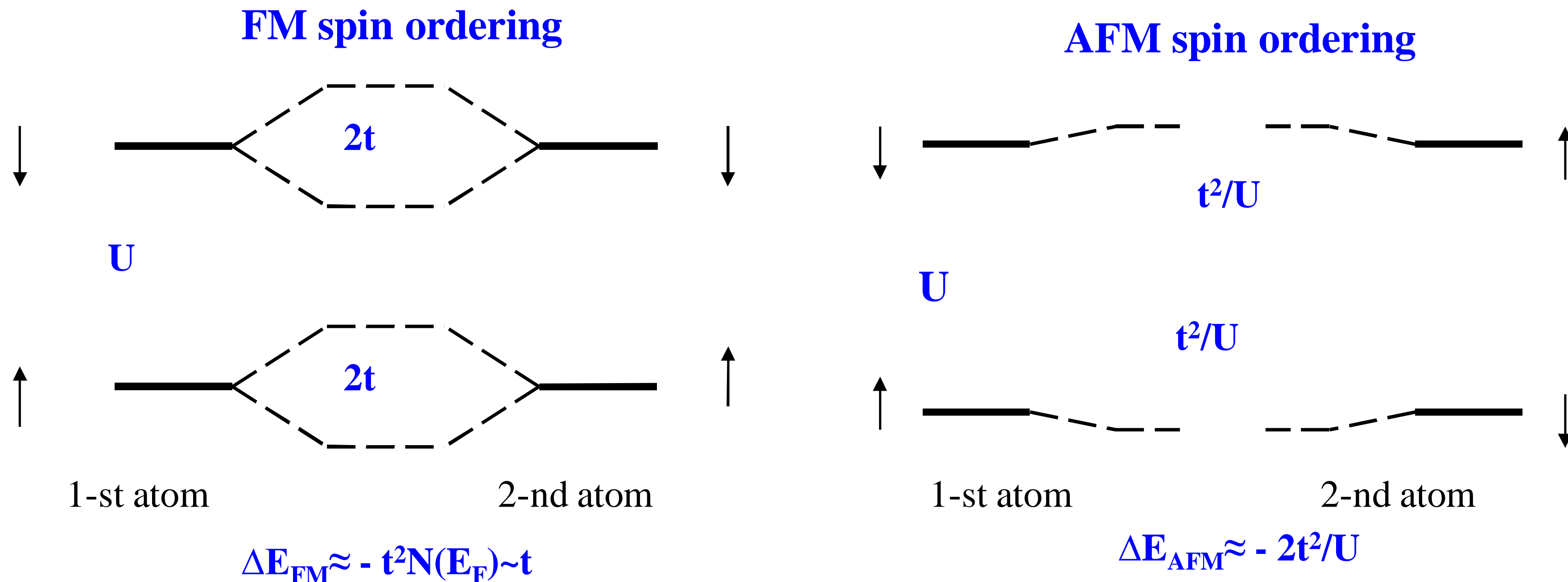


Gain in energy caused by FM and AFM spin ordering.

Qualitative explanation in terms of the double exchange and superexchange models.

$$\det\begin{pmatrix} E_1 - E & t \\ t^* & E_2 - E \end{pmatrix} = 0, \quad E = \frac{E_1 + E_2}{2} \pm \sqrt{\left(\frac{E_2 - E_1}{2}\right)^2 + t^2}$$

Weak interatomic coupling: t<<U



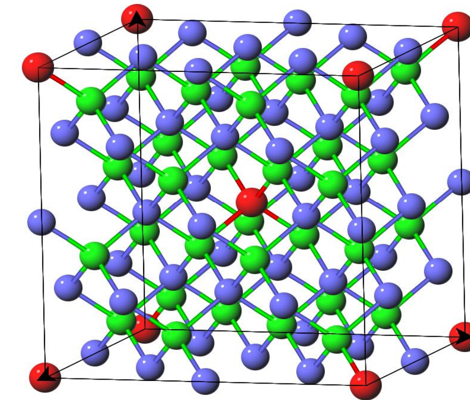
Spatial distributions of magnetic atoms used to simulate inhomogenuity of DMS samples (spinodal decomposition in DMS ?)

Ga

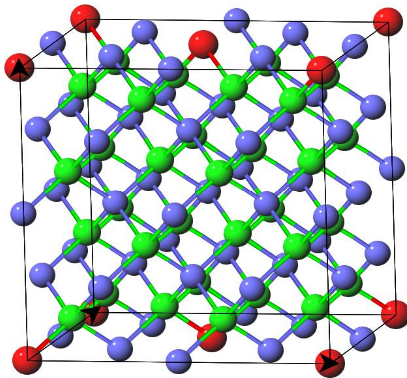
As

Mn

Uniform (random)



Intermediate



Short-range

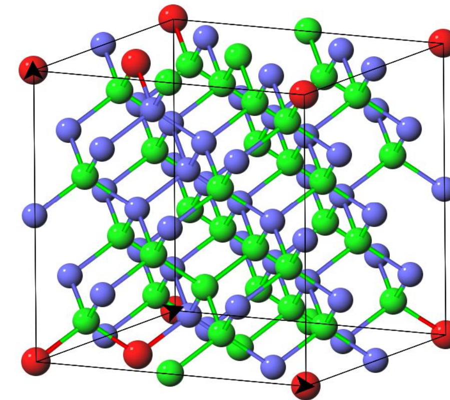


Table 1. The energies of short-range ordering $\Delta E_{sh.-range}=E_{random}-E_{sh.-range}$ and spin ordering $\Delta E_{AFM-FM}=E^{(AFM)}-E^{(FM)}$ in eV/cell.

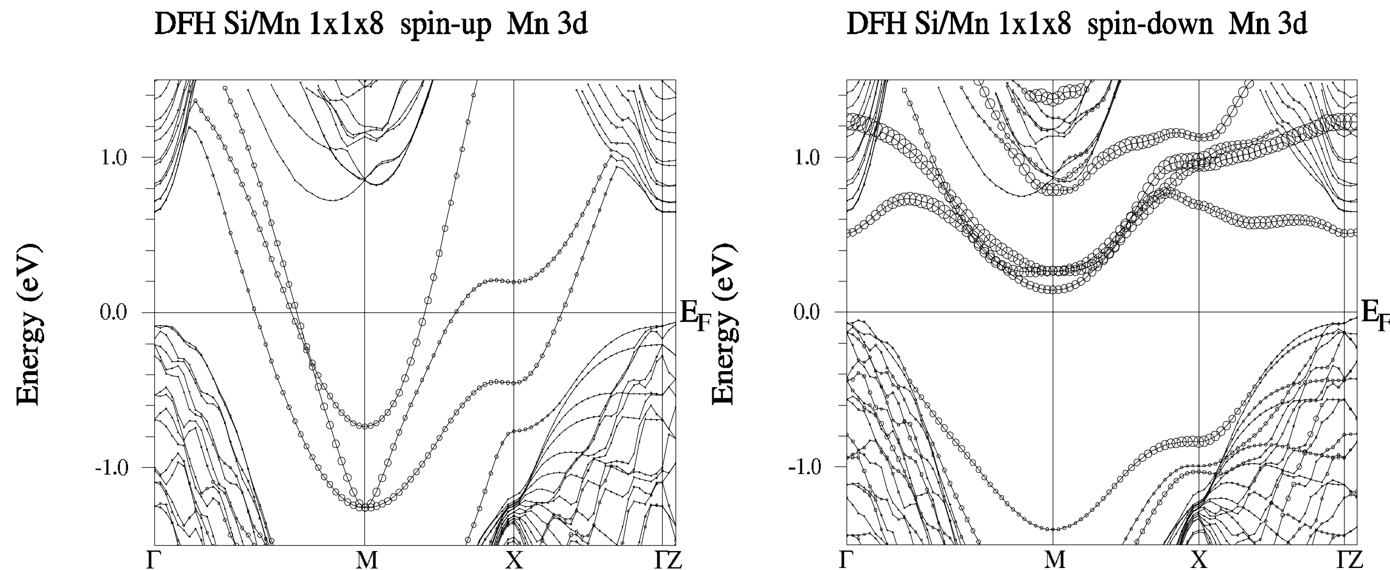
Material	Ferro- $\Delta E_{sh.-range}$	Antiferro- $\Delta E_{sh.-range}$	Random ΔE_{AFM-FM}	Short-range ΔE_{AFM-FM}	Lowest energy state
GaAs:Mn	0.141	0.059	0.167	0.249	Short-range FM
GaN:Mn	0.644	0.688	0.019	0.275	Short-range AFM
InAs:Mn	0.250	-0.107	0.110	0.467	Short-range FM
InSb:Mn	0.297	0.084	0.052	0.265	Short range FM
Ge:Mn	-0.374	0.122	-0.066	-0.562	Short-range AFM

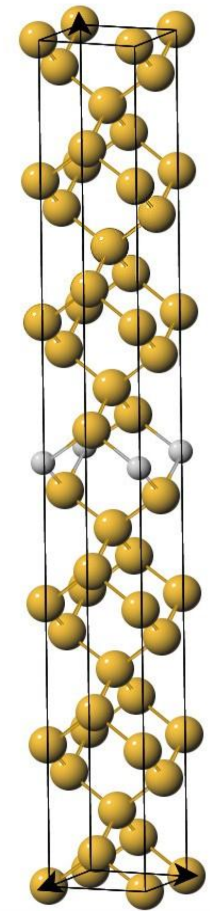
A simple qualitative explanation: Short-range ordering increases the width of the impurity 3d-band and by this means gives the gain in E_{total}. This effect is smaller when the 3d-band Is partially embedded into the valence band (GaAs:Mn).

3. Electronic structure and optical properties of digital magnetic heterostructures (DMH).

Band structure of Si/Mn

Si/Mn supercell



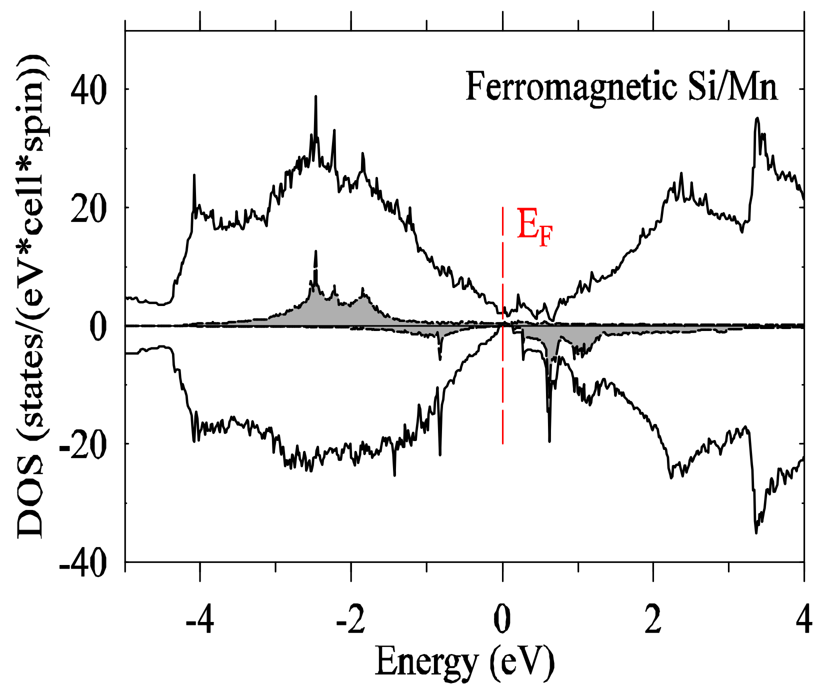


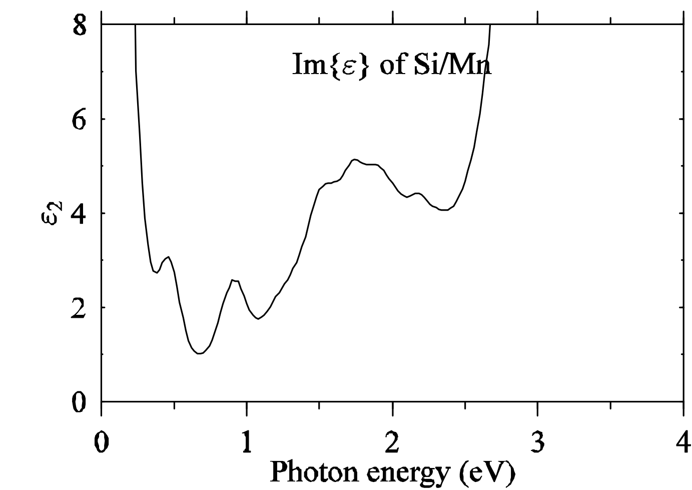
24 DMH were calculated:

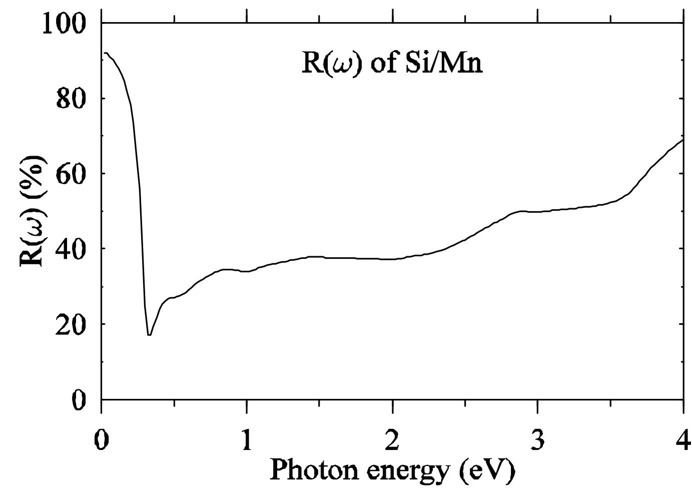
Si/M, Ge/M, GaAs/M, GaSb/M, GaN/M, GaN/M(50 %) (M=Cr, Mn, Fe, and Co).

Electron density of states and optical spectra of Si/Mn

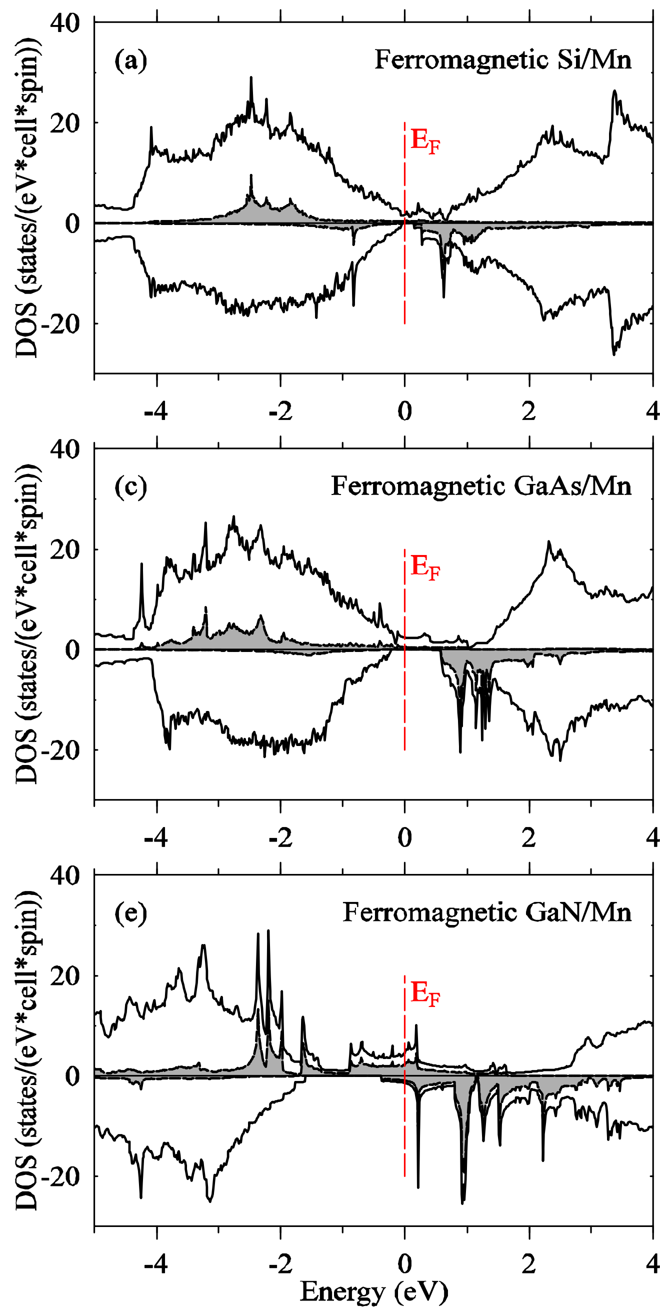
$\hbar\omega_p$=1.22 eV

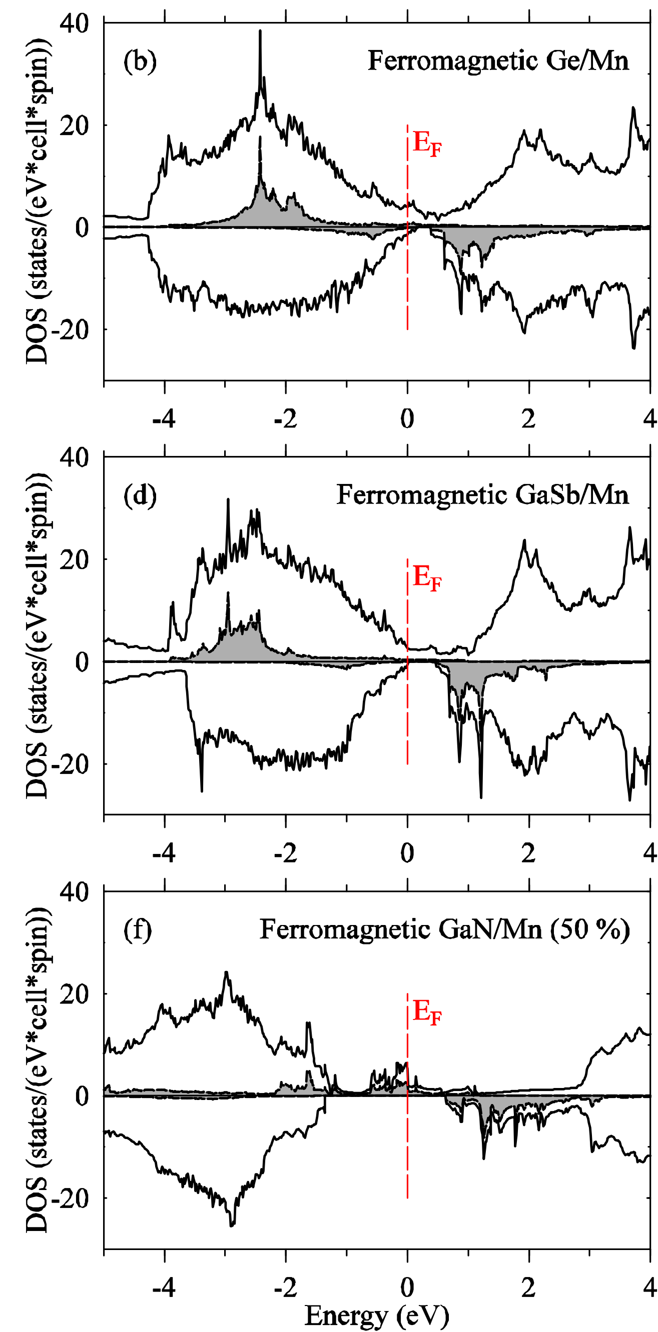






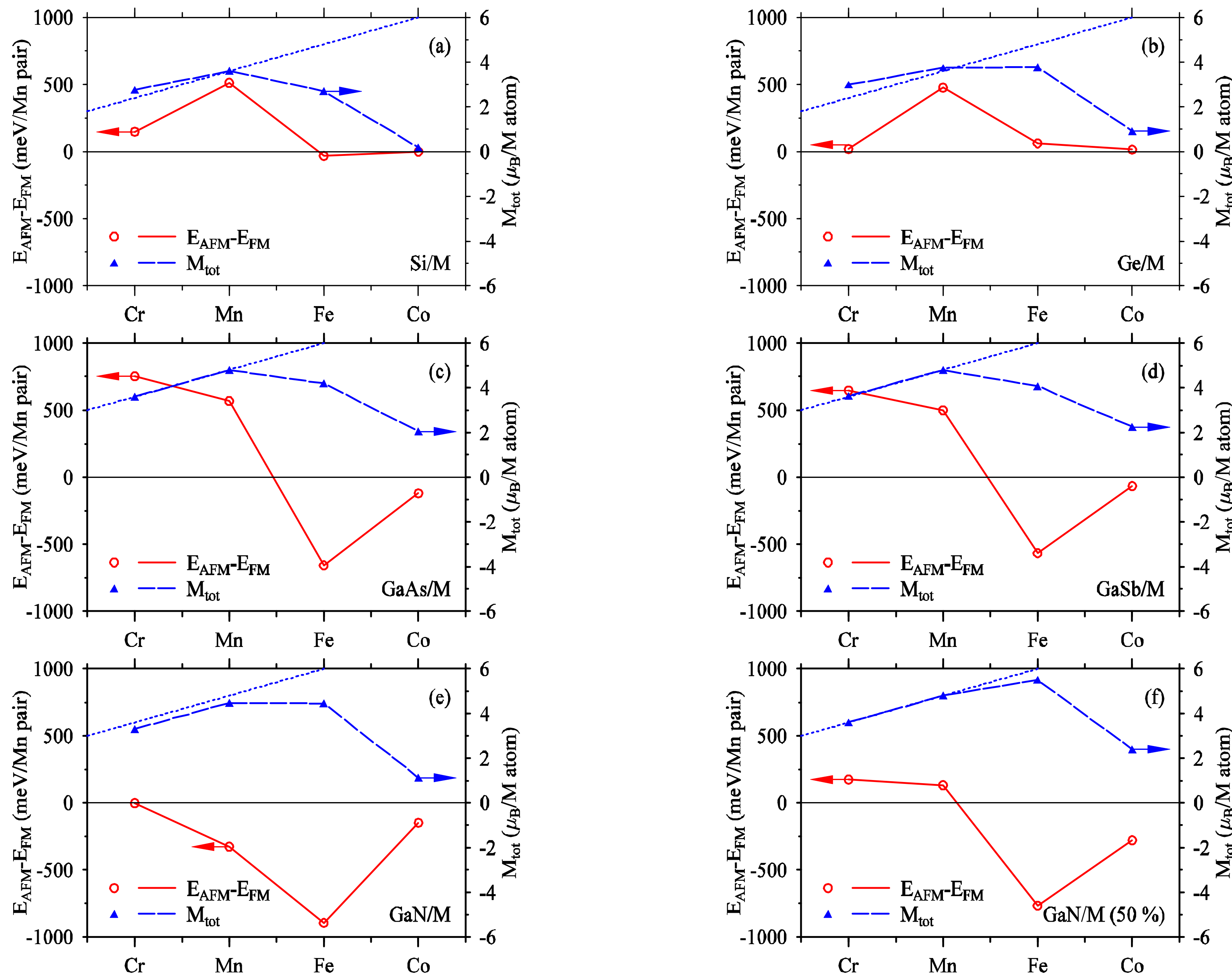
Density of electronic states in DMH.





$r(M\text{-}N\text{-}M) \approx 0.7 \cdot r(M\text{-}As\text{-}M)$

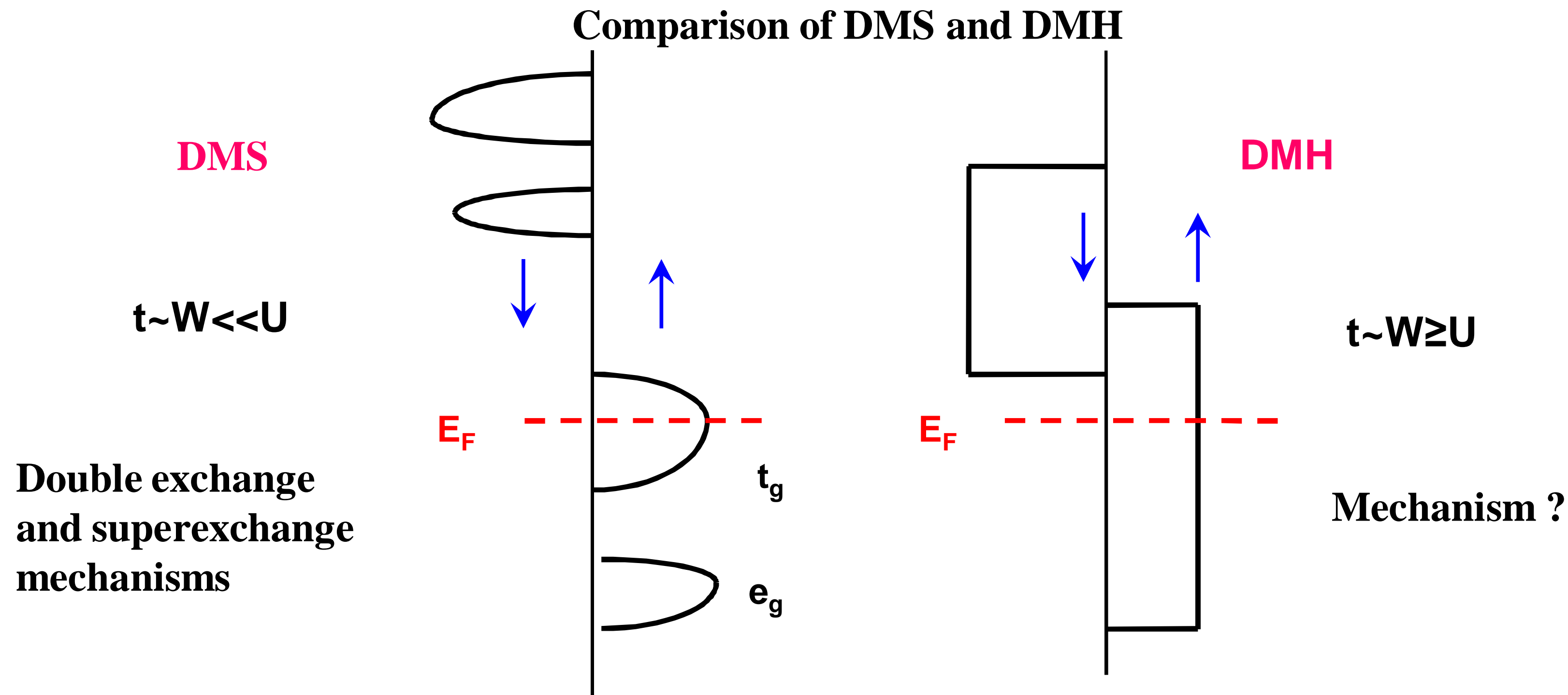
Correlation between $\Delta E = E_{AFM} - E_{FM}$ and magnetic moment M_{tot}



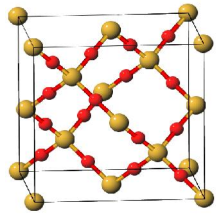
Qualitative explanation of the correlation.

- We found that the FM→AFM transition correlates well with the start of occupation of the spin-minority band of DMH.
- The occupation of the spin-minority band adds electrons with the highest energy $E \approx E_F$ that significantly increases the energy of the FM state.
- This contribution is large as 2D-DOS has a rectangular shape.
- In DMS, exchange interaction is large and impurity bands are narrow (**t<<U**). In this case the AFM state is highly localized and gives a negligible gain in kinetic energy. In DMH, impurity bands are wide (**t>U**). Therefore the AFM state is rather delocalized and its kinetic energy gain is comparable with that of the FM state.

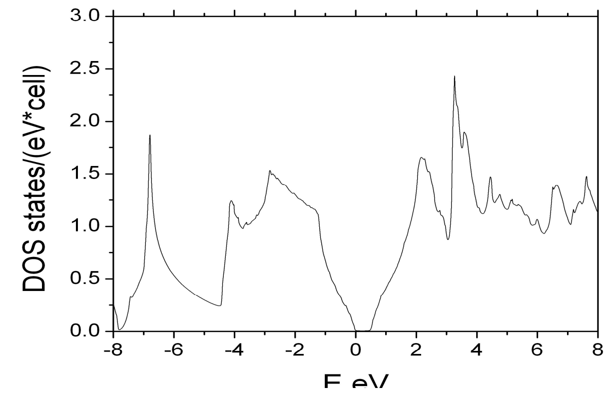
Comparison of DMS and DMH



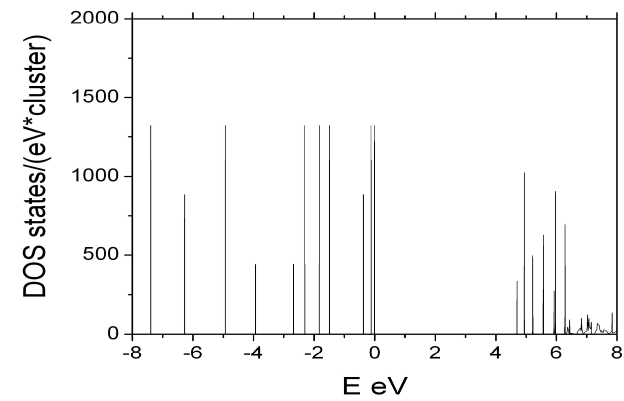
4. Electronic structure and carrier-induced gap narrowing in Si nanoclusters.

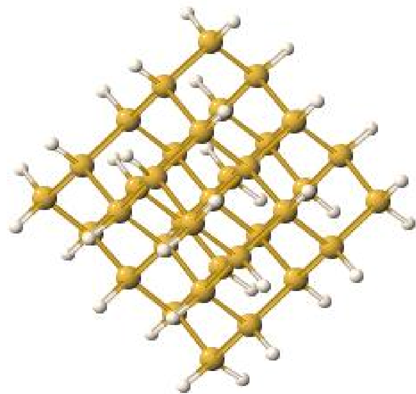


Bulk Si

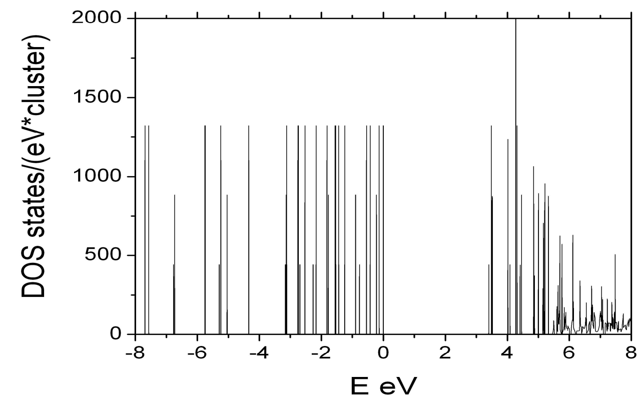


$Si_{10}H_{16}$ ($d_{cluster}$=0.5 nm)



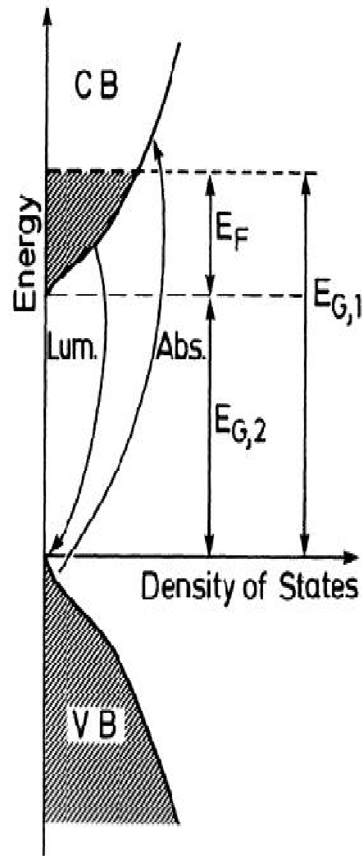


$Si_{35}H_{36}$ ($d_{cluster}$=1.0 nm)

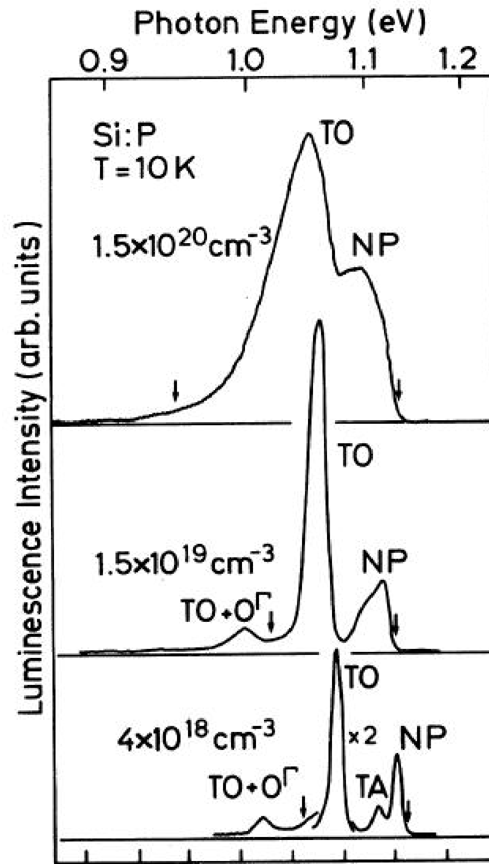


Gap narrowing in bulk Si caused by charging.

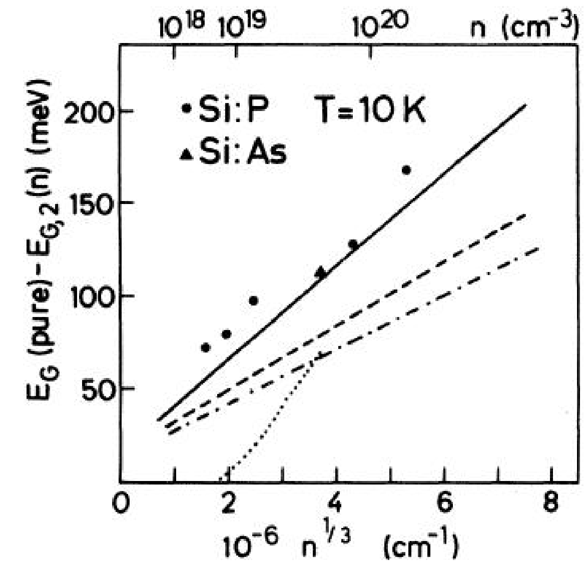
Electronic transitions



Photoluminiscence



Dependence on carrier density



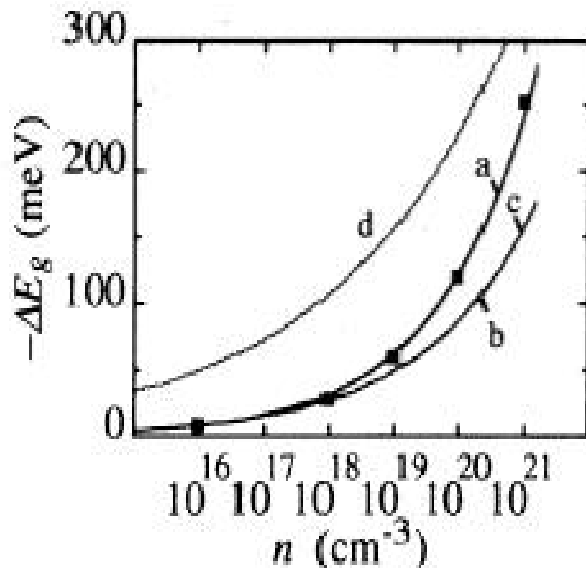
*Borrowed from: J.Wagner PRB 29, 2002 (1984)

Calculation of gap narrowing in bulk Si.

Gap	LDA	G_0W_0	experiment
E_G^{min}, eV	0.47	1.11	1.17
E_G^{direct}, eV	2.52	3.16	3.40

LDA: $E_G^{LDA} < E_G^{exp}$, ΔE_G^{LDA}=-3.5 meV at $4 \cdot 10^{20}$ cm^{-3} is too small for effect explanation.

GW method: $E_G^{GW} \approx E_G^{exp}$, $\Delta E_G^{GW} \approx \Delta E_G^{exp}$



*A.Oschlies et al. PRB 51, 1527 (1995)

Qualitative explanation:

Neutral Si: $\varepsilon(q) \approx \varepsilon_0 \approx 1+\omega_p^2/\Delta^2$,

Charged Si: $\varepsilon(q) \approx \varepsilon_0 + 1/(qr_D)^2$,

Metallic screening by induced carriers

$n=1.0*10^{20}$ r_D=2.5 Å,

$n=1.0*10^{21}$ r_D=1.4 Å

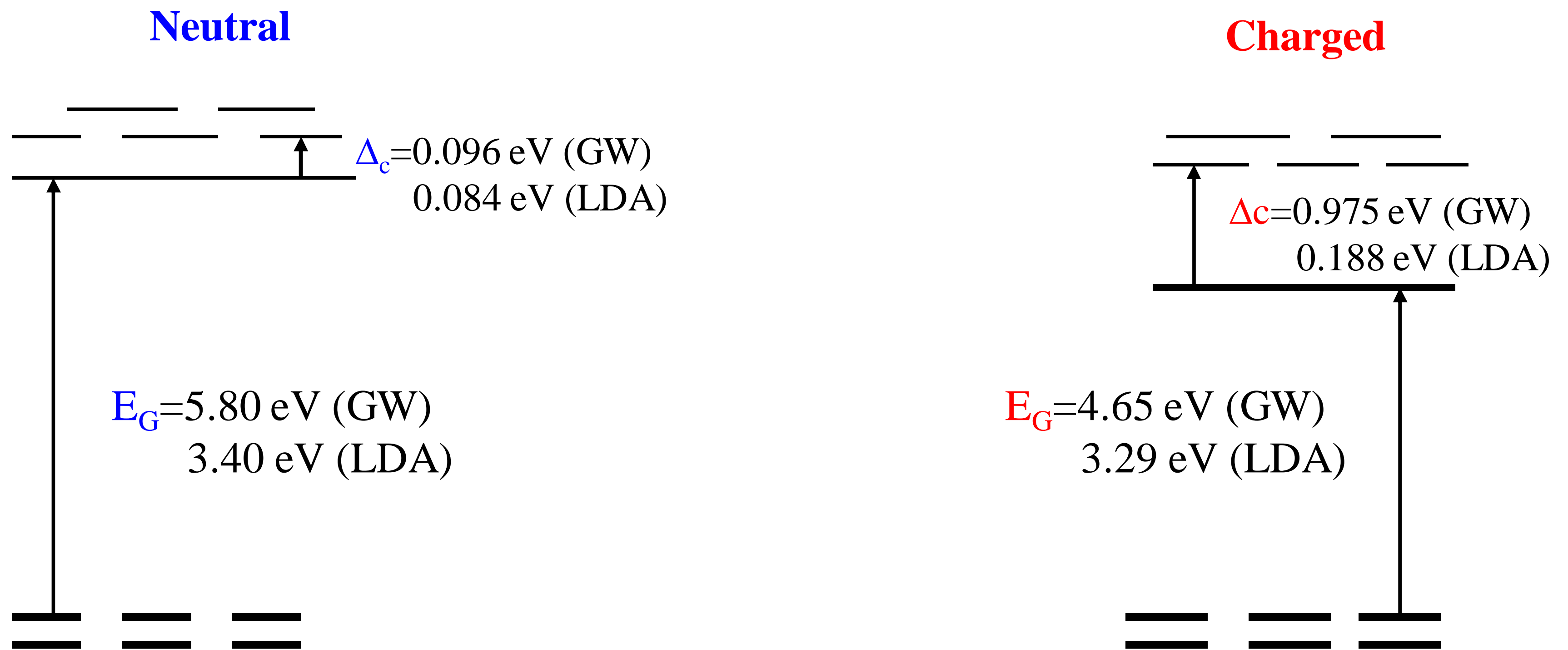
l(Si-Si)=2.25 Å

Electronic transitions and carrier-induced screening in Si nanoclasters.

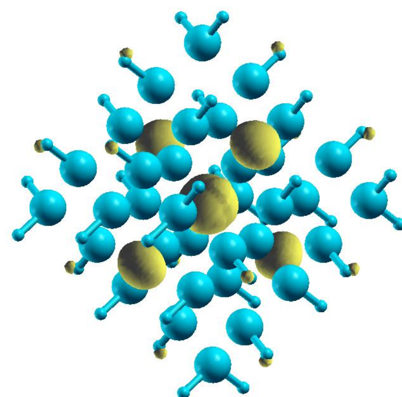
$\varepsilon_{neutral} \approx 1 + \omega_p^2 / E_G^2$, $\varepsilon_{charged} \approx \varepsilon_{neutral} + (\omega_p^{induced})^2 / \Delta_c^2$, $\omega_p^{induced} = 1.4$ eV

$\Delta E_G \approx (E_G^{GW} - E_G^{LDA}) * \varepsilon_{neutral} / \varepsilon_{charged}$,

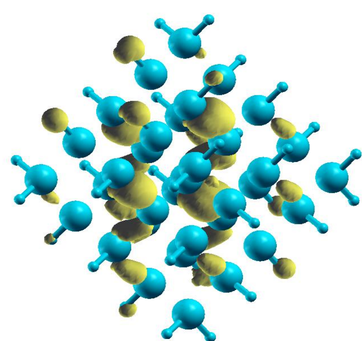
Exact $\Delta E_G = -1.15$ eV, Estimated $\Delta E_G \approx -1.4$ eV

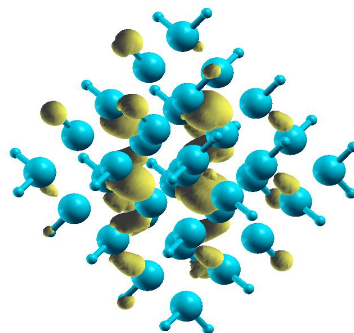


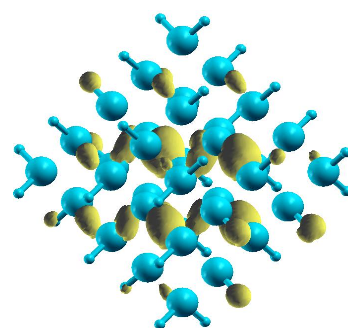
Wave functions of $Si_{35}H_{36}$



Conducting states

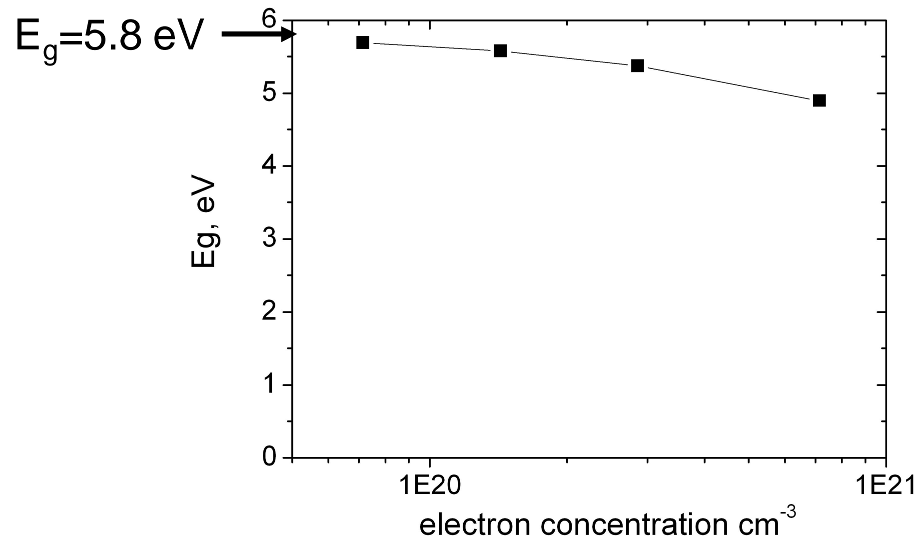


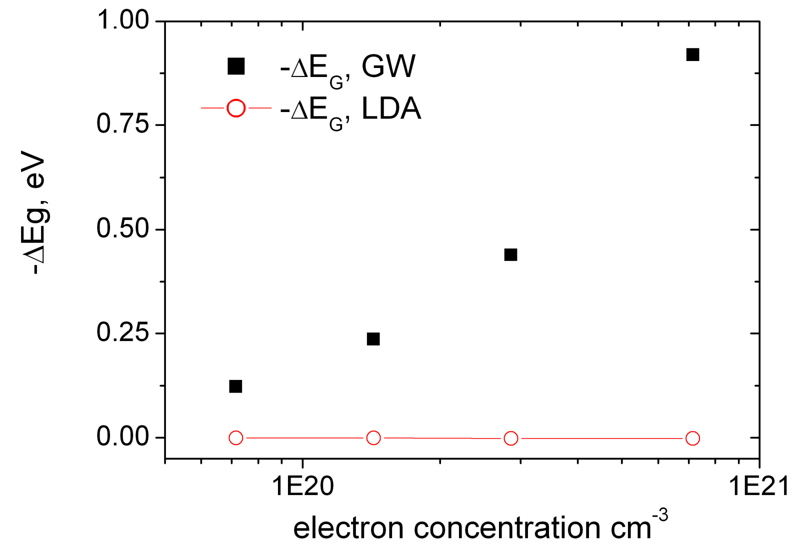




Valence states

Gap narrowing in Si_{35}





LDA gap narrowing is small :

-Electrostatic effects are small

-Correlation effects are dominant

Gap narrowing upon charging and co-doping

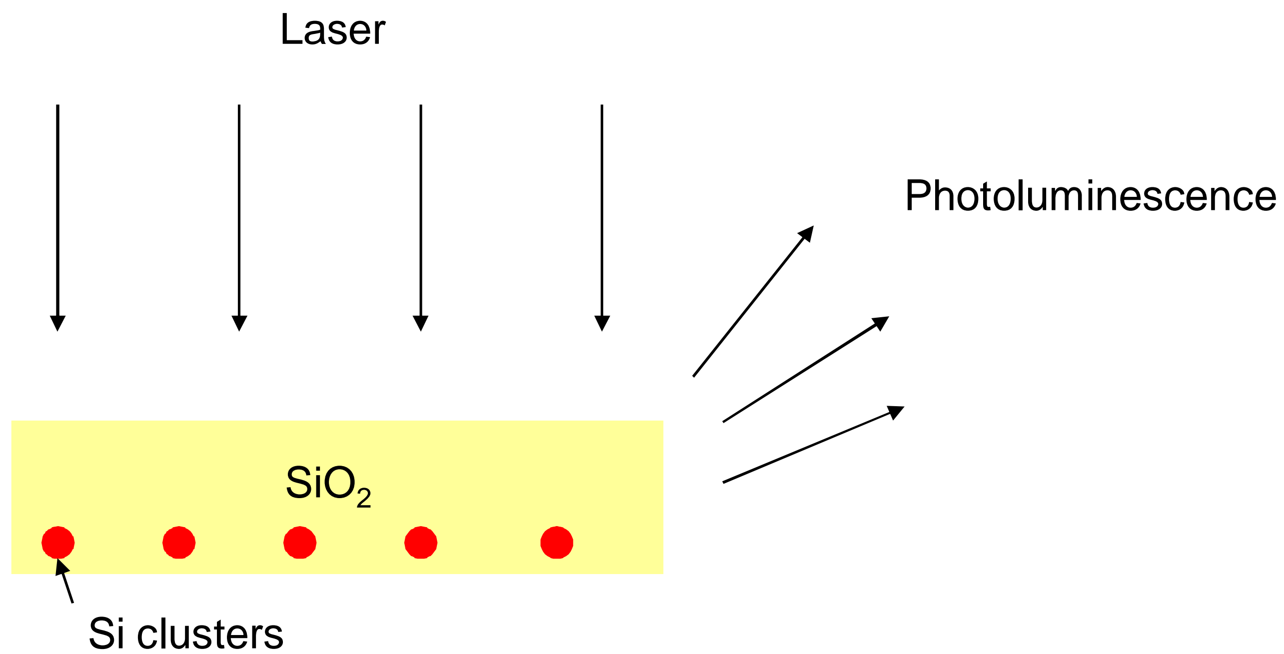
Cluster	1e (Si_{10})	1e (Si_{35})	P	As	Sb
$-\Delta E_G$, eV	2.27	1.15	1.21	1.42	1.36

The main factors caused the dependence of ΔE_G from the cluster size

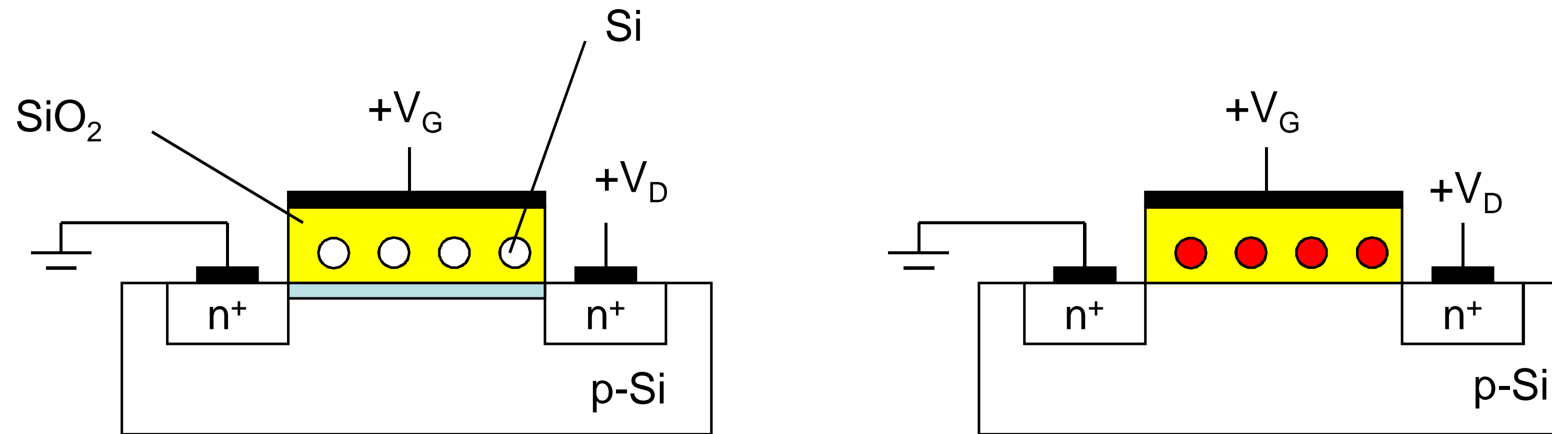
- Cluster size determines $n_{induced}$,
- Discrete electronic spectrum. In simple models $\Delta_c \approx 1/d_{cluster}^2$,
- EG is significantly increased by Si-H bonds (Si-O bonds for Si in SiO_2 matrix) on the cluster surface.
- Screening becomes stronger with the cluster size for a fixed $n_{induced}$.
- This dependence can be of importance for practice.

Experiment

Effect: Gap narrowing induced by cluster charging for electron concentration measurements



Flash memory



Channel conductivity depends on charge state of Si clusters

Advantage:

high possibility of miniaturization of the memory element

5. Conclusions

Three considered types of materials have their own special features:

1. In DMS the main effect is short-range ordering of magnetic atoms.

2. In DMH the too strong interaction of magnetic atoms caused their AFM spin ordering instead of FM one.
3. There is a significant dependence of gap narrowing caused by induced carriers on the cluster size.

Gap narrowing upon charging and co-doping