A03:「スピンエレクトロニクス材料の探索」

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研究組織　「スピンエレクトロニクス材料の探索」

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理論、デザイン

実証実験

理論、デザイン

実験グループとの緊密な連携。

スピンエレクトロニクス材料のデザインとその実証。

役割分担

半導体スピントロニクス	デザイン	佐藤、下司、吉田	ナノ構造制御による半導体スピントロニクス
		小倉、赤井	N 半導体スピントロニクスデ イスデザイン
	実証実験	黒田、朝日	ナノ構造制御による半導体スピントロニクス デザイン 実証実験 ZnTe系、GaN系
金属系スピントロニクス	デザイン	小田	による 制御
	実証実験	野崎、鈴木	実証実験

LiZnAsベース磁性半導体の材料設計
Computational materials design for LiZnAs-based magnetic semiconductors

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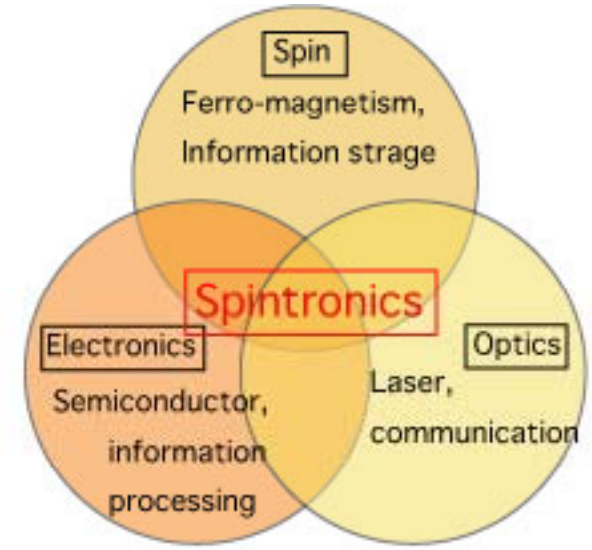
S. Fujimoto, K. Sato, H. Katayama-Yoshida
Osaka Univ.

Introduction

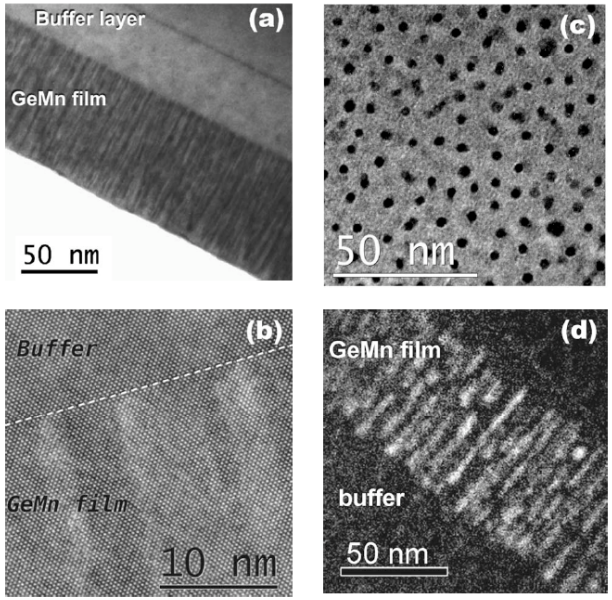


- Spintronics = charge + spin
- Dilute magnetic semiconductors(DMS)
  - Carrier induced ferromagnetism
  - (Ga, Mn)As, (In, Mn)As: T_C < RT.

- **For high-T_C, high concentration doping is necessary.**

S. A. Wolf et al, Science 294 (2001) 1488
T. Dietl Semicond. Sci. Tech. 17 (2002) 377,
K. Sato et al., Semicond. Sci. Tech. 17 (2002) 367

Homogeneous high concentration doping is difficult because of the phase separation.



Experiments. Singh et al., APL 86 (2005)12504
Gu et al., JMMM 290-291(2005)1395.
T. Devillers et al., PRB 76 (2007) 205306.

Propose new materials, where homogeneous high concentration doping is possible. LiZnAs-based DMS

Filled tetrahedral semiconductors LiZnAs

Masek et al., PRL 98 (2007) 067202

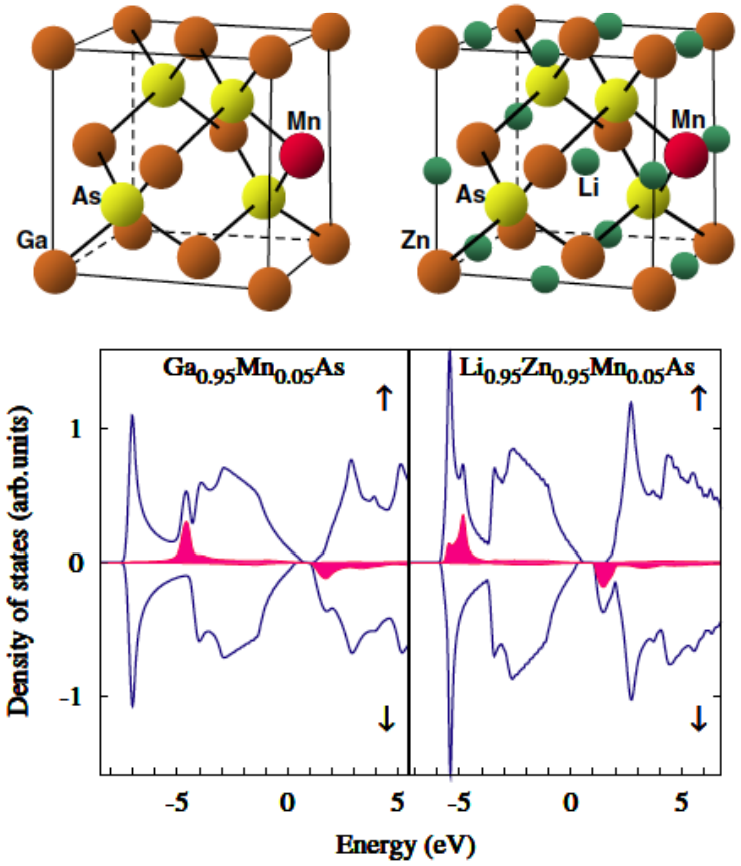


FIG. 1 (color online). Top panel: Schematics of (Ga,Mn)As and Li(Zn,Mn)As crystal structures. Bottom panel: *ab initio* total and Mn *d*-orbital projected density of states of $Ga_{0.95}Mn_{0.05}As$ and $Li_{0.95}(Zn_{0.95}, Mn_{0.05})As$ mixed crystals. Energy is measured from the Fermi energy.

- Zinc blende structure + interstitial Li (half-Heusler)
- $Ga^{3+}As^{3-}$

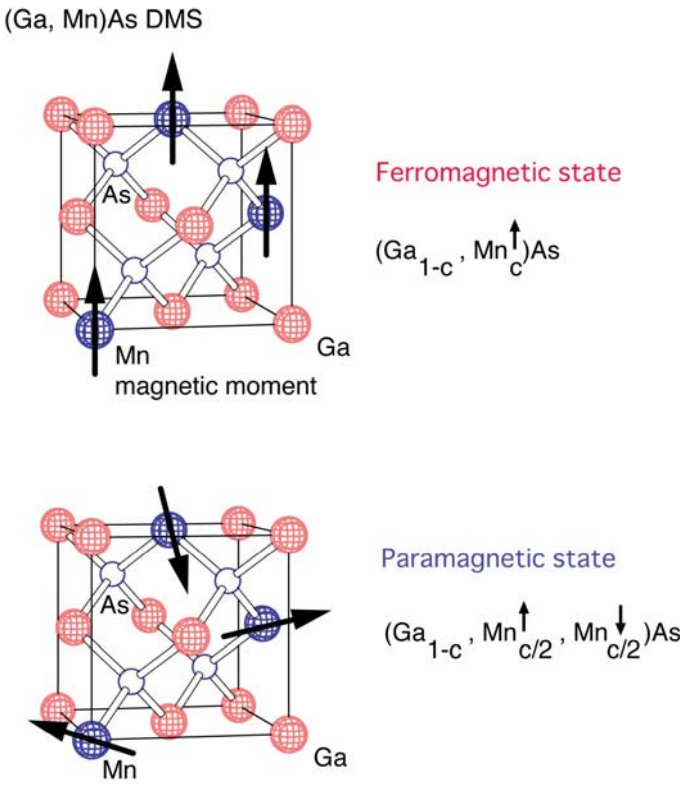
  $Zn^{2+}As^{3-} + Li^{1+}$
- Zn^{2+} Mn^{2+}: High solubility
  - $E_{Form}(Mn_{Zn}$ in LiZnAs)=~ -3 (eV)
  - $E_{Form}(Mn_{Ga}$ in GaAs)=~ -1 (eV)

  Mahadevan et al., PRB 68 (2003) 075202.
- Carrier control by Li addition (removal)
- Phase separation is also controlled by carrier doping.

Juza et al., Angew. Chem. 7 (1968) 360
v. G. Achenbach et al., Z. Anorg. Allg. Chem. 476 (1981) 9.

Calculation of magnetic properties of DMS

K. Sato et al., RMP 82 (2010) 1633.
L. Begqvist et al., PRL 93 (2004) 137202
K. Sato et al., PRB 70 (2004) 201202

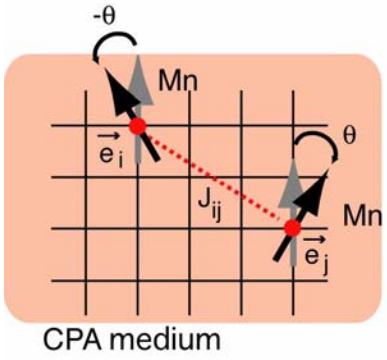


- KKR-CPA-LDA

→MACHIKANEYAMA2002 (Akai)

- Exchange interactions by Liechtenstein's formula

Energy difference due to the rotation is mapped to classical Heisenberg model (Liechtenstein et al.)



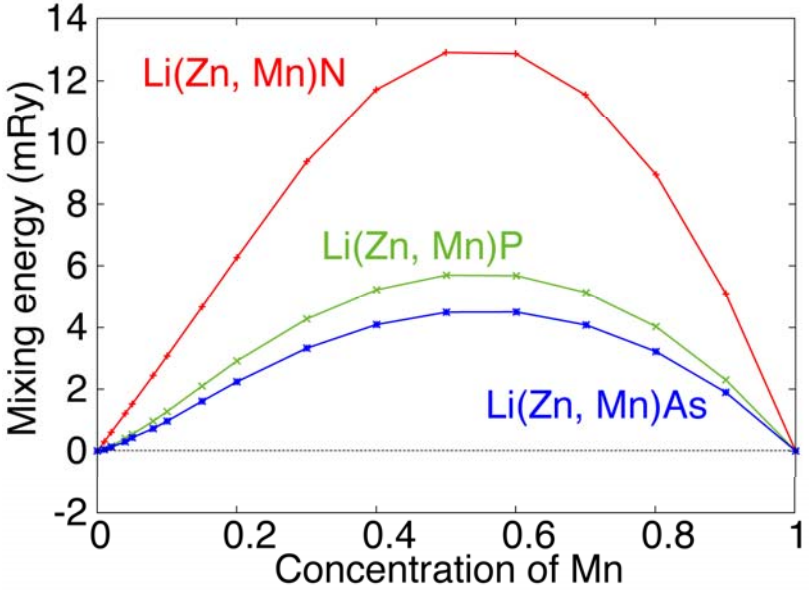
$$H = -\sum_{i \neq j} J_{ij} \vec{e}_i \cdot \vec{e}_j$$

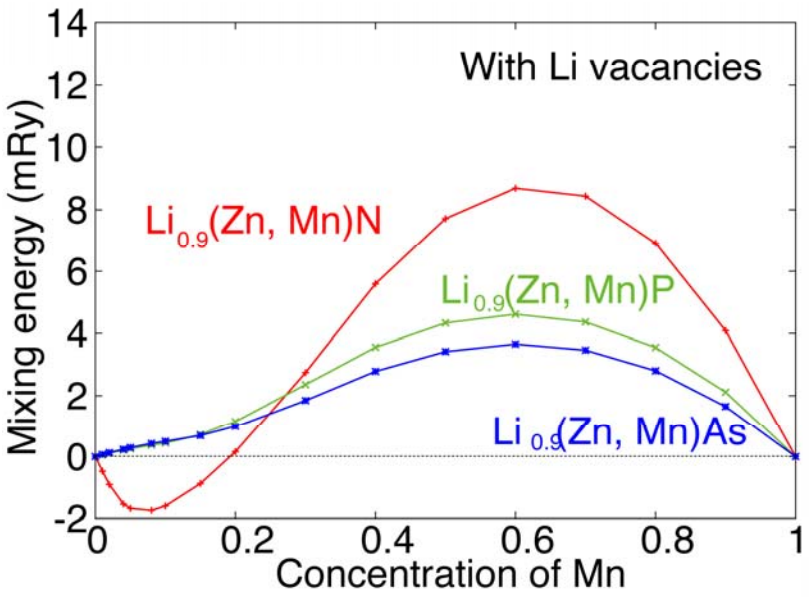
J_{ij} : Exchange interactions between 2 impurities in a CPA medium

$\vec{e}_i$: direction of magnetic moment of the impurity at site i

- Statistical method for T_C
  - Mean field approximation (MFA)
  - Random phase approximation (RPA)
  - Monte Carlo simulation (MCS)

Stability of homogeneous Li(Zn, Mn)As





- Mixing energy of Li(Zn, Mn)As

$$E_M = E[LiZn_{1-x}Mn_xAs] - xE[LiMnAs] - (1-x)E[LiZnAs]$$

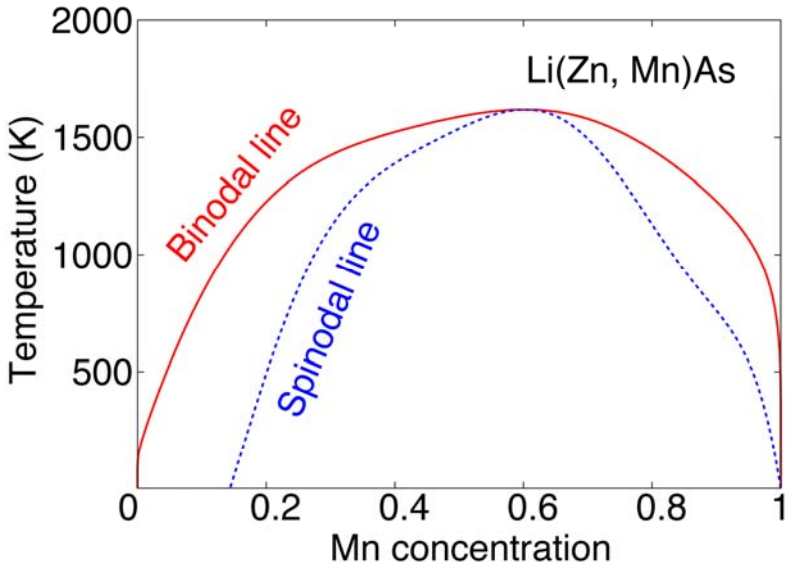
E: Total energy
x: concentration of Mn

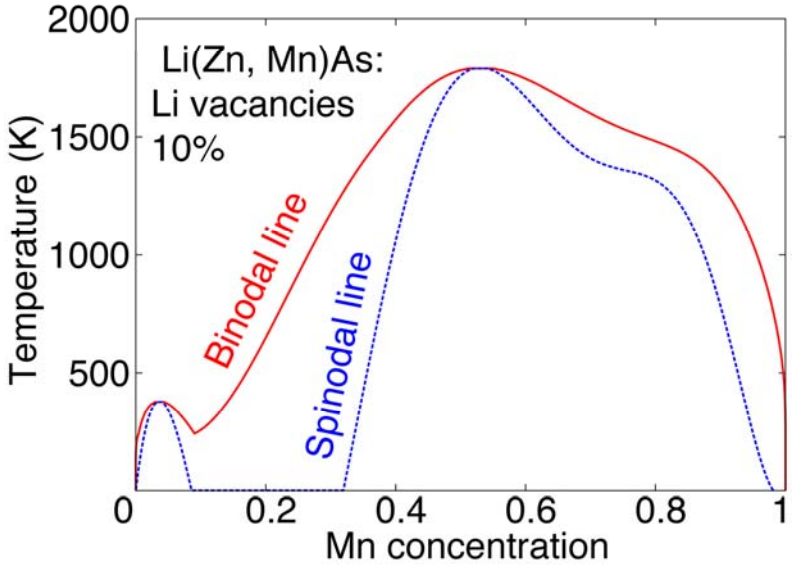
  - Upward convexity
    Phase separation
  - Downward convexity
    homogeneous mixing
    ordered phase
  - The presently investigated systems favor phase separation.

- By introducing Vc_{Li}, we can reduce the mixing energy.

co-doping method:
L. Bergqvist et al. PRB 83 (2011) 165201.
H. Fujii et al., APEX 4 (2011) 043003.

Phase diagram of Li(Zn, Mn)As





- Free energy F of two component alloy

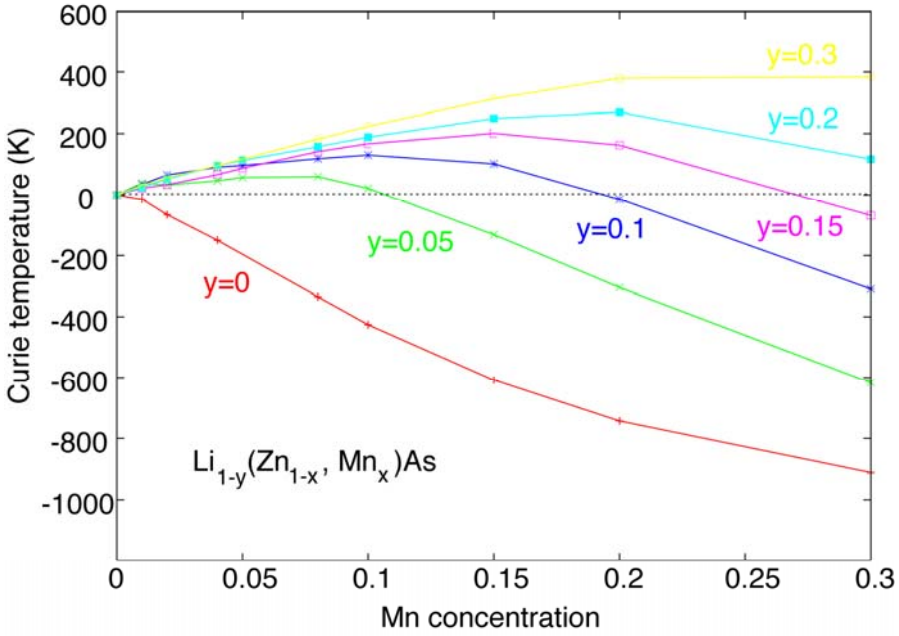
$$F = E_M - TS$$

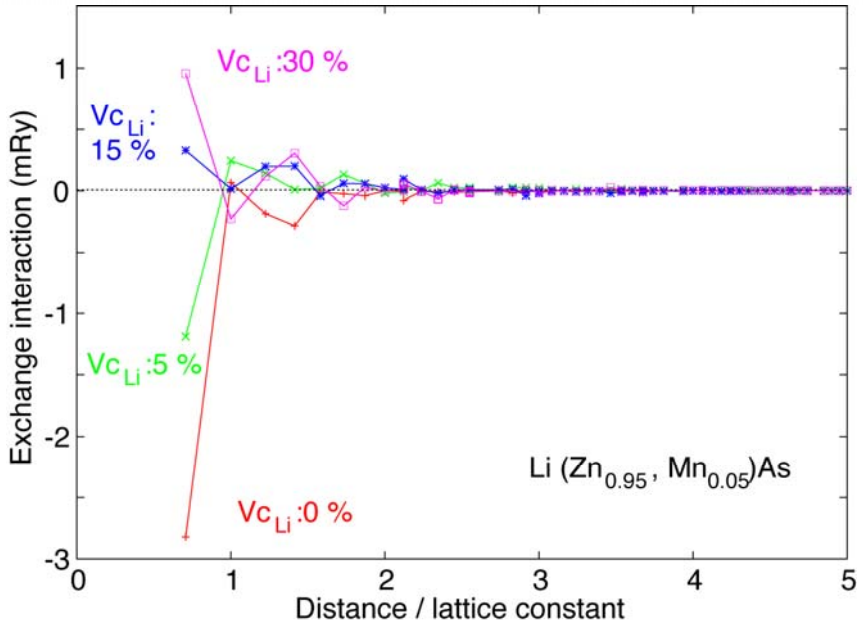
T: temperature
S: entropy

$$S = -k_B\left[(1-x)\log(1-x) + x\log(x)\right]$$

- Phase diagram
  - Binodal line: common tangent
  - Spinodal line: $\dfrac{\partial^2 F}{\partial c^2} = 0$

- Spinodal decomposition is suppressed by introducing Li vacancies.





T_C(MFA) and DOS of Li(Zn, Mn)As

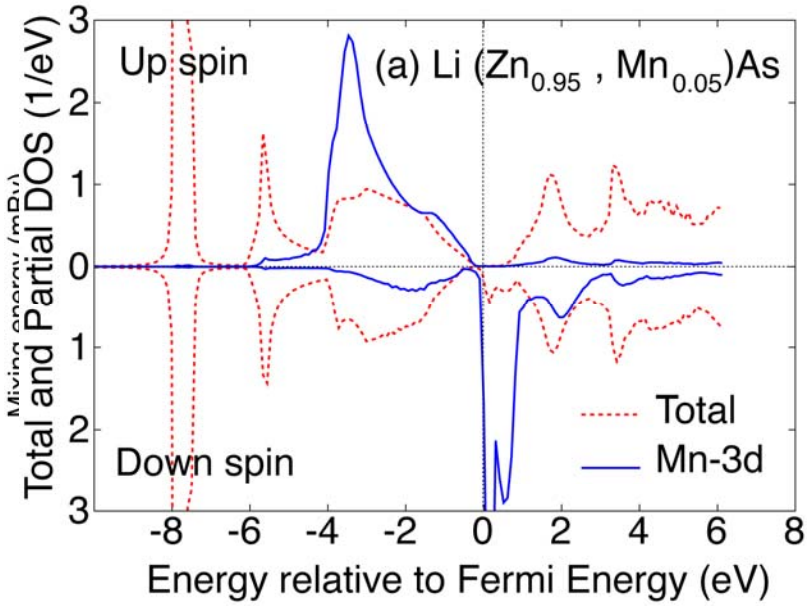
- T_C by the mean field approximation.

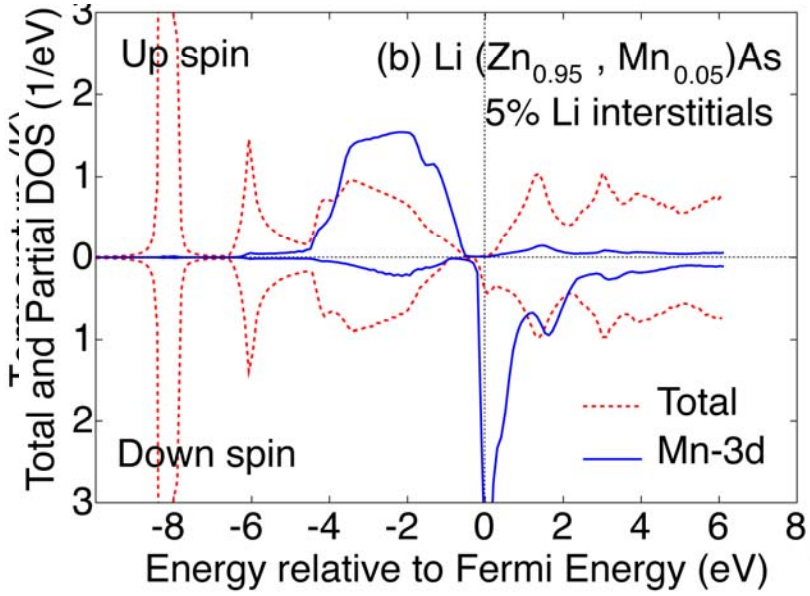
PM: paramag.
FM: ferromag.

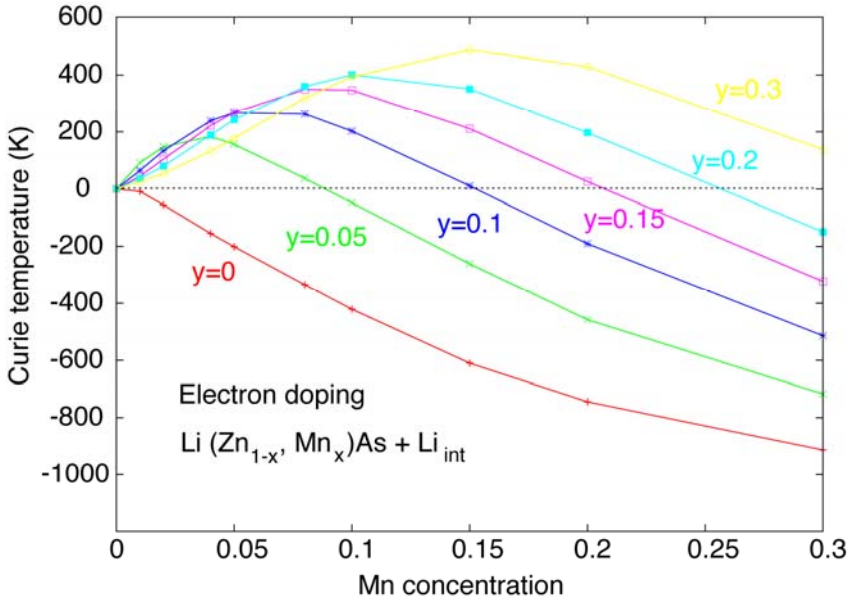
$$k_B T_C = \frac{2}{3}\frac{E(PM) - E(FM)}{x}$$

- Li(Zn, Mn)As
  - Li vacancy introduces holes and induces ferromagnetism
  - *p*-*d* exchange mediates ferromagnetic interactions.

Electron doping in Li(Zn, Mn)As



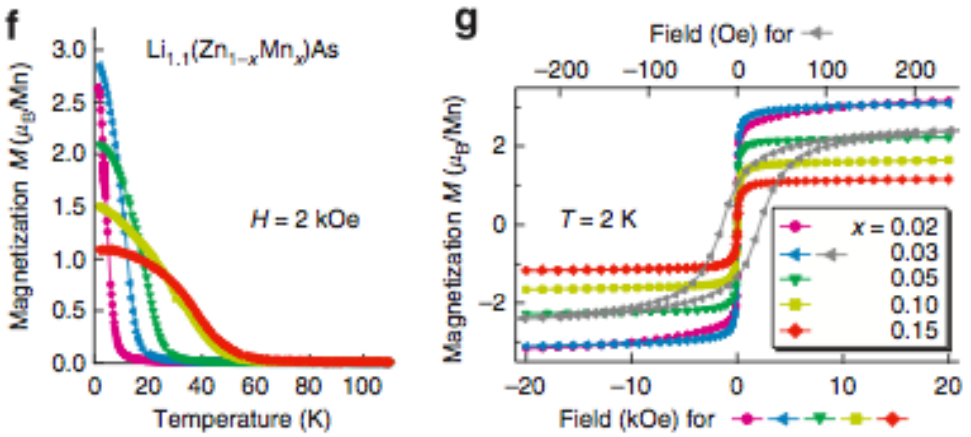




- Electron doping by Li_{int}
  - $E_{form}(Li_{int}$ in LiZnAs)= 0 ~ -1 (eV)
- Suppression of spinodal decomposition
- Ferromagnetism is induced by the electron doping.

Recent experiment

Z. Deng et al., Nature Commun. 2:422, (2011, Aug.) 1-5.



- Solid-state reaction
- XRD
- dc-magnetization, μSR
- Hall effect p-type
  - Li at Zn substitutional site

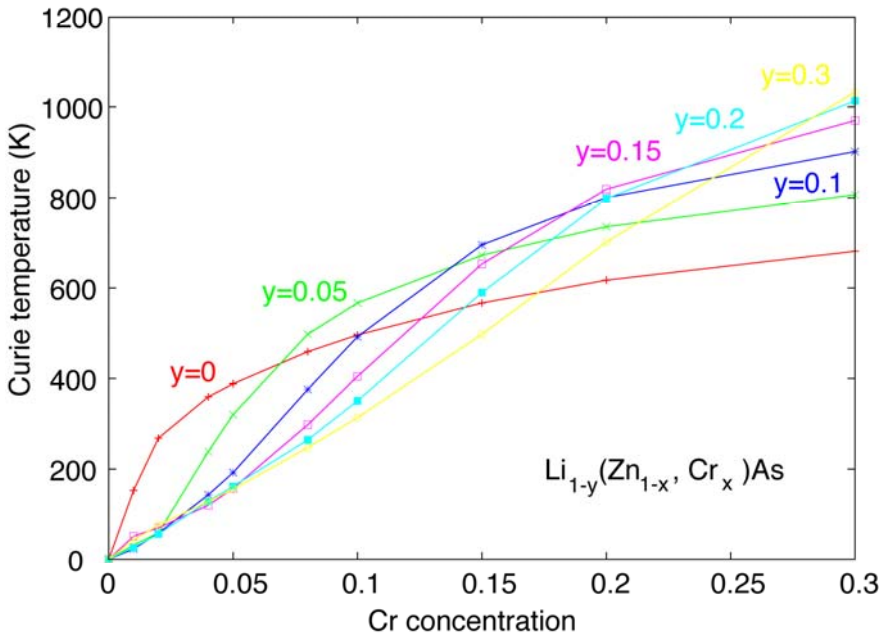
Table 1 | Ferromagnetic transition temperature and ordered moment size.

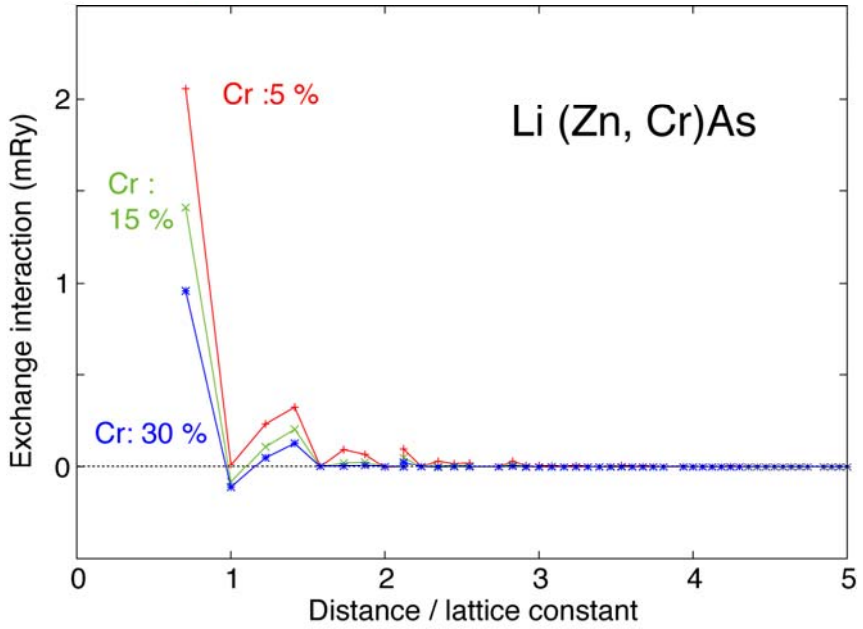
Li concentration	1.05		1.1		1.2	
	T_c (K)	M (T=2 K)	T_c (K)	M (T=2 K)	T_c (K)	M (T=2 K)
Mn concentration						
0.03			17	2.9		
0.05			29	2.1	14	1.8
0.1	22	0.6	49	1.5	22	1.4
0.15	38	0.5	50	1.1	23	0.7

M (Bohr magneton per Mn).

The values of T_c and the average ordered moment size M per Mn of $Li_{1+y}(Zn_{1-x}Mn_x)As$ at T=2K and H=2 kOe derived from magnetization measurements for several combinations of Li and Mn concentrations.

T_C(MFA) and DOS of Li(Zn, Cr)As





- T_C is calculated by the mean field approximation.
- Li(Zn, Cr)As
  - Ferromagnetic state is stable.
  - double exchange mechanism dominates
  - Hole doping is effective to raise T_C for Cr high concentration region.

Summary

- First-principles T_C calc. of DMS
  - Hybrid method = ab initio exchange const. + Monte Carlo
  - Reliable T_C calculations are possible.
  - For high-T_C, high concentration doping is needed, however solubility of Mn is very low in DMS.

- New material: Li(Zn, Mn)As
  1. Formation energy of Mn_{Zn} is negative.
  2. By introducing Vc_{Li} , Li_{int} ('co-doping'), we can control the phase separation and magnetism.
  3. Recent experiments: $Li_{1.1}(Zn_{0.85}, Mn_{0.15})As$, $T_C \sim 50$ (K)
  4. Cr doping is also promising.