μSR Applications in the Research of Diluted Magnetic Semiconductors

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Department of Physics, Zhejiang University
(Material synthesis + muSR + NMR)

2nd Muon Source Workshop
Dec-13th, 2019

Supported by MOST, NSFC and ZJ-NSF

In collaboration with:

Y.J. Uemura’ Group (Columbia)
Changqing Jin’s Group (IOP)

Experiments:

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Cui Ding (now a postdoc at Tsinghua with Prof. Qikun Xue)
Shengli Guo
Licheng Fu
Yilun Gu

Acknowledgement

Jianhua Zhao(Semi), Kai Chang (Semi), Kaiyou Wang(semi)， Igor Zutic (Buffalo), S. Maekawa (JAEA), Bo Gu(KITP), Igor Mazin (Navy), Ravin Bhatt (Princeton), Xin Wan (ZJU), Chao Cao (HZNU), Ni Ni (UCLA)

Outline

a. Introduction of some newly fabricated DMSs

“111”, 122”,”1111”, “42622”,”32522”

----- **$Li_{1+y}(Zn_{1-x}Mn_x)P$**

----- n-type **$Ba(Zn_{1-x}Co_x)_2As_2$**

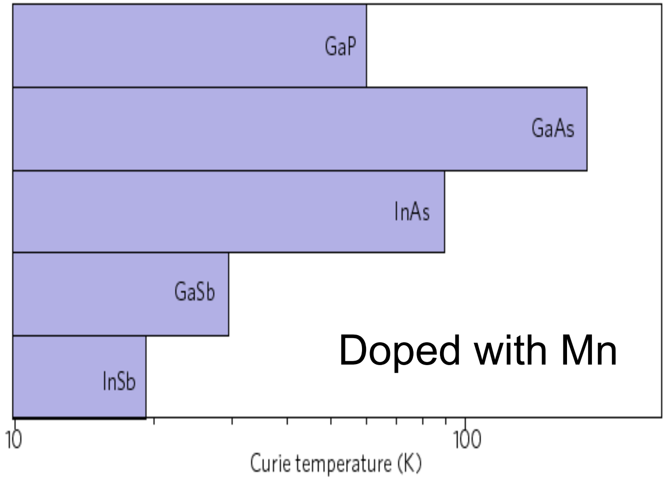
b. Microscopic characterization

----- **μSR results** on bulk form DMSs

-----**NMR results** on $Li_{1.1}(Cd_{1-x}Mn_x)P$ and $Li_{1.15}(Zn_{1-x}Mn_x)P$

Why bulk form DMS?

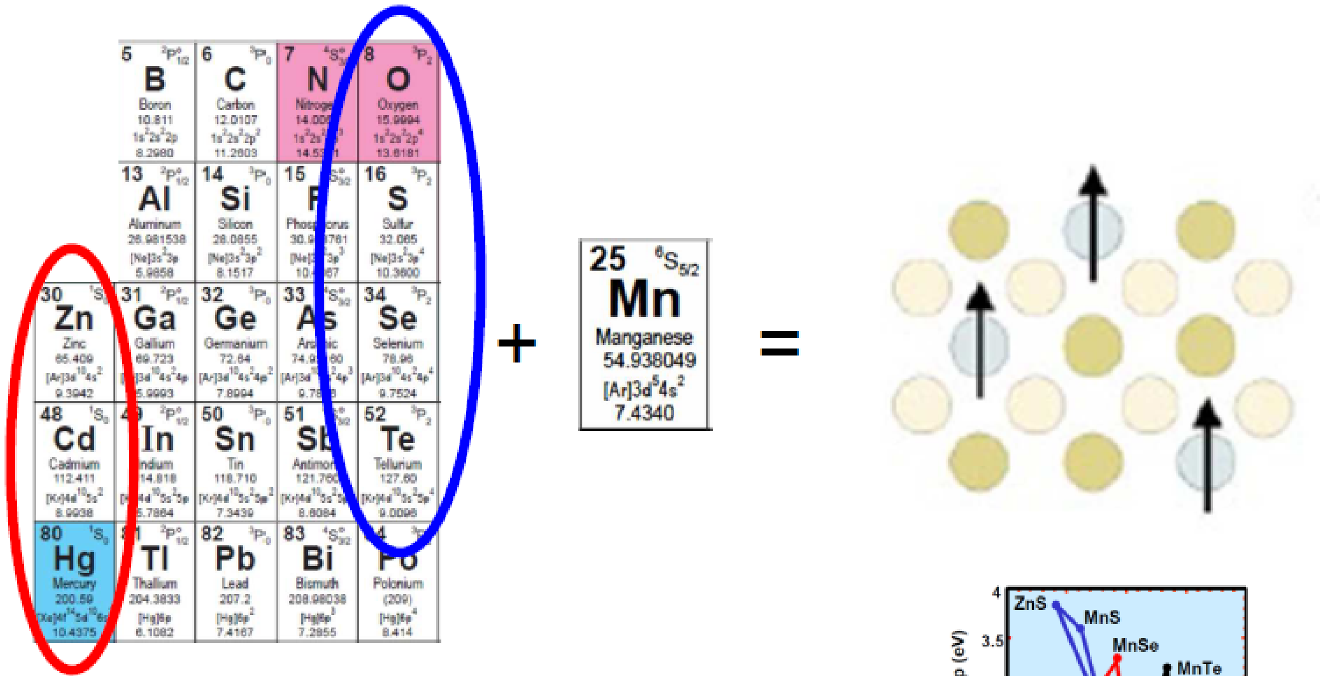
- We want to create "spintronics", and use not only charge but also spin information
- $Ga_{1-x}Mn_xAs$, T_C~200K, limited for practical applications; holes and spins are all introduced by Mn atoms (Jianhua Zhao's group in Institute of Semiconductor, Beijing)
- Mismatch of valences for Mn^{2+} and Ga^{3+} atoms, chemical solubility is less than 1% in bulk form
- Only low dimensional thin film can be fabricated with Molecular Beam Epitaxy
- Mn^{2+} substitution for Ga^{3+} introduces holes and spins
- NMR, μSR and neutron scattering are limited to investigate thin film.
- No NMR work ever done on DMS
- DMS in bulk form is highly expected!

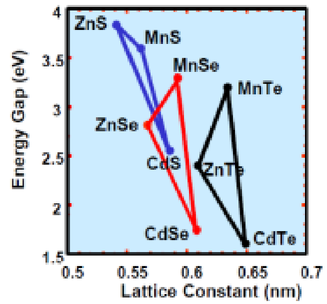


Currently achieved highest Tc in various III-V DMS thin films

(Dietl et al, Nature Materials, 2010, (9)965)

II-VI Diluted Magnetic Semiconducotors





Spin Glass Ordering, saturation moment ~0.01μ_B

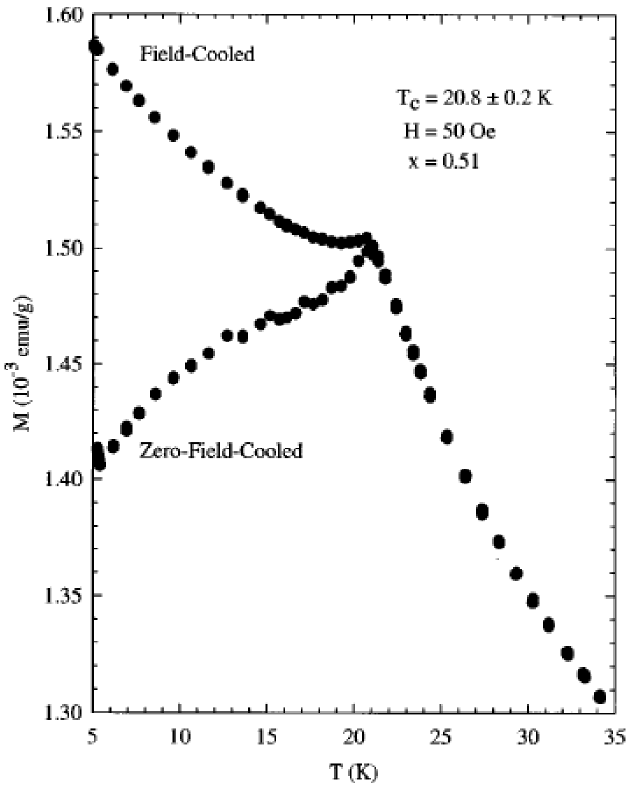


FIG. 6. Zero-field-cooled and field-cooled magnetization vs temperature T for $Zn_{0.49}Mn_{0.51}Te$. The cusp in the magnetization at $T = 20.8 \pm 0.2$ K for the zero-field-cooled case is characteristic of a transition to the spin-glass phase.

Phys Rev B, 58, 12876 (1998)

$Zn_{0.49}Mn_{0.51}Te$

- **Zn and Mn valences of "+2",**
- **No solid solution limit**
  the doping can be as high as ~70%
- **Mn ions do not provide carriers, only provide local moment**
- **Difficult to control density and type of carriers**

ZnSe/ZnTe→FeSe
("11" family of Fe-based SC)

PRL 98, 067202 (2007) PHYSICAL REVIEW LETTERS week ending 9 FEBRUARY 2007

Dilute Moment *n*-Type Ferromagnetic Semiconductor Li(Zn,Mn)As

J. Mašek,[1] J. Kudrnovský,[1] F. Máca,[1] B. L. Gallagher,[2] R. P. Campion,[2] D. H. Gregory,[3] and T. Jungwirth[4,2]
[1]*Institute of Physics ASCR, Na Slovance 2, 182 21 Praha 8, Czech Republic*
[2]*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*
[3]*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom*
[4]*Institute of Physics ASCR, Cukrovarnická 10, 162 53 Praha 6, Czech Republic*
(Received 6 September 2006; published 7 February 2007)

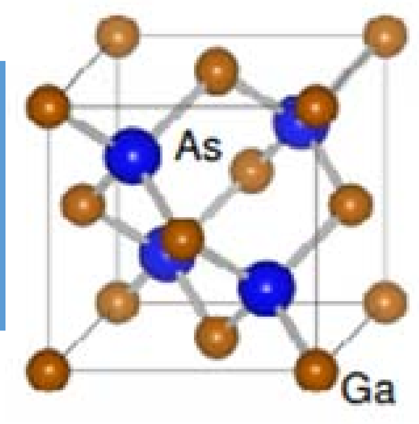
We propose to replace Ga in (Ga,Mn)As with Li and Zn as a route to high Curie temperature, carrier mediated ferromagnetism in a dilute moment *n*-type semiconductor. Superior material characteristics, rendering Li(Zn,Mn)As a realistic candidate for such a system, include high solubility of the isovalent substitutional Mn impurity and carrier concentration controlled independently of Mn doping by adjusting Li-(Zn,Mn) stoichiometry. Our predictions are anchored by *ab initio* calculations and comparisons with the familiar and directly related (Ga,Mn)As, by the physical picture we provide for the exchange interaction between Mn local moments and electrons in the conduction band, and by analysis of prospects for the controlled growth of Li(Zn,Mn)As materials.

DOI: 10.1103/PhysRevLett.98.067202 PACS numbers: 75.50.Pp, 73.61.Ey, 75.30.Hx

"III-V" ⟷ "I-II-V" ⟷ "II-VI"

$(Li^{+}Zn^{2+}) = Ga^{3+}$
→ LiZnAs = GaAs

$(Li^{+}As^{3-}) = Se^{2-}$
→ Zn(LiAs) = ZnSe



GaAs (1.42ev)

LiZnAs (1.6ev)
LiZnP (2.04ev)
LiCdP (1.30ev)

$Ga_{1-x}Mn_xAs$: Mn dope both spins and holes

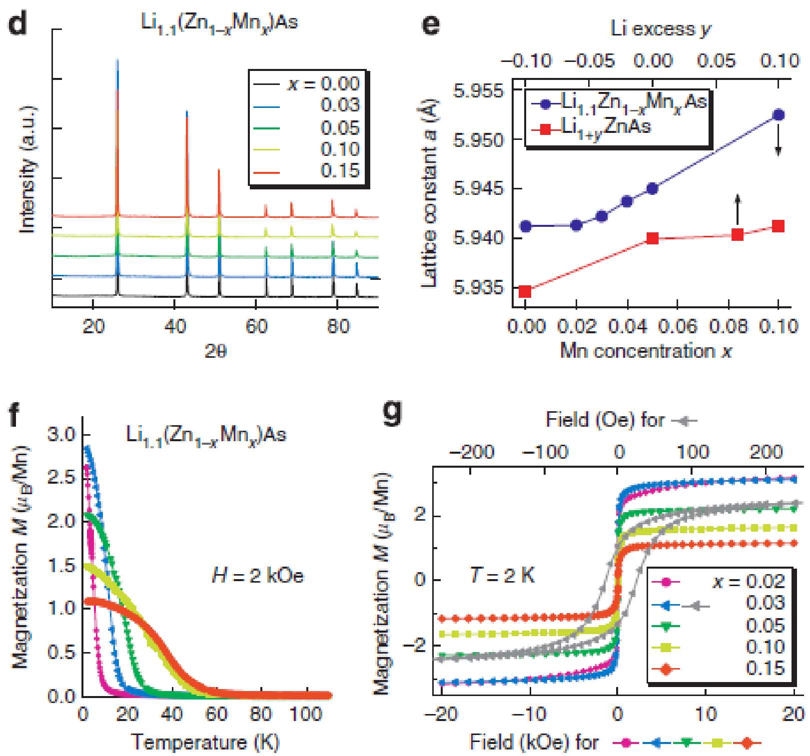
$Li_{1+y}(Zn^{+2}_{1-x}Mn^{+2}_{x})As$, $Li_{1+y}(Zn^{+2}_{1-x}Mn^{+2}_{x})P$, $Li_{1+y}(Cd^{+2}_{1-x}Mn^{+2}_{x})P$ (T_C ~40-50K)
: decouple spins and carriers

- Mn doping induc
- Li extra or defici ... rriers

(C.Q. Jin's group

LiZnAs → LiFeAs
("111" family of Fe-based SC)

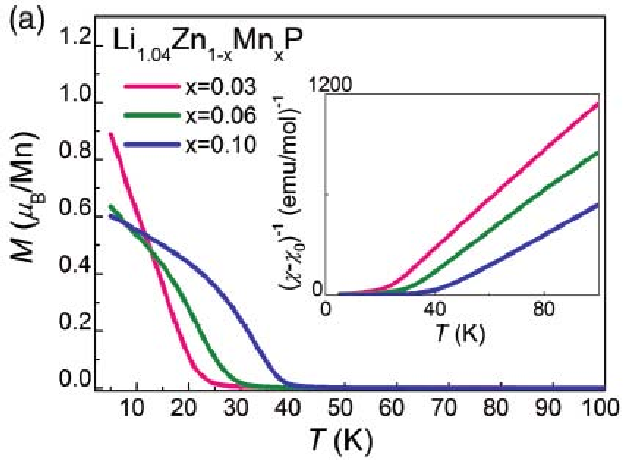
"111"- $Li_{1+y}(Zn^{+2}_{1-x}Mn^{+2}_{x})As$ （$T_C \sim 50$ K)

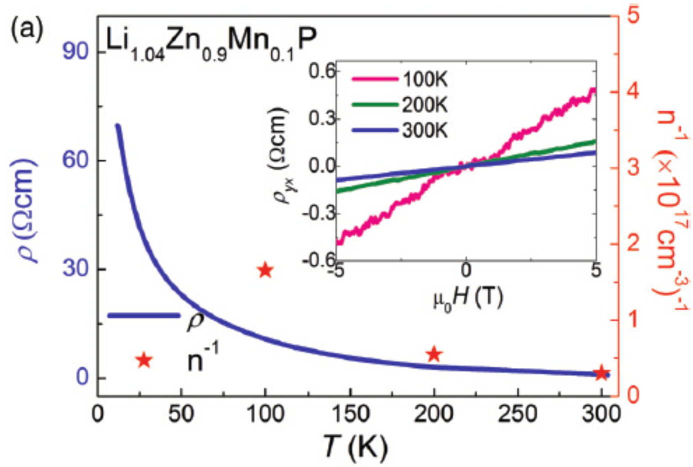


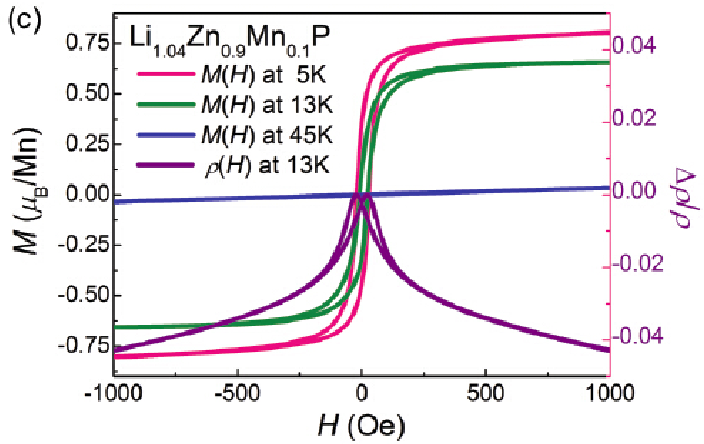
Z. Deng et al, Nature Communications (2011)

- **Saturation moments continuously decrease with more Mn**
- **Effective moment is 5~6μ_B/Mn, high spin state**
- **Coercive field ~ 50 Oe, for magnetic manipulation**

$Li_{1+y}(Zn^{+2}_{1-x}Mn^{+2}_{x})P$: Max T_C ~ 40 K



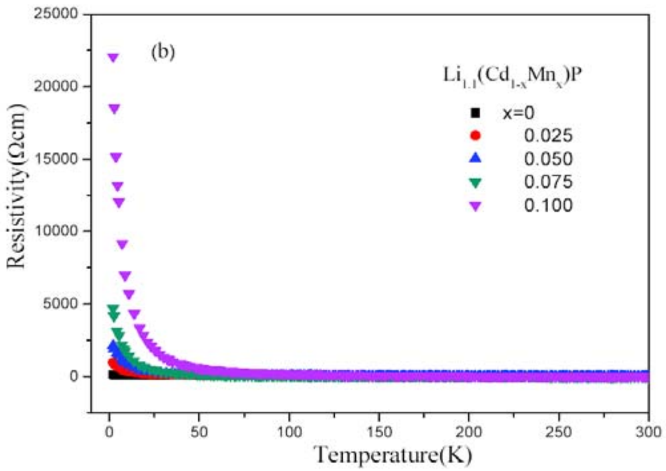


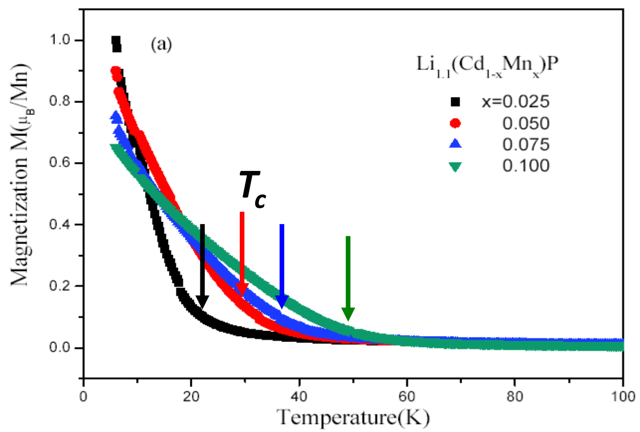


Deng et al, PRB 88,081203(R) (2013)

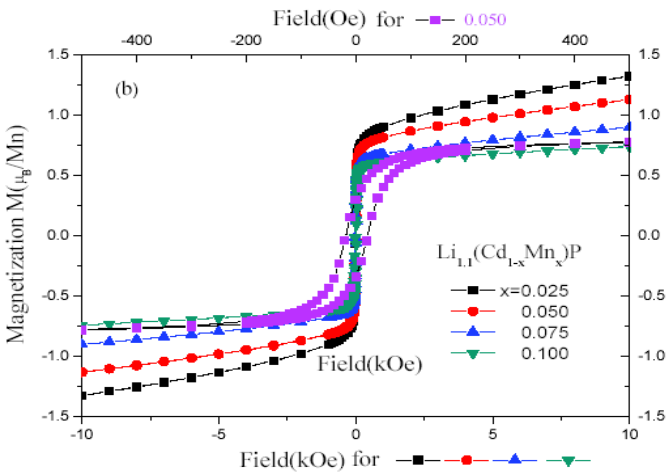
$Li_{1+y}(Cd^{+2}_{1-x}Mn^{+2}_{x})P$

Wei Han et al, Scientific Reports 9, 7490 (2019)





Magnetizations of Li1.1(Cd,Mn)P as function of Mn content

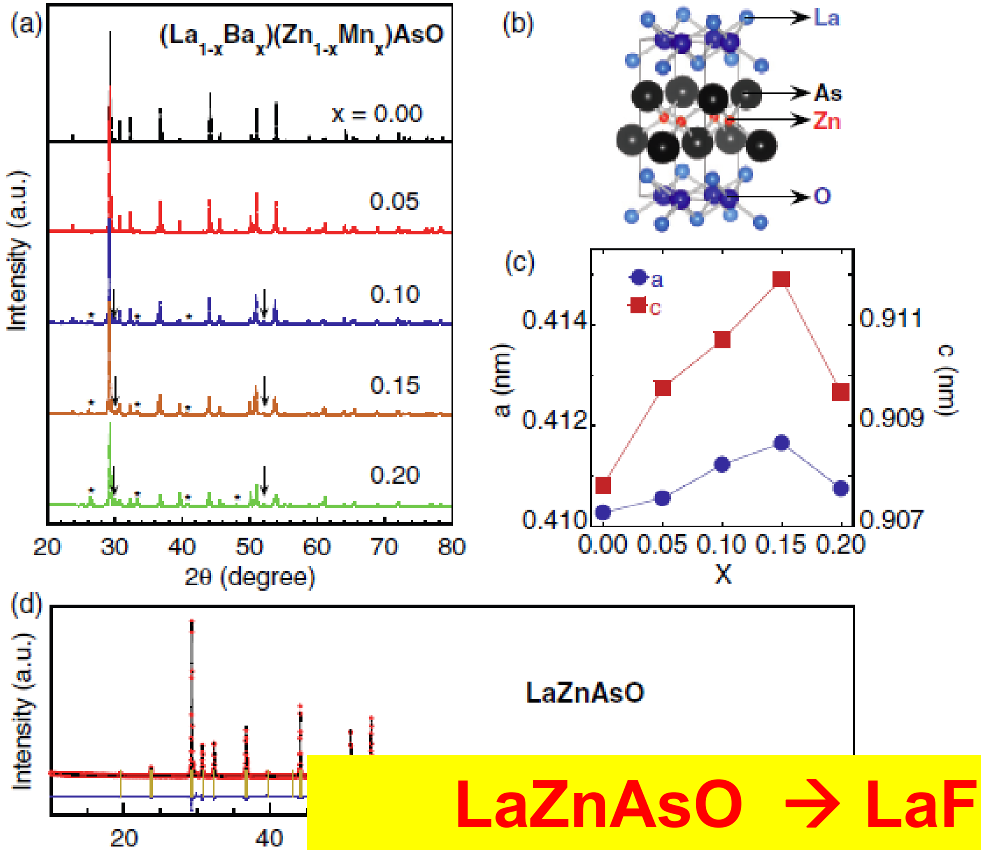


The MH curves of Li1,1(Cd,Mn)P

T_c and moment size at 6K

x*(100%)	T_c	Mn(6K)
2.5	21	1.00
5.0	28	0.90
7.5	35	0.75
10	43	0.65

$(La_{1-x}Ba_x)(Zn_{1-x}Mn_x)AsO$ T_C ~40K

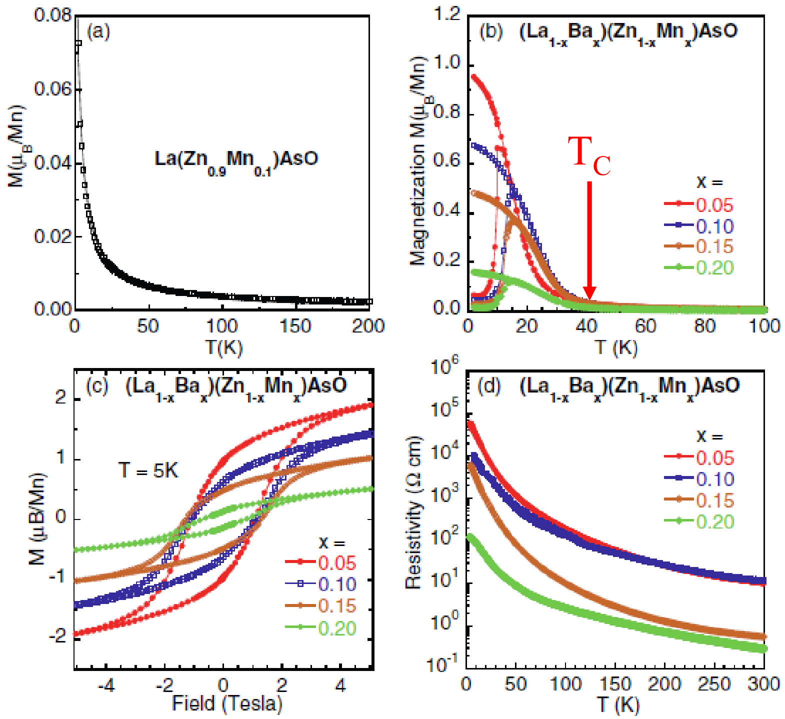


- Isostructral to Fe-based SC "1111"-$LaFeAsO_{1-x}F_x$

LaZnAsO → LaFeAsO
("1111" family of Fe-based SC）

C. Ding and F.L. Ning, PRB 88, 041102 (2013)

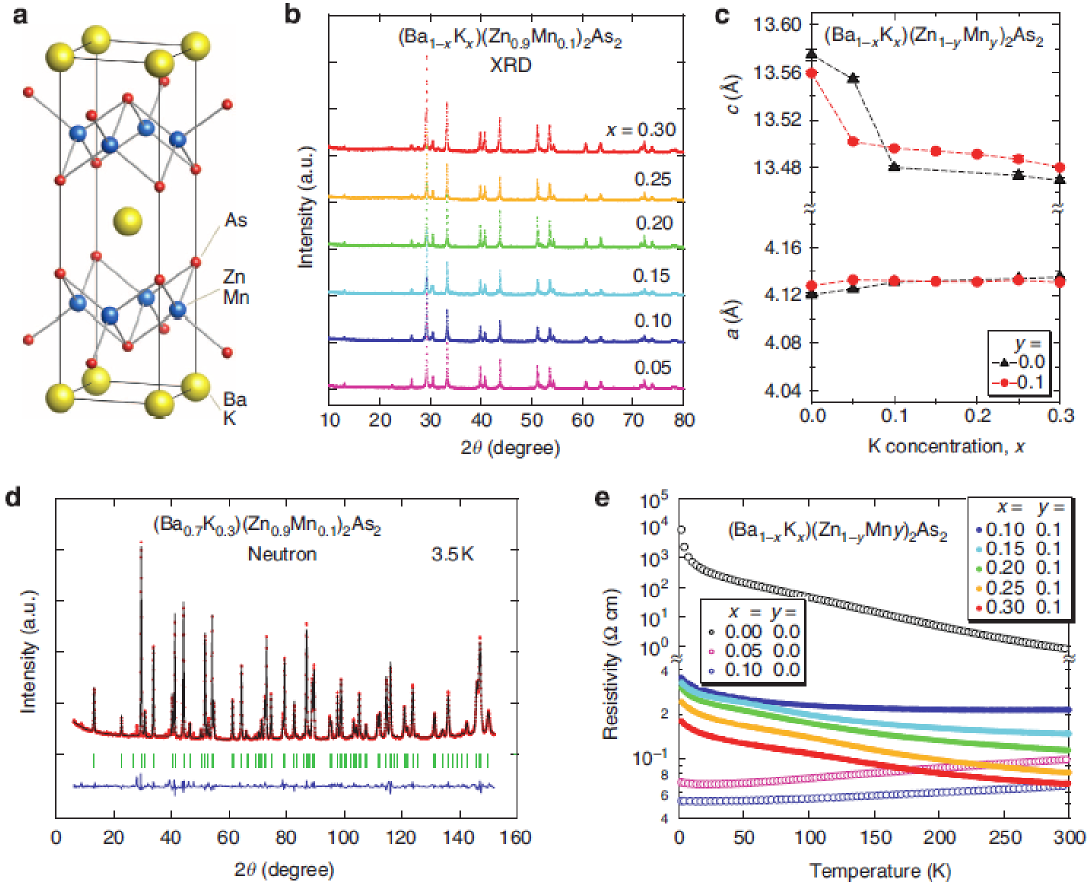
$(La_{1-x}Ba_x)(Zn_{1-x}Mn_x)AsO$ T_C ~40K



- **doping Mn only, paramagnetic state**
- **Only when carriers are doped via Ba substitution for La, FM ordering is observed**
- **From resitivity, semiconducting behavior**
- **Large coercive field ~ 1 Tesla**

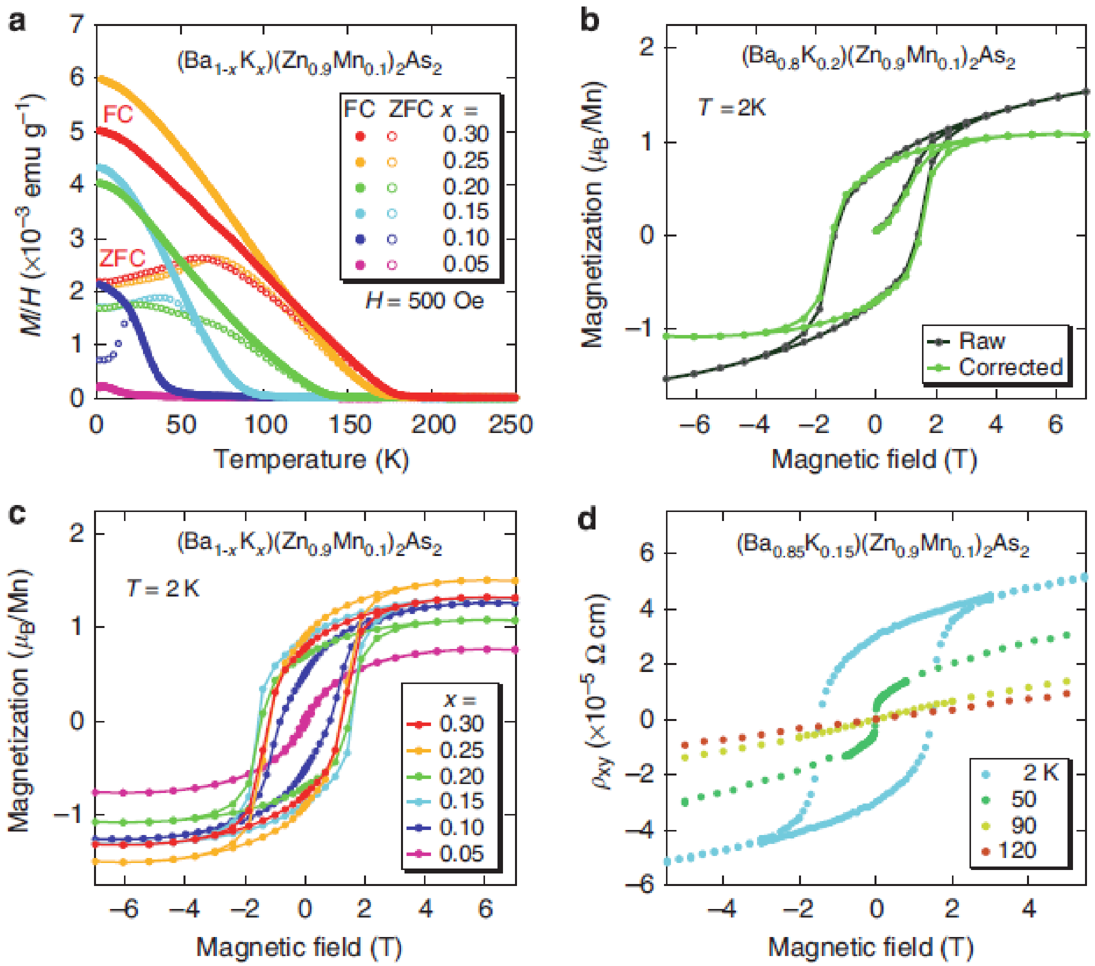
C. Ding and F.L. Ning, PRB 88, 041102 (2013)

$(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ T_C ~180K



K. Zhao et al, Nature Communications, 4, 1442 (2013)

$(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ T_C ~180K



K. Zhao et al, Nature Communications, 4, 1442 (2013)

Chin. Sci. Bull. (2014) 59(21):2524–2527
DOI 10.1007/s11434-014-0398-z

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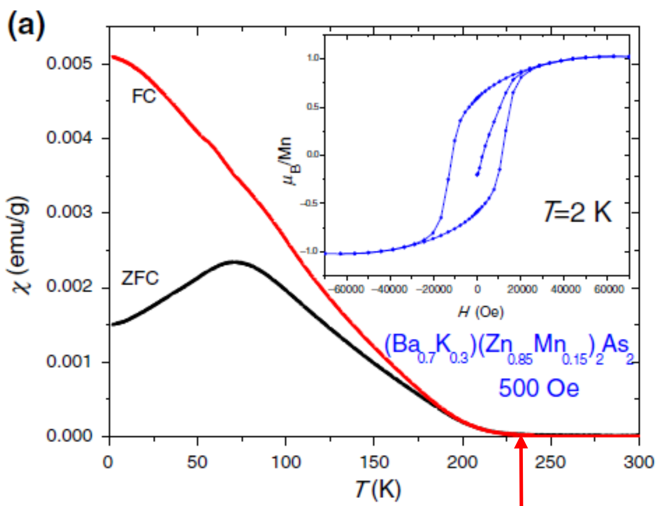
www.springer.com/scp

Letter

Condensed Matter Physics

Ferromagnetism at 230 K in $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ diluted magnetic semiconductor

Kan Zhao · Bijuan Chen · Guoqiang Zhao ·
Zhen Yuan · Qingqing Liu · Zheng Deng ·
Jinlong Zhu · Changqing Jin



T_C ~ 230K

$BaZn_2As_2$ → $BaFe_2As_2$
(“122” family of Fe-based SC）

Fabricate new DMS and what we have

GaAs ------------ $Ga_{1-x}Mn_xAs$ ------------------------ MnAs

FM, T_c ~ 210K(film) FM, T_c ~ 320K

LiZnAs --------- $LiZn_{1-x}Mn_xAs$ ----------------------- LiMnAs

"111" FM, T_c ~ 55K(bulk) AFM, T_N~ 400K

I-II-V (Nature Comm. 2011, IOP)

$BaZn_2As_2$ ---- $Ba_{1-y}K_y(Zn_{1-x}Mn_x)_2As_2$ ---------------- $BaMn_2As_2$

"122" FM, T_c ~ 230K(bulk) AFM, T_N~ 620K

II-II-V (Nature Comm. 2013, IOP)

LaZnAsO ---- $La_{1-y}Ba_yZn_{1-x}Mn_xAsO$ --------------- LaMnAsO

"1111" FM, T_c ~ 40K(bulk) AFM, T_N ~ 320K

(PRB 2013, Zhejiang)

"32522" ---- $(Sr_3La_2O_5)(Zn_{1-x}Mn_x)_2As_2$ --------------- AFM(?)

FM, Tc ~ 40K(bulk)

(EPL 2014, Zhejiang)

"42622" ---- $(Sr_{1-x}K_x)_4Ti_2O_6(Zn_{1-x}Mn_x)_2As_2$ --------------- AFM(?)

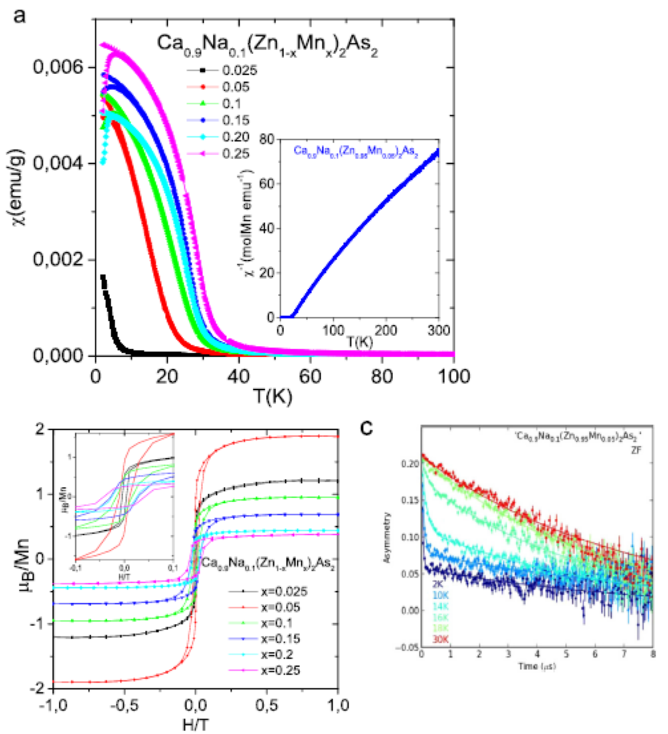
FM, Tc ~ 25K(bulk)

(To be submitted, Zhejiang)

JOURNAL OF APPLIED PHYSICS 116, 163906 (2014)

(Ca,Na)(Zn,Mn)$_2$As$_2$: A new spin and charge doping decoupled diluted ferromagnetic semiconductor

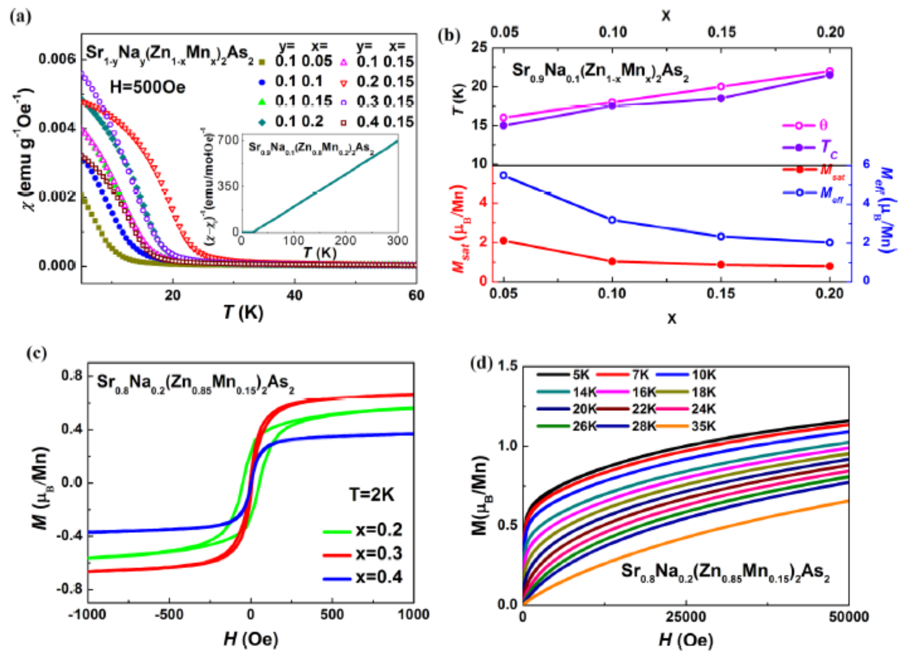
K. Zhao,[1] B. J. Chen,[1] Z. Deng,[1] W. Han,[1,2] G. Q. Zhao,[1] J. L. Zhu,[1] Q. Q. Liu,[1]
X. C. Wang,[1] B. Frandsen,[3] L. Liu,[3] S. Cheung,[3] F. L. Ning,[4] T. J. S. Munsie,[5] T. Medina,[5]
G. M. Luke,[5] J. P. Carlo,[6] J. Munevar,[7] G. M. Zhang,[8] Y. J. Uemura,[3] and C. Q. Jin[1,3,a)]



PHYSICAL REVIEW B 90, 155202 (2014)

(Sr,Na)(Zn,Mn)$_2$As$_2$: A diluted ferromagnetic semiconductor with the hexagonal CaAl$_2$Si$_2$ type structure

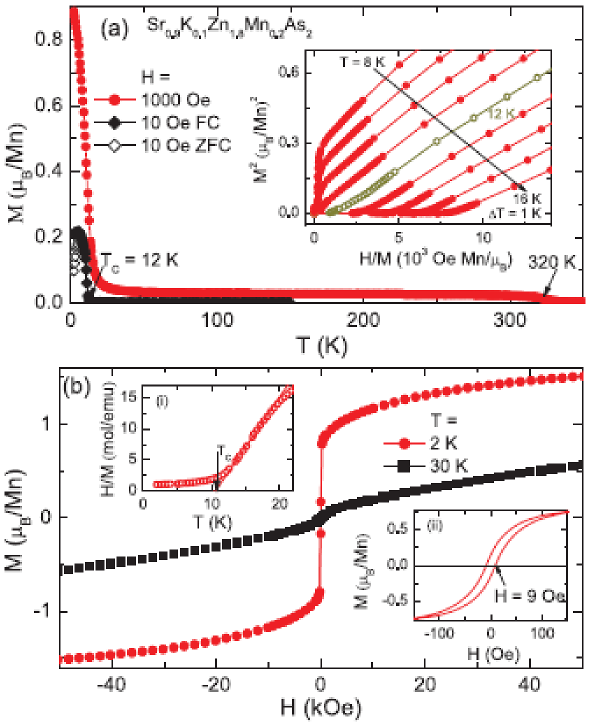
B. J. Chen,[1] K. Zhao,[1] Z. Deng,[1] W. Han,[1] J. L. Zhu,[1] X. C. Wang,[1] Q. Q. Liu,[1] B. Frandsen,[2] L. Liu,[2] S. Cheung,[2] F. L. Ning,[3]
T. J. S. Munsie,[4] T. Medina,[4] G. M. Luke,[4] J. P. Carl,[5] J. Munevar,[6] Y. J. Uemura,[2] and C. Q. Jin[1]



epl A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS
September 2014
EPL, **107** (2014) 67007
www.epljournal.org
doi: 10.1209/0295-5075/107/67007

$Sr_{0.9}K_{0.1}Zn_{1.8}Mn_{0.2}As_2$: A ferromagnetic semiconductor with colossal magnetoresistance

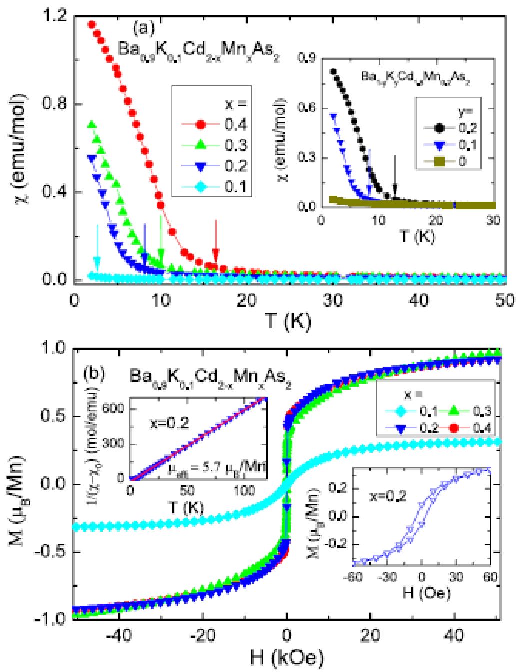
Xiaojun Yang[1], Qian Chen[1], Yupeng Li[1], Zhen Wang[1], Jinke Bao[1], Yuke Li[2], Qian Tao[1], Guanghan Cao[1] and Zhu-An Xu[1(a)]



JOURNAL OF APPLIED PHYSICS **114**, 223905 (2013)
CrossMark

K and Mn co-doped $BaCd_2As_2$: A hexagonal structured bulk diluted magnetic semiconductor with large magnetoresistance

Xiaojun Yang,[1] Yuke Li,[2] Pan Zhang,[1] Hao Jiang,[1] Yongkang Luo,[1] Qian Chen,[1] Chunmu Feng,[1] Chao Cao,[2] Jianhui Dai,[2] Qian Tao,[1] Guanghan Cao,[1] and Zhu-An Xu[1,a)]
[1]*Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China*
[2]*Department of Physics, Hangzhou Normal University, Hangzhou 310036, China*



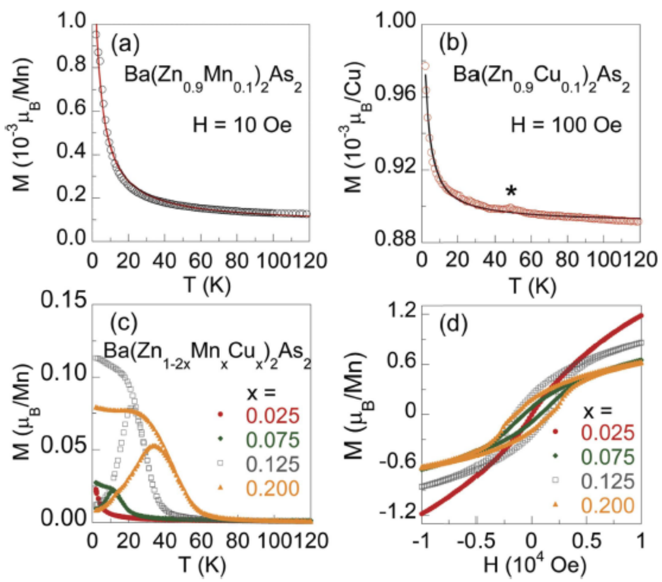
SCIENTIFIC REPORTS

OPEN

$Ba(Zn_{1-2x}Mn_xCu_x)_2As_2$: A Bulk Form Diluted Ferromagnetic Semiconductor with Mn and Cu Codoping at Zn Sites

Received: 07 April 2015
Accepted: 28 September 2015
Published: 23 October 2015

Huiyuan Man[1,2], Shengli Guo[1,2], Yu Sui[3], Yang Guo[4], Bin Chen[4], Hangdong Wang[4], Cui Ding[1,2] & F.L. Ning[1,2]



Contents lists available at ScienceDirect
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journal homepage: www.elsevier.com/locate/jmmm
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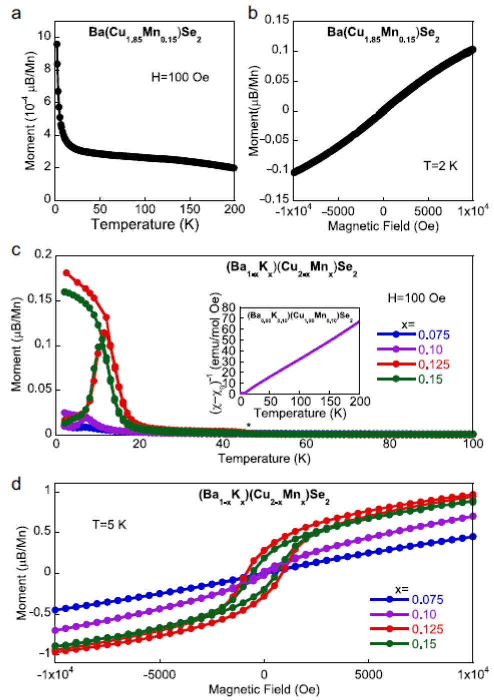
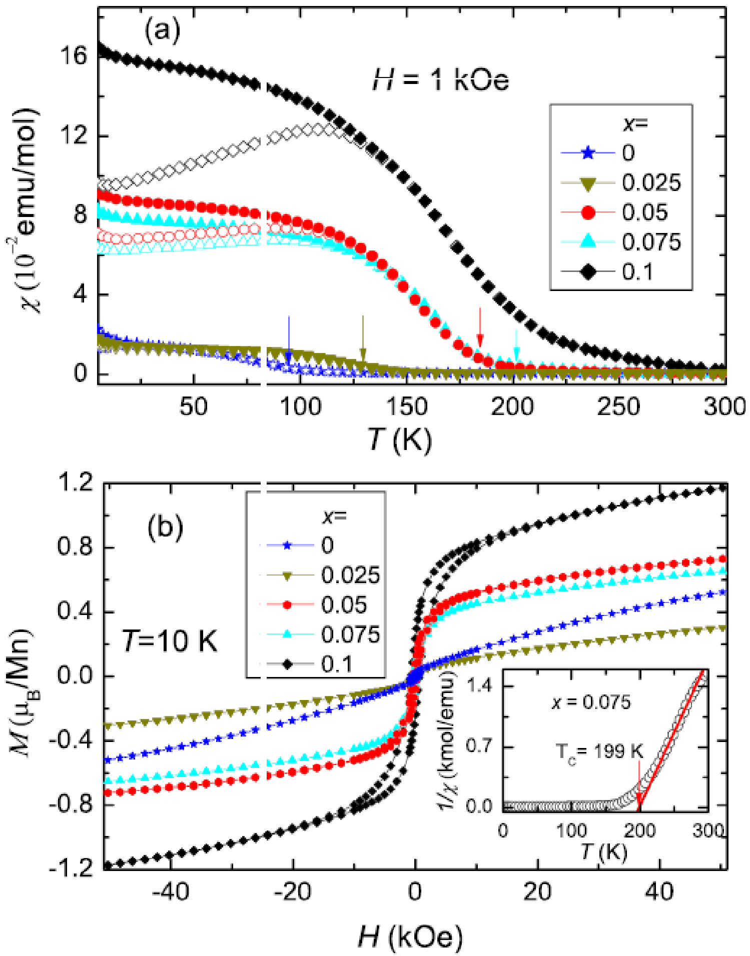
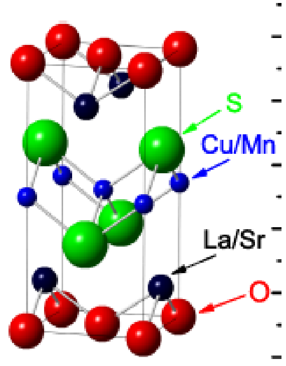
$(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$: A copper-based bulk form diluted magnetic semiconductor with orthorhombic $BaCu_2S_2$-type structure

Shengli Guo[a,b], Huiyuan Man[a,b], Xin Gong[a,b], Cui Ding[a,b], Yao Zhao[a,b], Bin Chen[c], Yang Guo[c], Hangdong Wang[c], F.L. Ning[a,b,*]

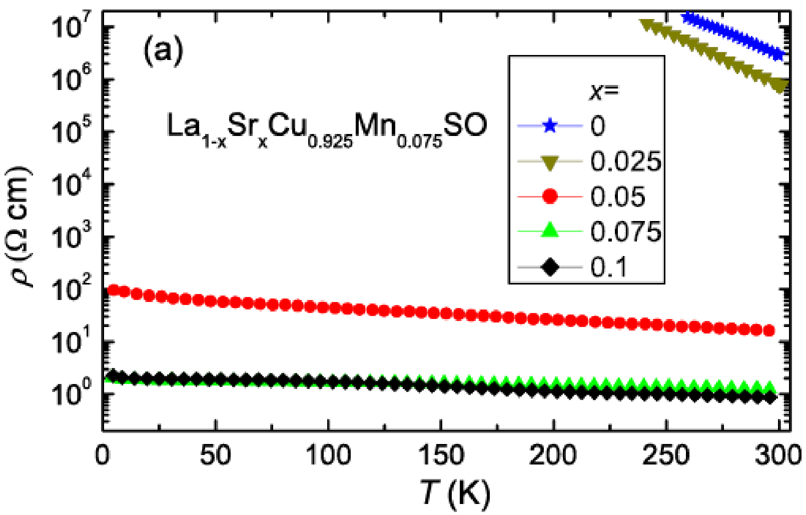


Sr and Mn co-doped LaCuSO: “1111”- type DMS



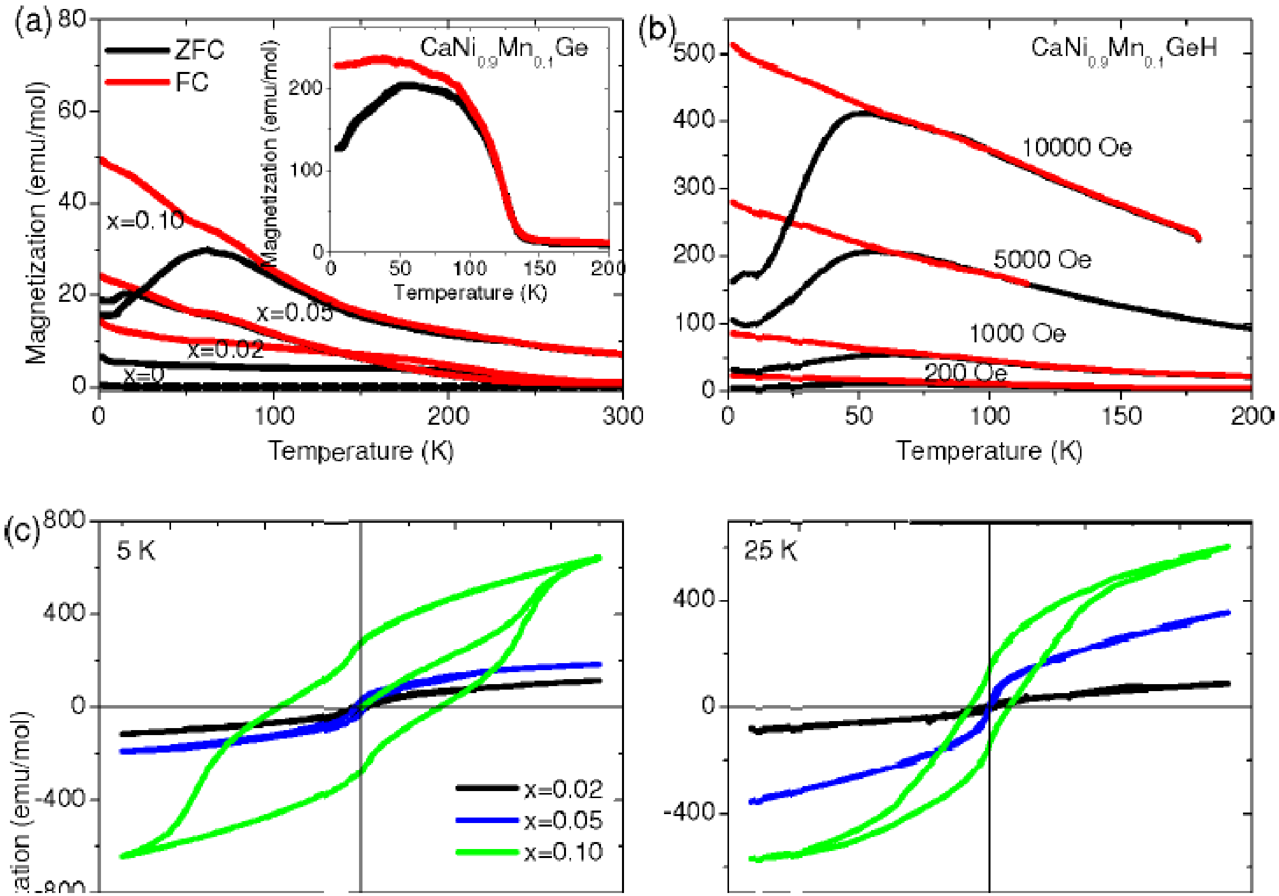


$T_C \sim 200$ K



Z.A. Xu et al, Applied Physics Letters 103, 022410 (2013)

$CaNi_{1-x}Mn_xGe$ $CaNi_{1-x}Mn_xGeH$



H. Hosono et al, JACS, 134, 11687 (2012)

H. Hosono et al, Physical Review B **84**, 214439 (2011)

$Ga_{1-x}Mn_xAs$ *Tc* ~ 200K(film)

$LiZn_{1-x}Mn_xAs$ *Tc* ~ 55K(bulk)-----"111"

$Ba_{1-y}K_y(Zn_{1-x}Mn_x)_2As_2$ *Tc* ~ 230K(bulk)---"122" → **P-type DMS**

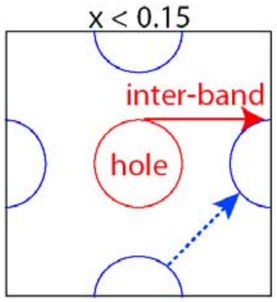
$La_{1-y}Ba_yZn_{1-x}Mn_xAsO$ *Tc* ~ 40K(bulk) ---"1111"

$(Sr_3La_2O_5)(Zn_{1-x}Mn_x)_2As_2$ *Tc* ~ 40K(bulk)---"32522"

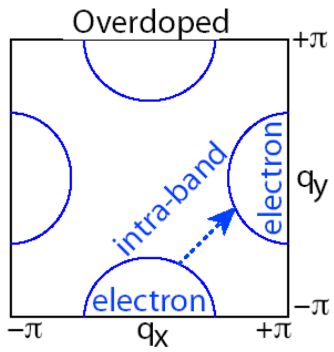
$(Sr_{1-x}K_x)_4Ti_2O_6(Zn_{1-x}Mn_x)_2As_2$ *Tc* ~ 25K(bulk)---"42622"

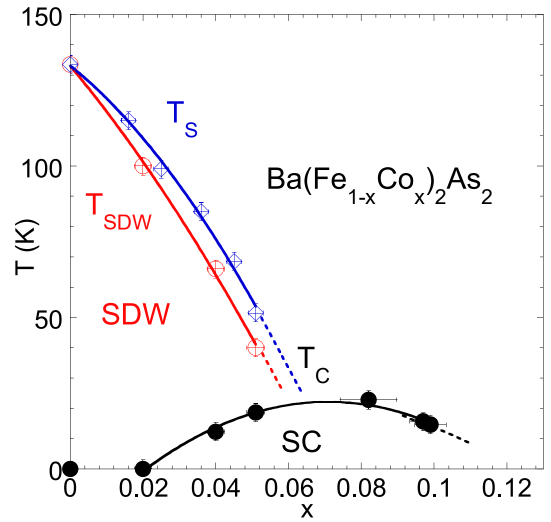
For making junctions, n-type DMS are expected!

"122" – $Ba(Fe_{1-x}Co_x)_2As_2$- SC
Tc = 25 K



Doping Co, introduce electrons

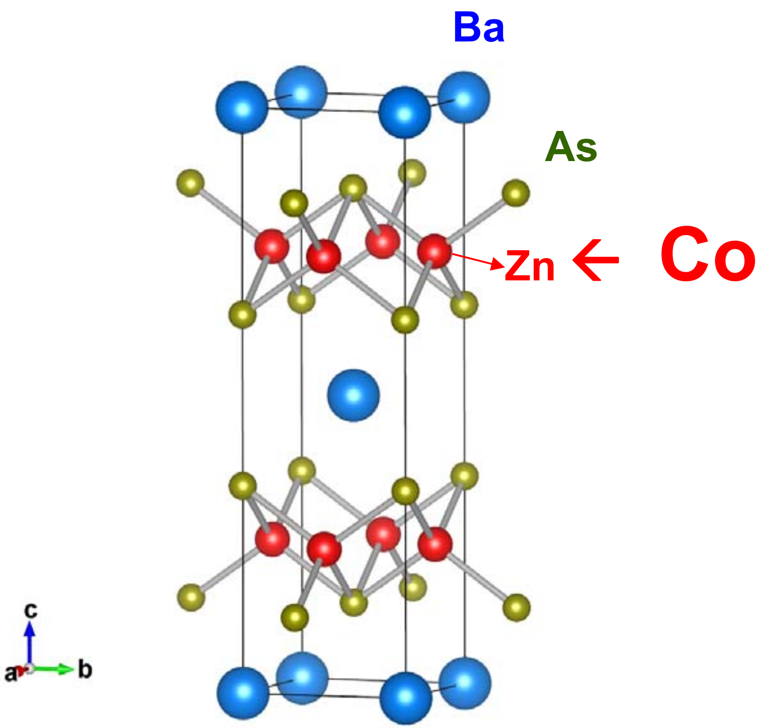




(F.L. Ning et al, JPSJ 78, 013711(2009))

(T_S is from Fisher et al, PRB 79, 014506(2009)).

“122” - $BaZn_2As_2$

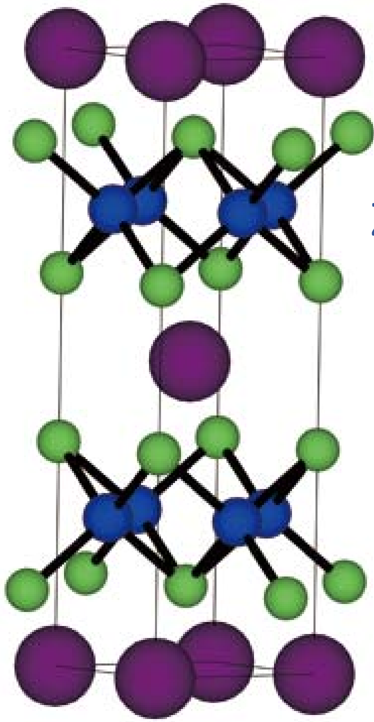


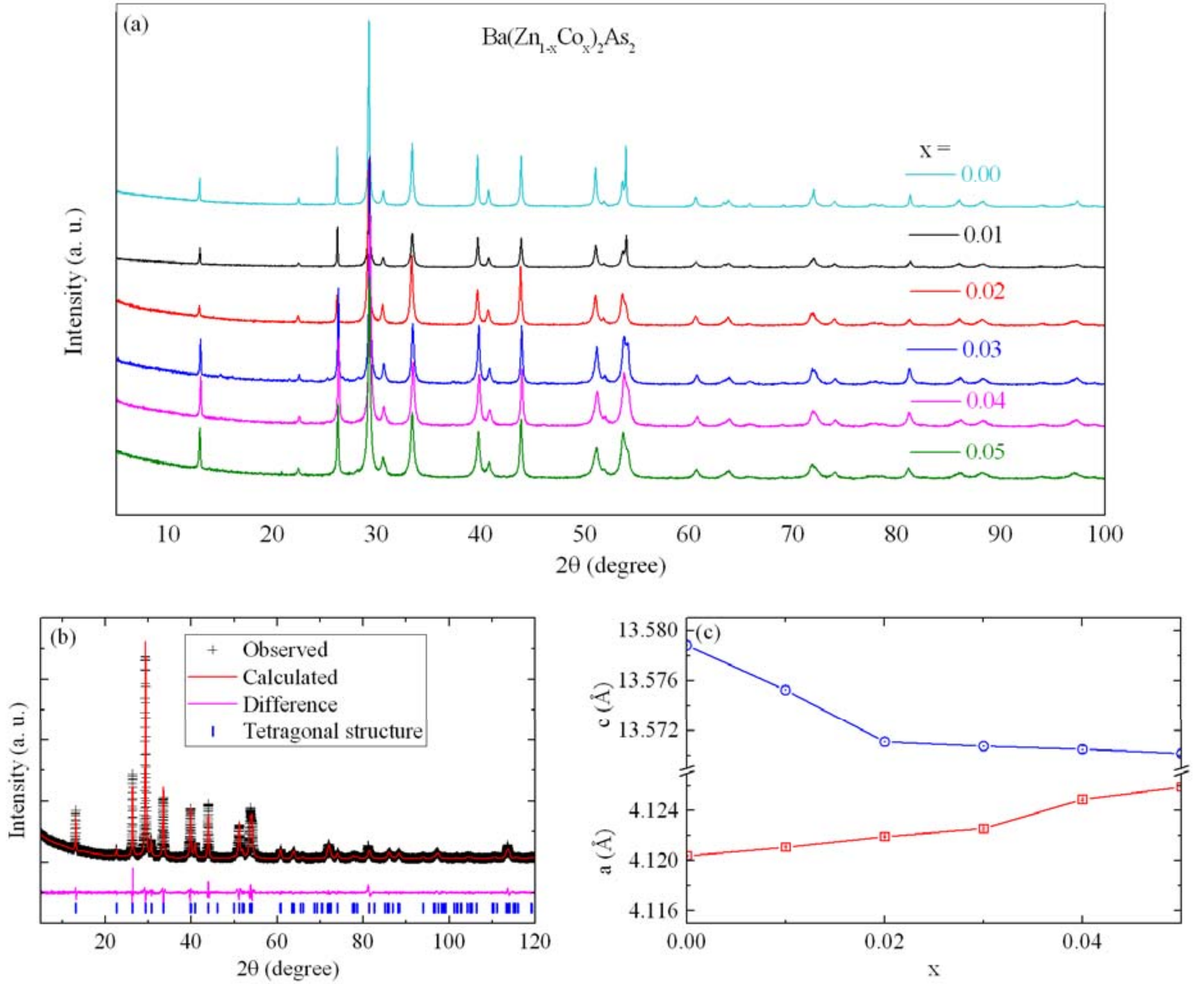
The idea here is:

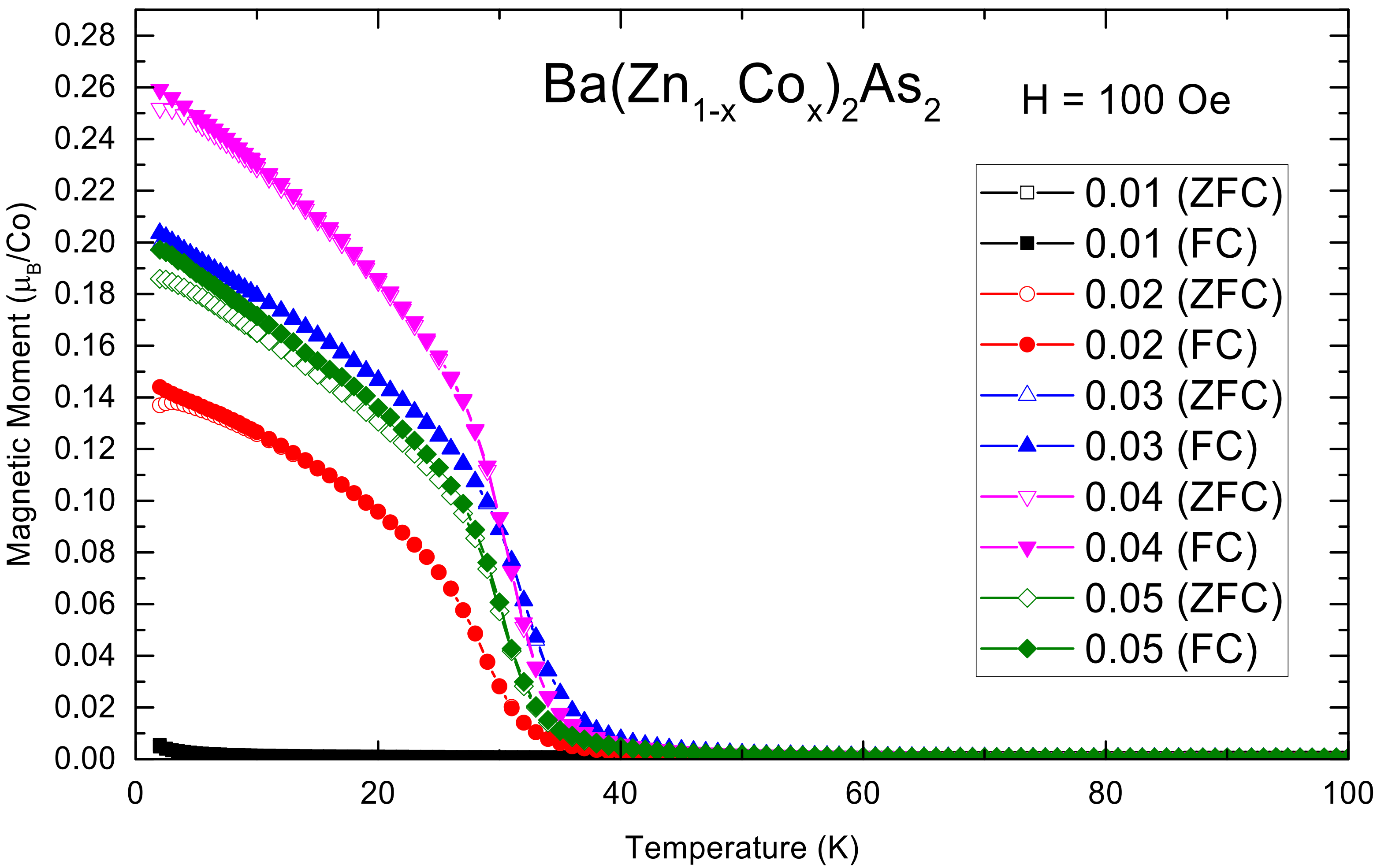
---Co introduce both moments and electrons

（Started the work in 2013)

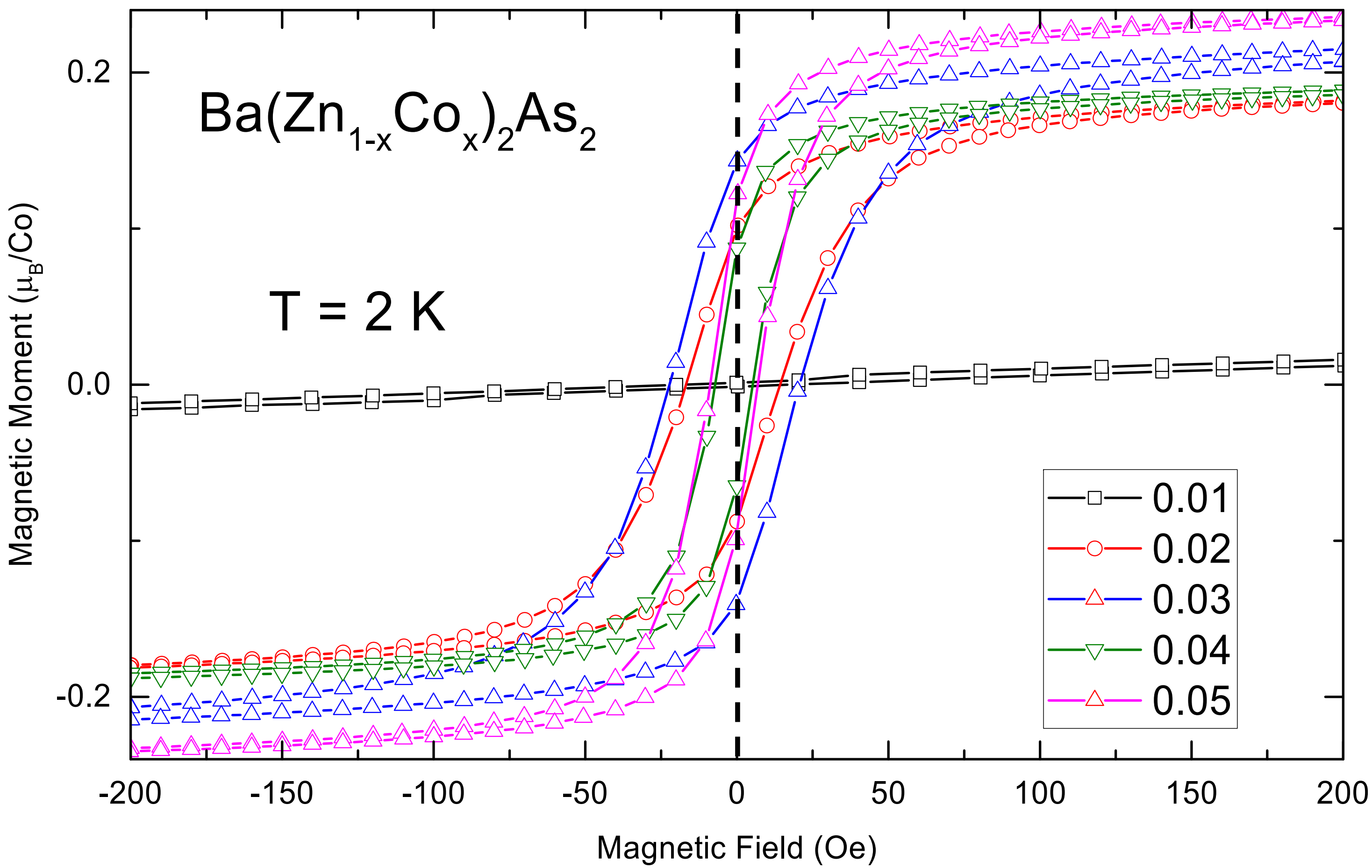
Until 2016: Shengli Guo obtained pure phase





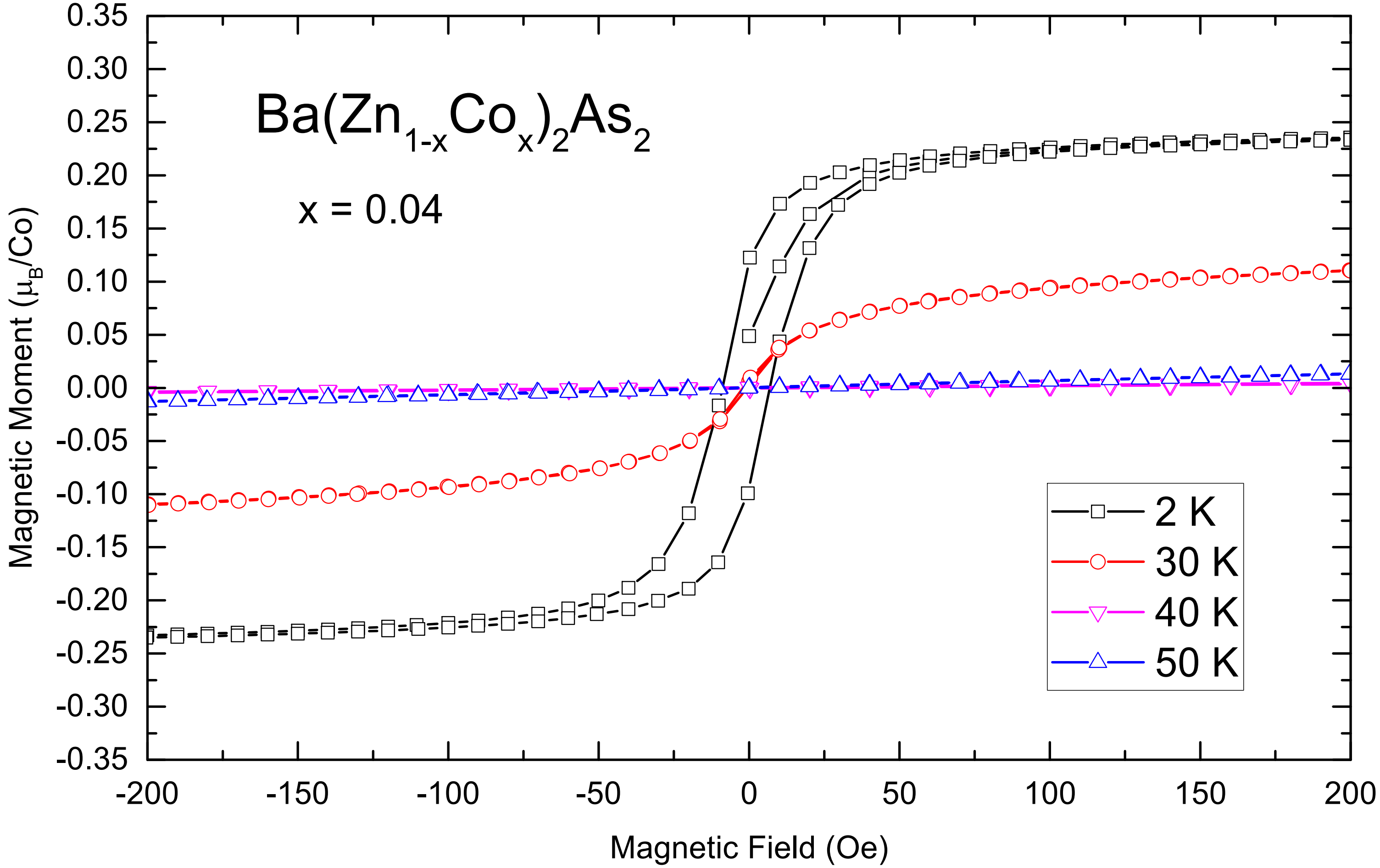


Ba(Zn1-xCox)2As2
H = 100 Oe
0.01 (ZFC)
0.01 (FC)
0.02 (ZFC)
0.02 (FC)
0.03 (ZFC)
0.03 (FC)
0.04 (ZFC)
0.04 (FC)
0.05 (ZFC)
0.05 (FC)
Magnetic Moment (μB/Co)
Temperature (K)
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
20
40
60
80
100

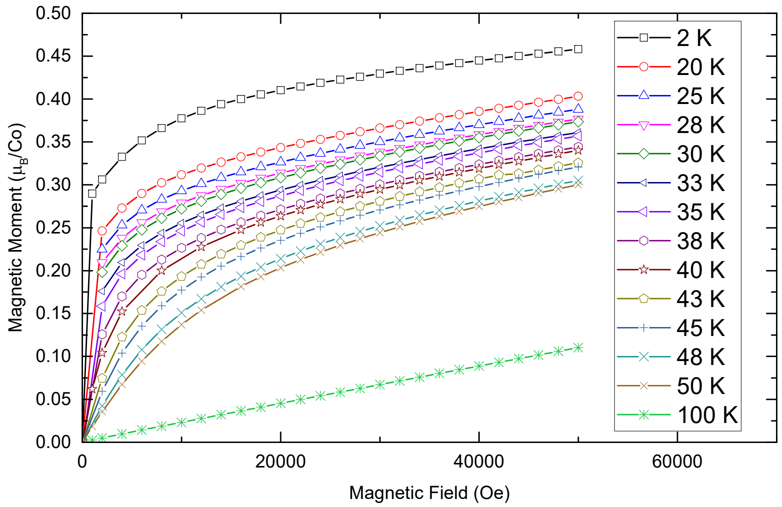


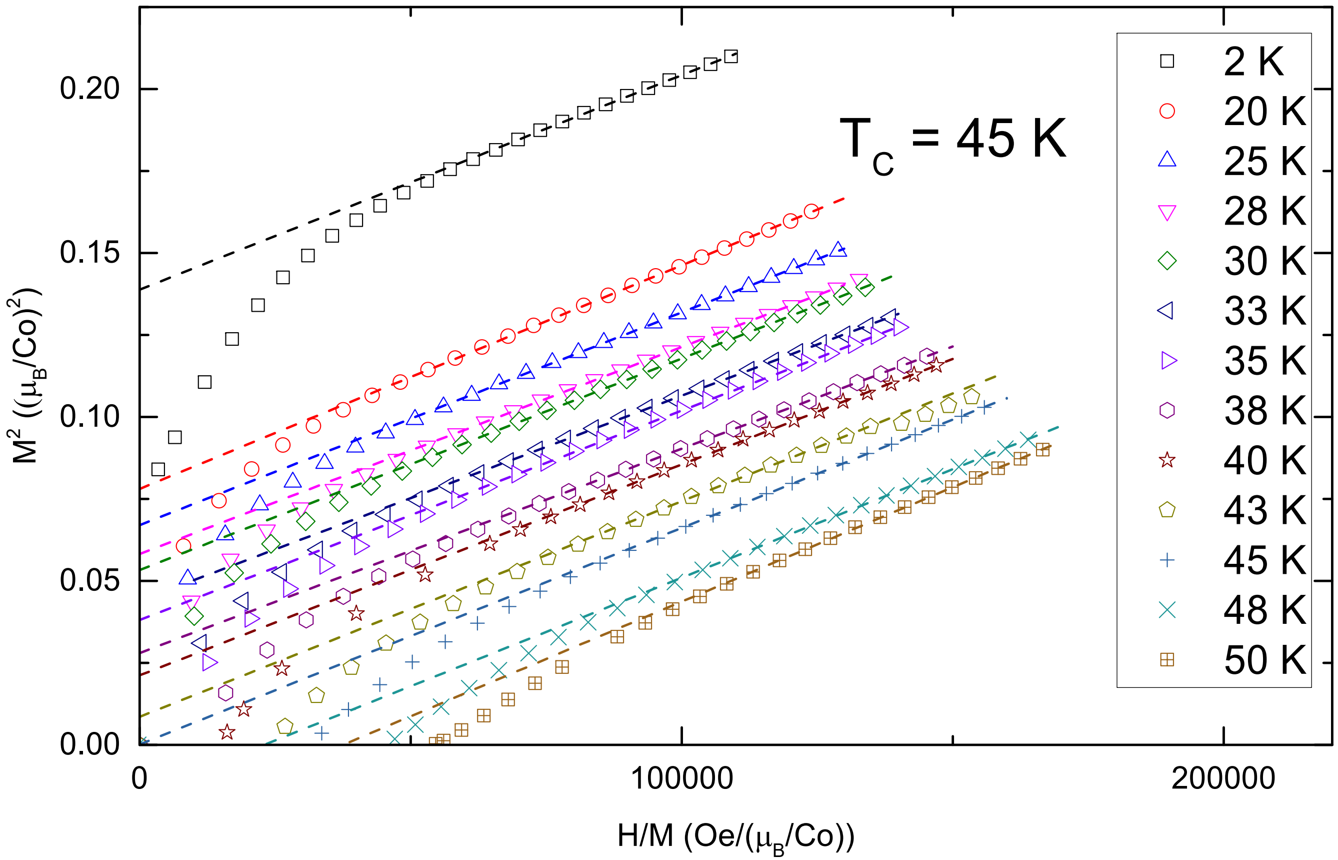
Ba(Zn1-xCox)2As2
T = 2 K
Magnetic Moment (μB/Co)
Magnetic Field (Oe)
0.2
0.0
-0.2
-200
-150
-100
-50
0
50
100
150
200
0.01
0.02
0.03
0.04
0.05

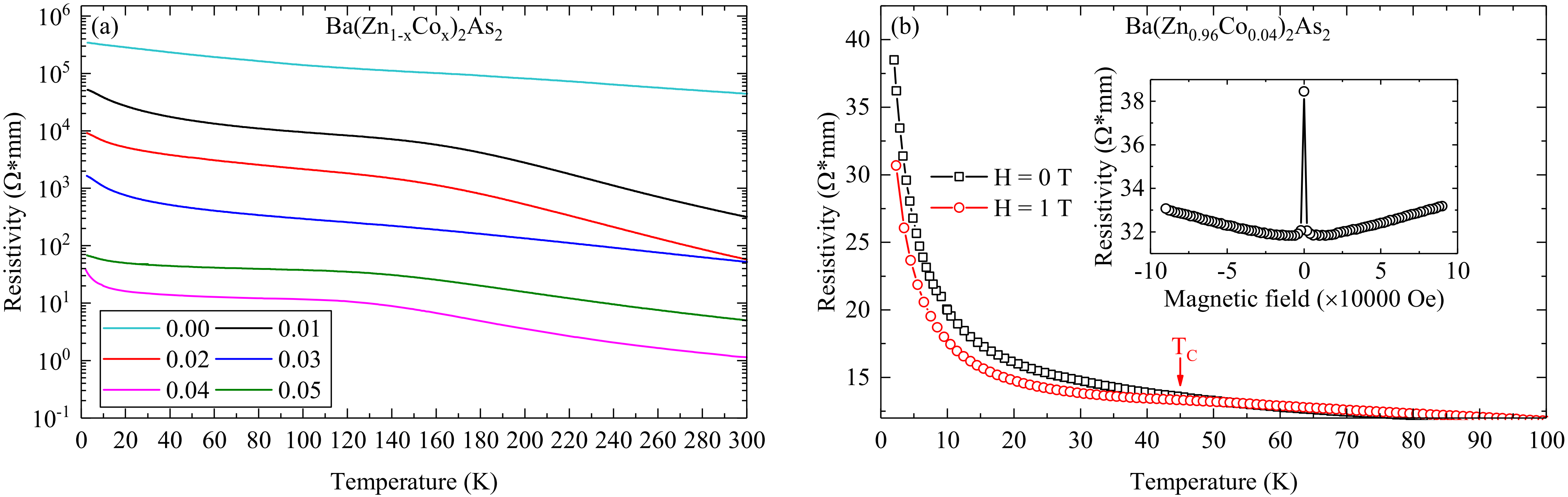
$Ba(Zn_{0.96}Co_{0.04})_2As_2$



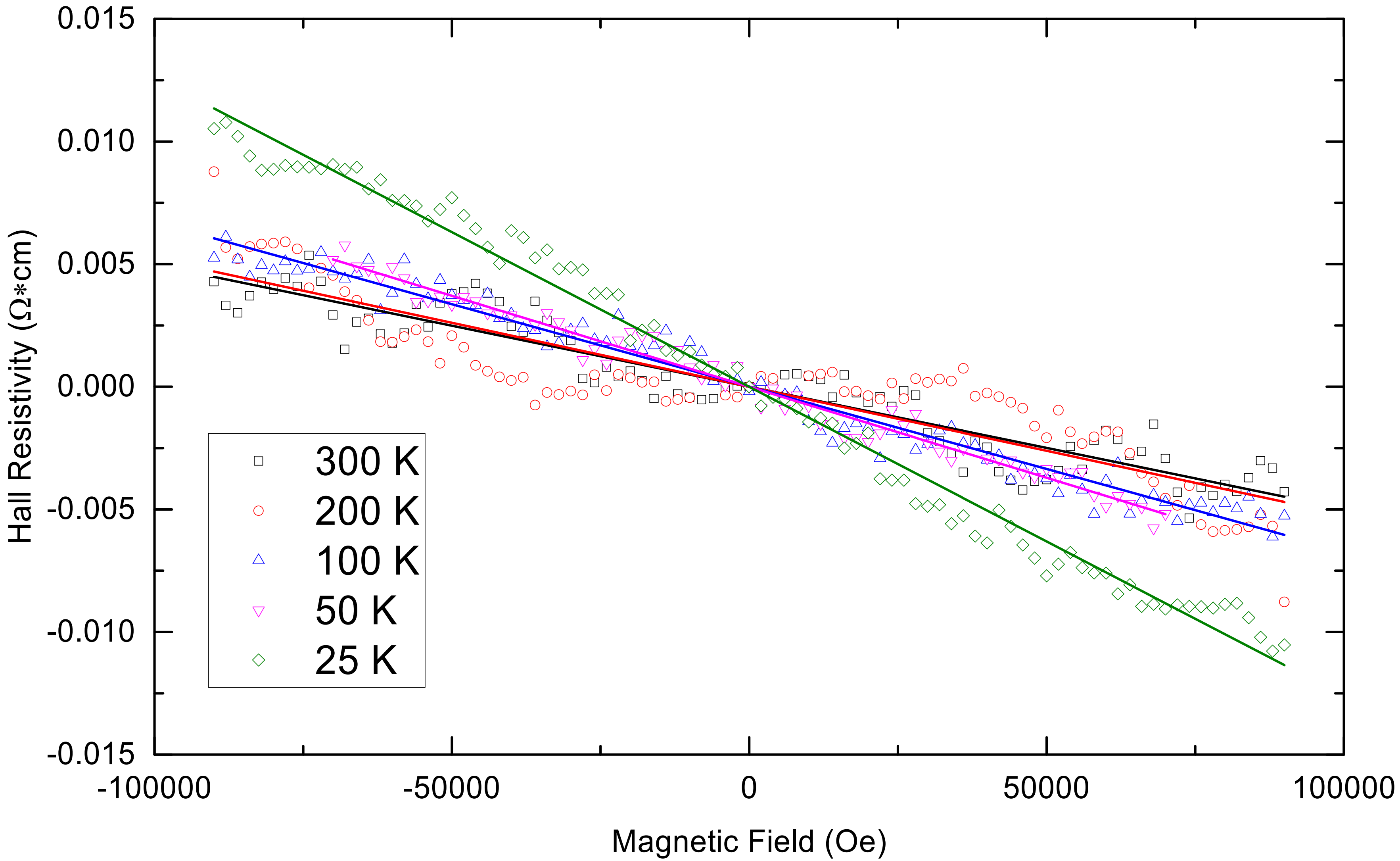
$Ba(Zn_{0.96}Co_{0.04})_2As_2$





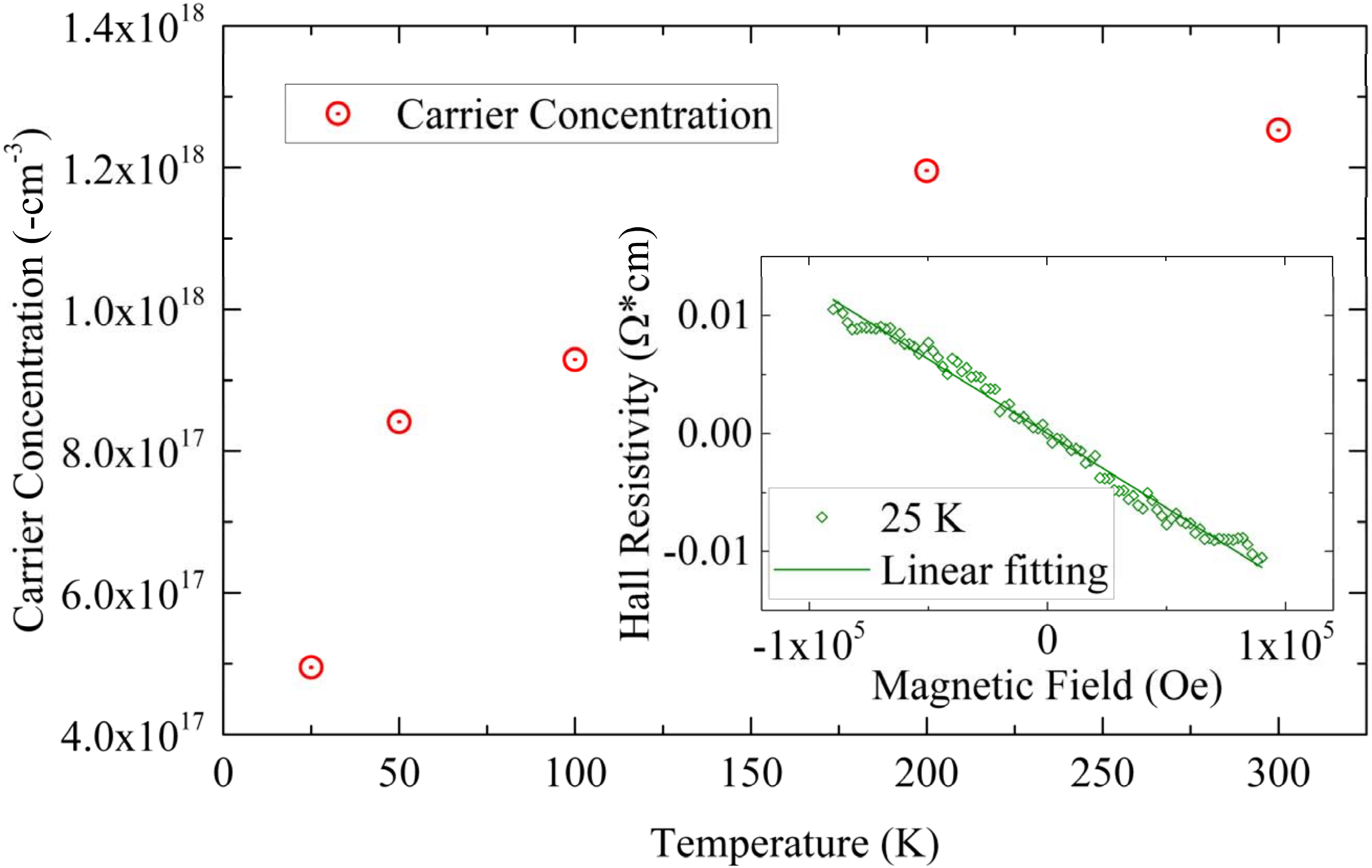


(a)
Ba(Zn1-xCox)2As2
Resistivity (Ω*mm)
Temperature (K)
0.00
0.01
0.02
0.03
0.04
0.05
(b)
Ba(Zn0.96Co0.04)2As2
Resistivity (Ω*mm)
Temperature (K)
H = 0 T
H = 1 T
TC
Magnetic field (×10000 Oe)

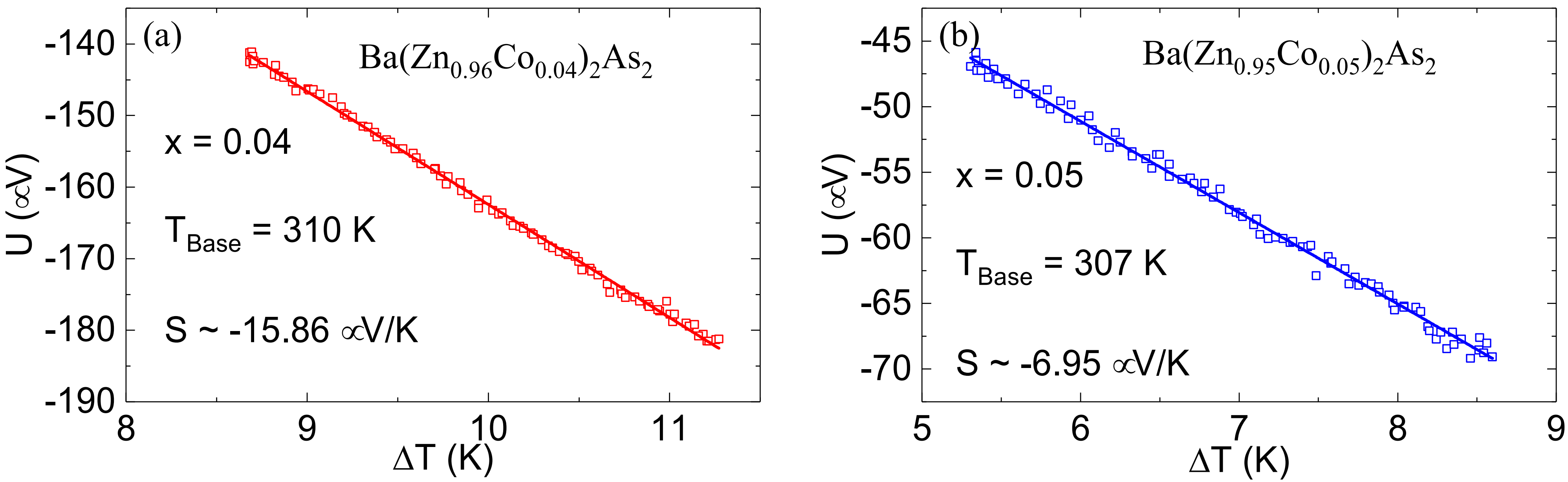


Hall Resistivity (Ω*cm)
Magnetic Field (Oe)
0.015
0.010
0.005
0.000
-0.005
-0.010
-0.015
-100000
-50000
0
50000
100000
300 K
200 K
100 K
50 K
25 K

-n VS. T plot


Carrier Concentration
Carrier Concentration (-cm^{-3})
1.4x10^{18}
1.2x10^{18}
1.0x10^{18}
8.0x10^{17}
6.0x10^{17}
4.0x10^{17}
0
50
100
150
200
250
300
Temperature (K)
Hall Resistivity (Ω*cm)
0.01
0.00
-0.01
25 K
Linear fitting
-1x10^5
0
1x10^5
Magnetic Field (Oe)

Negative Seebeck coefficient



New Diluted Ferromagnetic Semiconductors (Zhejing U)

1. $(La_{1-x}Ba_x)(Zn_{1-x}Mn_x)AsO$ (T_C =40K) (PRB，2013)
2. $(SrLa_2O_5)(Zn_{1-x}Mn_x)_2As_2$ (T_C =40K) (EPL，2014)
3. $Li_{1+y}(Zn_{1-x}Cr_x)As$ (T_C =210K) (JAP，2014)
4. $Ba(Zn_{1-2x}Mn_xCu_x)_2As_2$ (T_C =70K) (SR, 2015)
5. $(Ba_{1-x}K_x)(Cu_{1-x}Mn_x)Se_2$ (T_C =18K) (JMMM, 2016)
6. $Li(Zn_{1-2x}Mn_xCu_x)As$ (T_C =33K) (JPCM, 2016)
7. $La(Zn_{1-2x}Mn_xCu_x)AsO$ (T_C =8K) (EPL, 2016)
8. $(La_{1-x}Ca_x)(Zn_{1-x}Mn_x)AsO$ (T_C =30K) (JPCM, 2016)
9. $La(Zn_{1-2x}Mn_xCu_x)SbO$ (T_C =15K) (EPL, 2017)
10. $Ba(Zn_{1-x}Co_x)_2As_2$ (T_C =40K) (N-type, PRB, 2019)
11. $(Sr_{1-x}K_x)F(Zn_{1-x}Mn_x)Sb$ (T_C =40K) (JMMM, 2019)
12. $Cu_2(Zn_{1-x}Mn_x)(Sn_{1-y}Al_y)Se_4$ (T_C =5K) (Submitted, 2019)
13. $(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2Sb_2$ (In preparation, 2019)
14. $(Ca_{1-x}Na_x)(Zn_{1-y}Mn_y)_2Sb_2$ (T_C =10K) (In preparation, 2019)

In past several years, our collaboration team (Uemura & Jin & Ning) published ~ 40 papers on DMS

1, S.L. Guo et al, PRB 99, 155201 (2019)
2, L.C. Fu et al, JMMM 483, 95 (2019)
3, Y.L. Gu et al, JOS 40, 081506 (2019)
4, G.X. Zhi et al, Cond Matt 3, 42(2018)
5, S.L. Guo et al, CPB 27, 097502(2018)
6, Yao Zhao et al, EPL 120, 47005 (2017)
7, F.F. Zhu et al, APL 111, 062106 (2017)
8 S.L. Guo et al, EPL 114, 57008 (2016)
9, S.L. Guo et al, JMMM 400, 295 (2016)
10, Cui Ding et al, JPCM 28, 026003 (2016)
11, S.L. Guo et al, JPCM 28, 366001 (2016)
12, H.Y. Man et al, Scientific Reports 5, 15507 (2015)
13, Cui Ding et al, Science China (2014)
14, Cui Ding et al, EPL 107, 17004 (2014)
15, F.L. Ning et al, PRB 90, 185023 (2014)
16, H.Y. Man et al, EPL 105, 67004 (2014)
17, Q. Wang et al, JAP 115, 083917 (2014)
18, J.C. Lu et al, EPL 103, 67001 (2013)
19, C. Ding et al PRB 88, 041102(R) (2013)
20, C. Ding et al PRB 88, 041108(R) (2013)
21, W. Han et al, Scientific Reports 9, 7490 (2019)
22, Y. Peng et al, CPB 28, 057501 (2019)
23, G.Q. Zhao et al, JPCM 30, 254001 (2018)
24, G.X. Gu et al, APL 112, 032402 (2018)
25, Sun Fei et al, CPL 34, 0256 (2017)
26, R. Wang et al, AIP Advances 7, 045017 (2017)
27, Sun Fei et al, PRB 95, 094412 (2017)
28, B.J.Chen et al, Scientific Reports 6, 36578 (2016)
29, B.Frandsen and Uemura et al, PRB 94, 094102 (2016)
30, F. Sun et al, PRB 93, 224403 (2016)
31, H. Suzuki and Fujimori et al, PRB 92, 215320 (2015)
32, H. Suzuki and Fujimori et al, PRB 91, 140401 (2015)
33, K. Zhao et al, Chin. Sci. Bull. (2014)
34, B.J. Chen et al PRB 90, 155202 (2014)
35, B.J. Chen et al JAP 116,163906 (2014)
36, W. Han et al, Science China (2013)
37, Z. Deng et al, PRB 88, 081203(R) (2013)
38, K. Zhao et al, Nature Comm. 4, 1442 (2013)
39, Z. Deng et al, JPCS 400, 032033 (2012)
40, Z. Deng et al, Nature Comm. 2, 422 (2011)

Photoemission and X-ray Absorption Studies of the Diluted Magnetic Semiconductor $Ba_{1-y}K_y(Zn_{1-x}Mn_x)_2As_2$ Isostructural to Fe-based Superconductors

H. Suzuki[1], K. Zhao[2], G. Shibata[1], Y. Takahashi[1], S. Sakamoto[1], K. Yoshimatsu[1], B. J. Chen[2], H. Kumigashira[3], F.-H. Chang[4], H.-J. Lin[4], D. J. Huang[4], C. T. Chen[4], Bo Gu[5], S. Maekawa[5], Y. J. Uemura[6], C. Q. Jin[2] and A. Fujimori[1]

Theory of Mn-doped I-II-V Semiconductors

J. K. Glasbrenner,[1] I. Žutić,[2] and I. I. Mazin[3]
[1] *National Research Council/Code 6393, Naval Research Laboratory, Washington, DC 20375, USA*
[2] *Department of Physics, University at Buffalo, State University of New York, NY 14260, USA and*
[3] *Code 6393, Naval Research Laboratory, Washington, DC 20375, USA*
(Dated: May 13, 2014)

Re: APS Invited Symposium Nomination Notification

From: Jacek K. Furdyna <furdyna@nd.edu>
Time: 22:02:31 Sep 14, 2014 (Sunday)
To: ningfl@zju.edu.cn, furdyna.1@nd.edu

Dear Fanlong,
It was a real pleasure to be able to nominate y
beautiful and ground-breaking work at the APS March r
APS accepts this nomination. It should be a very str
And I hope we get a chance to meet sometime in
With my best regards,
Jacek

Re: APS Invited Symposium Nomination Notification

From: zigor <zigor@buffalo.edu>
Time: 01:11:15 Sep 10, 2014 (Wednesday)
To: ningfl@zju.edu.cn

My pleasure Fanlong,

there will be lots of politics involved,
but it was certainly worth trying for
such an exciting work.

Regards,
Igor

P- and N-type diluted magnetic semiconductors with narrow band gaps

Bo Gu [1*] and Sadamichi Maekawa[1,2]
[1] *Advanced Science Research Center, Japan Atomic Energy Agency, Tokai 319-1195, Japan*
[2] *ERATO, Japan Science and Technology Agency, Sendai 980-8577, Japan*

(Dated: January 19, 2016)

We propose a method to realize diluted magnetic semiconductors (DMS) with p- and n-type carriers by choosing host semiconductors with a narrow band gap. By employing a combination of the density function theory and quantum Monte Carlo simulation, we demonstrate such semiconductors using Mn-doped $BaZn_2As_2$, which has a band gap of 0.2 eV. In addition, we found a new non-toxic DMS Mn-doped $BaZn_2Sb_2$, of which the Curie temperature T_c is predicted to be higher than that of Mn-doped $BaZn_2As_2$, the T_c of which was up to 230 K in the recent experiment.

PACS numbers: 75.50.Pp, 75.30.Hx, 02.70.Ss

After the discovery of ferromagnetism in (Ga,Mn)As, diluted magnetic semiconductors (DMS) have received considerable attention owing to potential applications based on the use of both their charge and spin degrees of freedom in electronic devices [1, 2]. Thus far, the highest Curie temperature of (Ga,Mn)As has been $T_c = 190$ K [3]. The substitution of divalent Mn atoms into trivalent Ga sites introduces hole carriers; thus, (Ga,Mn)As is a p-type DMS. The valence mismatch between Mn and Ga leads to severely limited chemical solubility for Mn in GaAs. Moreover, owing to simultaneous doping of charge and spin induced by Mn substitution, it is difficult to individually optimize charge and spin densities.

To overcome these difficulties, a new type of DMS, i.e., Li(Zn,Mn)As was proposed [4] and later fabricated with $T_c = 50$ K [5]. It is based on LiZnAs, a I–II–V semiconductor. Spin is introduced by isovalent (Zn^{2+}, Mn^{2+}) substitution, which is decoupled from carrier doping with excess/deficient Li concentration. Although

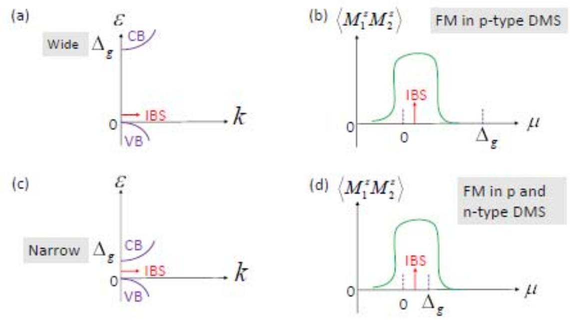


FIG. 1. (Color online) Schematic pictures of impurity bound state (IBS) and ferromagnetic (FM) coupling in diluted magnetic semiconductors (DMS). (a) Host bands $\epsilon(k)$ with a wide band gap Δ_g between the valence band (VB) and the conduction band (CB). The position of the IBS ω_{IBS} (arrow) is close to the top of the VB owing to strong mixing between the impurity and the VB, and usually no IBS appears below the

Diluted Ferromagnetic Semiconductors in Bulk Form

with decoupling spins and carriers

REVIEWS OF MODERN PHYSICS, VOLUME 86, JANUARY–MARCH 2014

Dilute ferromagnetic semiconductors: Physics and spintronic structures

By Tomasz Dietl and Hideo Ohno

In addition to current interest in various magnetically doped semiconductors, oxides, and organic materials, a lot of attention will be devoted to four emerging families of compounds: (i) high Curie temperature ferrimagnetic spinel oxides and Heusler compounds such as Mn_2CoAl (Ouardi *et al.*, 2013), awaiting for mastering of defect and carrier control; (ii) high Néel temperature semiconductors, e.g., LiMnAs, for antiferromagnetic spintronics (Jungwirth *et al.*, 2011); (iii) topological insulators, in which ferromagnetism might be mediated by Dirac electrons, e.g., $(Bi, Mn)_2Te_3$ (Checkelsky *et al.*, 2012); and (iv) derivatives of FeAs superconductors, such as $(K, Ba)(Zn, Mn, Fe)_2As_2$ compounds for studies of interplay between *p-d* Zener ferromagnetism, antiferromagnetic superexchange, and superconductivity (Zhao *et al.*, 2013). Here nanocharacterization protocols, elaborated over the recent years for DMSs (Bonanni, 2011), will play an essential role in the meaningful development of new materials.

Uemura, Jin, Ning started the research topic.

Dietl and Ohno, RMP, 86, 187 (2014): "a lot of attention will be devoted to four emerging families of compounds,…., **IV: FeAs derived compound,….,** for studies of interplay between p-d Zener ferromagnetism, antiferromagnetic, superexchange, and superconductivity."

Advances in Magnetics

Roadmap for Emerging Materials for Spintronic Device Applications

Atsufumi Hirohata[1], Hiroaki Sukegawa[2], Hideto Yanagihara[3], Igor Žutić[4], Takeshi Seki[5], Shigemi Mizukami[6], and Raja Swaminathan[7]

[1]Department of Electronics, University of York, York YO10 5DD, U.K.
[2]Magnetic Materials Unit, National Institute for Materials Science, Tsukuba 305-0047, Japan
[3]Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8577, Japan
[4]Department of Physics, University at Buffalo–The State University of New York, Buffalo, NY 14260 USA
[5]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[6]WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[7]Intel Corporation, Chandler, AZ 85226 USA

The Technical Committee of the IEEE Magnetics Society has selected seven research topics to develop their roadmaps, where major developments should be listed alongside expected timelines: 1) hard disk drives; 2) magnetic random access memories; 3) domain-wall devices; 4) permanent magnets; 5) sensors and actuators; 6) magnetic materials; and 7) organic devices. Among them, magnetic materials for spintronic devices have been surveyed as the first exercise. In this roadmap exercise, we have targeted magnetic tunnel and spin-valve junctions as spintronic devices. These can be used, for example, as a cell for a magnetic random access memory and a spin-torque oscillator in their vertical form as well as a spin transistor and a spin Hall device in their lateral form. In these devices, the critical role of magnetic materials is to inject spin-polarized electrons efficiently into a nonmagnet. We have accordingly identified two key properties to be achieved by developing new magnetic materials for future spintronic devices: 1) half-metallicity at room temperature (RT) and 2) perpendicular anisotropy in nanoscale devices at RT. For the first property, five major magnetic materials are selected for their evaluation for future magnetic/spintronic device applications: 1) Heusler alloys; 2) ferrites; 3) rutiles; 4) perovskites; and 5) dilute magnetic semiconductors. These alloys have been reported or predicted to be half-metallic ferromagnets at RT. They possess a bandgap at the Fermi level E_F only for its minority spins, achieving 100% spin polarization at E_F. We have also evaluated $L1_0$ alloys and $D0_{22}$–Mn alloys for the development of a perpendicularly anisotropic ferromagnet with large spin polarization. We have listed several key milestones for each material on their functionality improvements, property achievements, device implementations, and interdisciplinary applications within 35 years time scale. The individual analyses and the projections are discussed in the following sections.

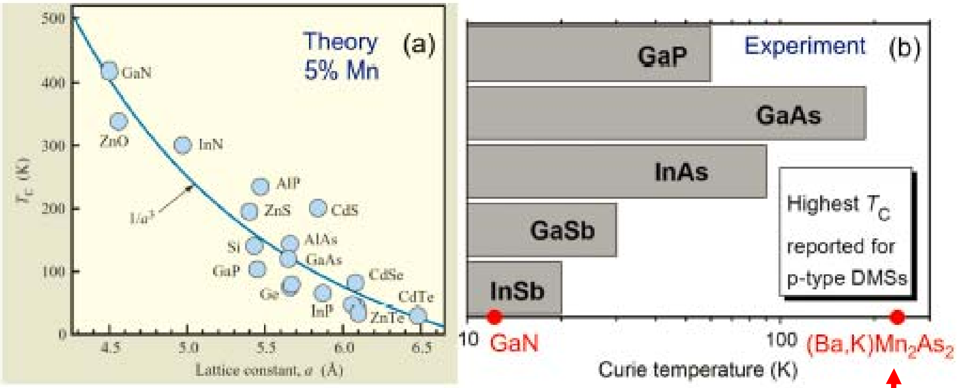


Fig. 8. (a) Theoretical predictions for T_C in DMS [41], adapted from [45]. (b) Reliable highest experimental T_C reported for Mn-doped DMS, adapted from [36].

some of the previous limitations are overcome: the absence of carriers in II–VIs and the low-Mn solubility in III–Vs. With 30% K and 15% Mn doping, their $T_C \sim 230$ K [48] exceeds the value in (Ga, Mn)As. Selected highest reliable experimental T_C reported for the Mn-doped DMS is shown in Fig. 8(b). Circles are given for GaN, which has about 30 times smaller T_C than predicted in Fig. 8(a), and (Ba, K)Zn_2As_2, a current record for DMS. The *ab initio* studies predict a further increase in T_C [49]. We expect that the tunable RT carrier-mediated ferromagnetism will be realized in II–II–V DMS within 5 years.

Regarding (m3.2), while DMS is often viewed as the

II-II-V DMS

$(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ T_C ~230K

Uemura, Jin, Ning started the research topic.

Several advantages of bulk form DMS materials:

- Synthesized in thermally equilibrium condition, **less defects** are expected;
- **Bulk form, single crystals** are available, for NMR, neutron, μSR measurements;
- Carriers can be doped **at different ionic sites**, for example for $BaZn_2As_2$, K substitution for Ba introduces holes, while Mn substitution for Zn introduces electrons;
- Charge and spin doping are **decoupled**, each can be precisely controlled and tuned;
- **Iso-structural** to its superconductor, antiferromagnet variant, junctions via As layer can be made;
- **Thin films** of parent compound LaZnAsO and $BaZn_2As_2$ have been successfully made;
- $(Ba_{1-y}K_y)(Zn_{1-x}Mn_x)_2As_2$: $T_C = 230$ K for now, thin film may achieve **higher T_C**? (FeSe-SC)
- Share **the same origin of ferromagnetism** as (Ga,Mn)As, helpful to understand the general mechanism;

Outline

a. Introduction of some newly fabricated DMSs

"111", 122","1111", "42622","32522"

----- $Li_{1+y}(Zn_{1-x}Mn_x)P$

----- n-type $Ba(Zn_{1-2x}Co_xMn_x)_2As_2$

b. Microscopic characterization

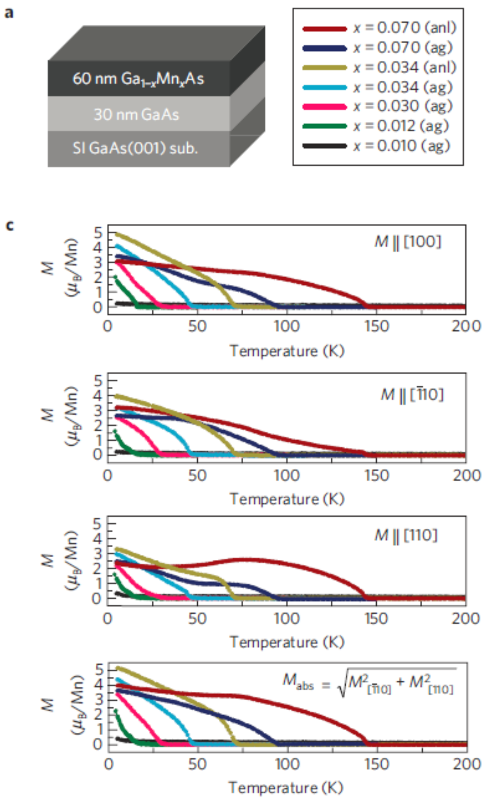
----- μSR results on (Ga,Mn)As and $Li_{1.15}(Zn_{1-x}Mn_x)P$

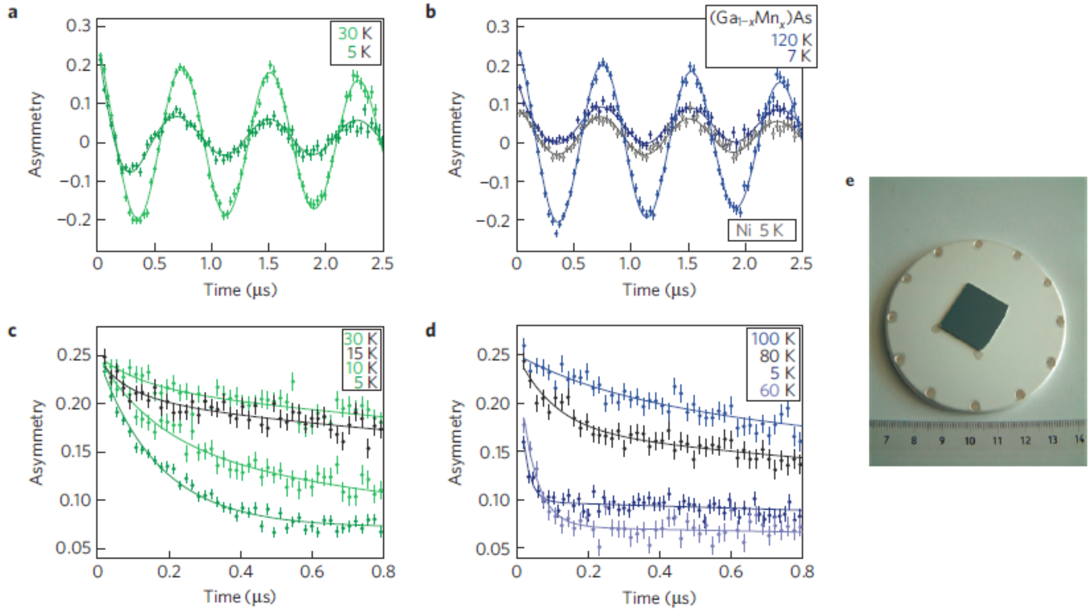
-----NMR results on $Li_{1.1}(Cd_{1-x}Mn_x)P$ and $Li_{1.15}(Zn_{1-x}Mn_x)P$

nature materials
LETTERS
PUBLISHED ONLINE: 21 MARCH 2010 | DOI: 10.1038/NMAT2715

Spatially homogeneous ferromagnetism of (Ga, Mn)As

S. R. Dunsiger[1,2], J. P. Carlo[1], T. Goko[1,3], G. Nieuwenhuys[4], T. Prokscha[4], A. Suter[4], E. Morenzoni[4], D. Chiba[5,6], Y. Nishitani[6], T. Tanikawa[5,6], F. Matsukura[5,6], H. Ohno[5,6], J. Ohe[7,8], S. Maekawa[7,8] and Y. J. Uemura[1]*





μ SR experiments were conducted in PSI

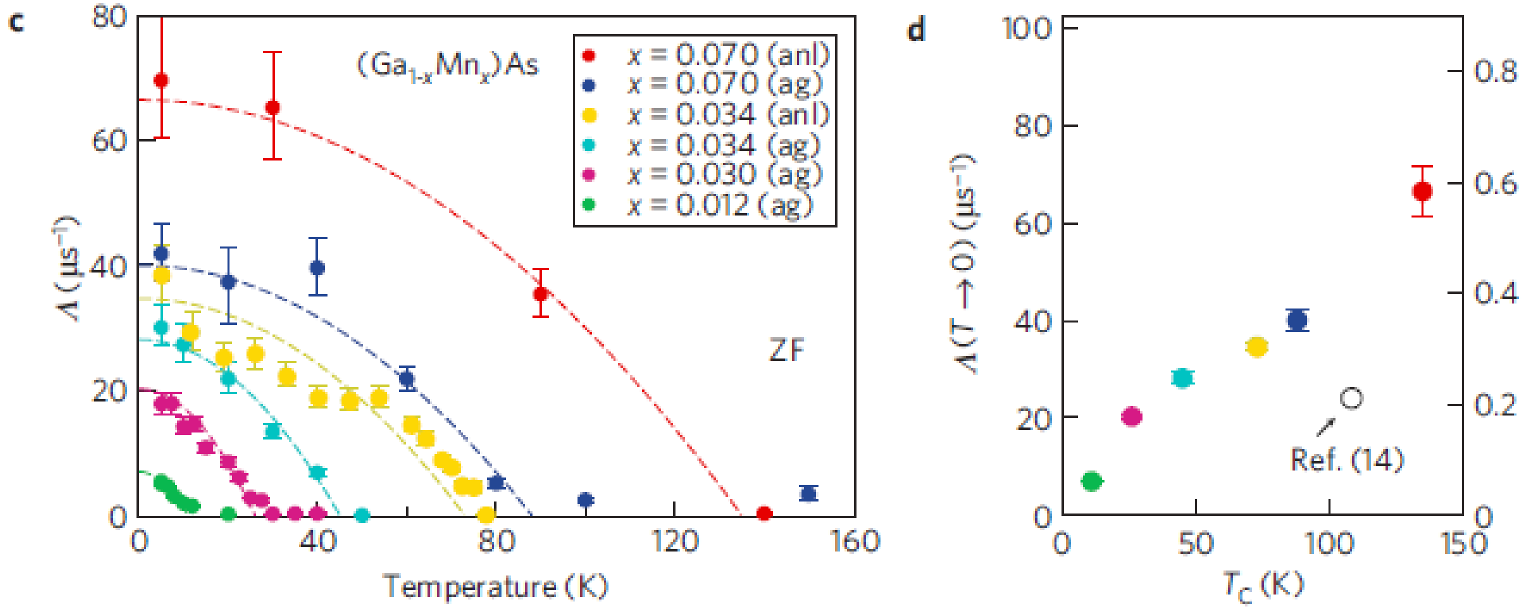
nature materials

LETTERS

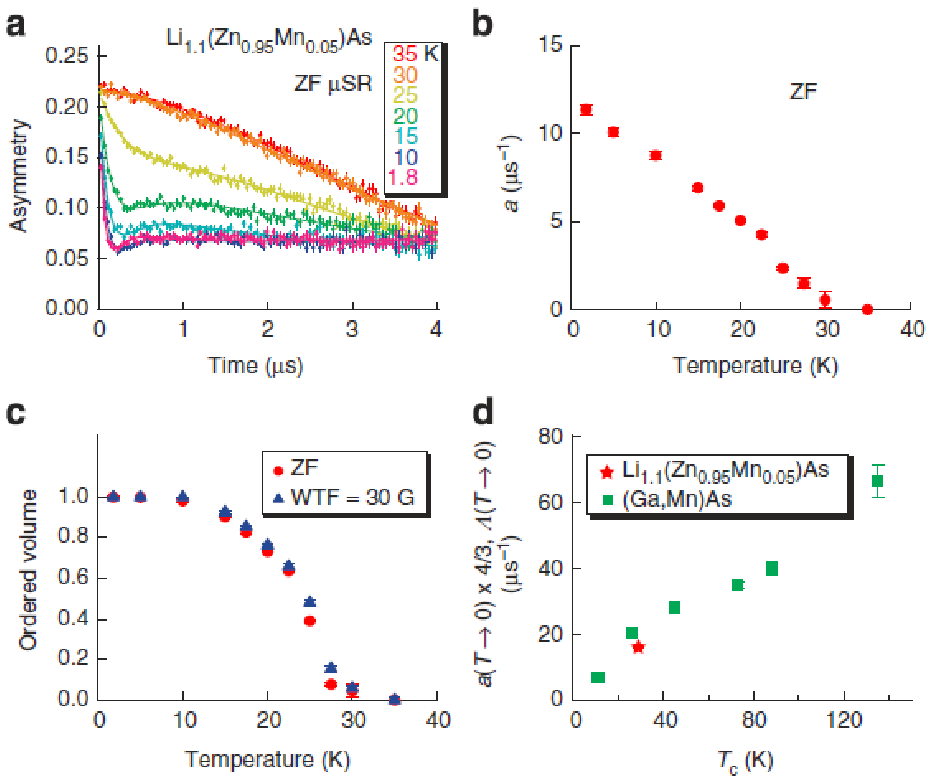
PUBLISHED ONLINE: 21 MARCH 2010 | DOI: 10.1038/NMAT2715

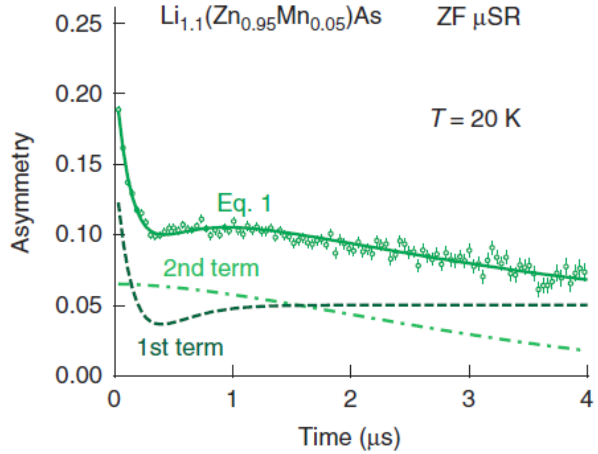
Spatially homogeneous ferromagnetism of (Ga, Mn)As

S. R. Dunsiger[1,2], J. P. Carlo[1], T. Goko[1,3], G. Nieuwenhuys[4], T. Prokscha[4], A. Suter[4], E. Morenzoni[4], D. Chiba[5,6], Y. Nishitani[6], T. Tanikawa[5,6], F. Matsukura[5,6], H. Ohno[5,6], J. Ohe[7,8], S. Maekawa[7,8] and Y. J. Uemura[1]*



$Li_{1.1}(Zn_{0.95}Mn_{0.05})As$ (T_C ~ 30 K)



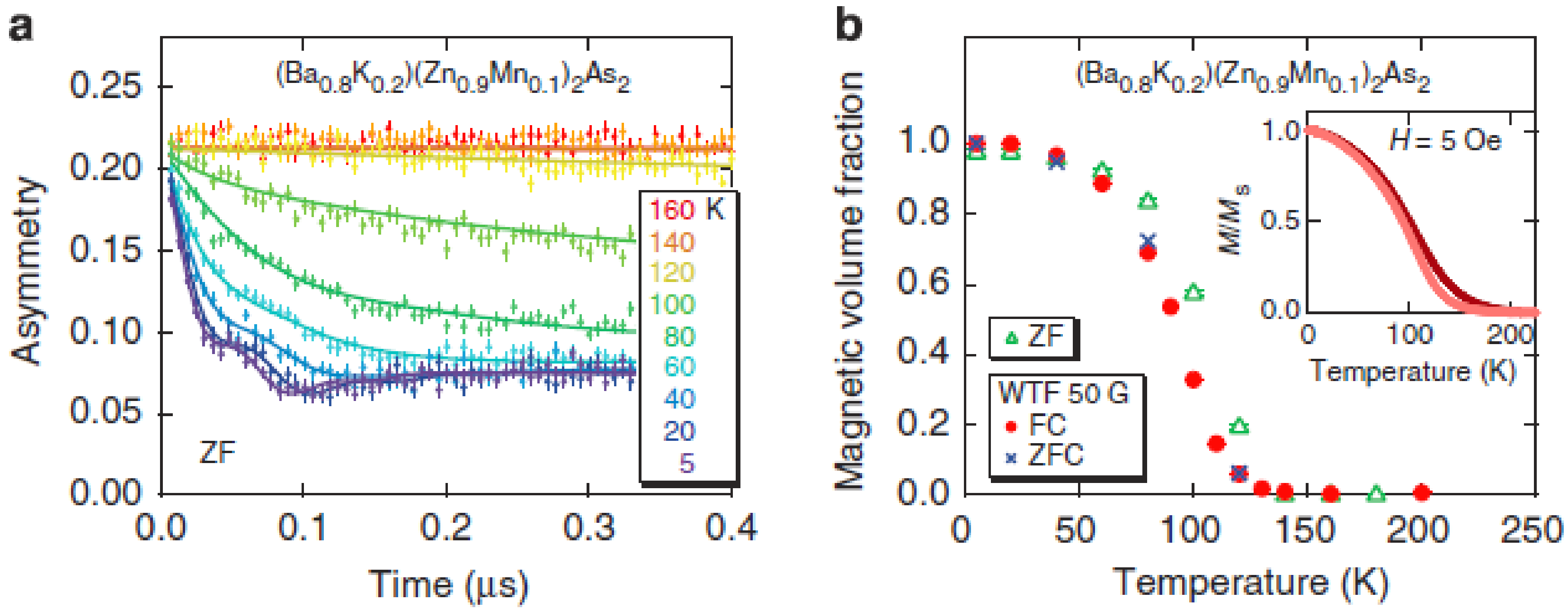


$$A_{\mathrm{mag}}\, G_z^{\mathrm{L}}(t) + A_{\mathrm{para}} \exp(-(\lambda t)^{\beta}).$$

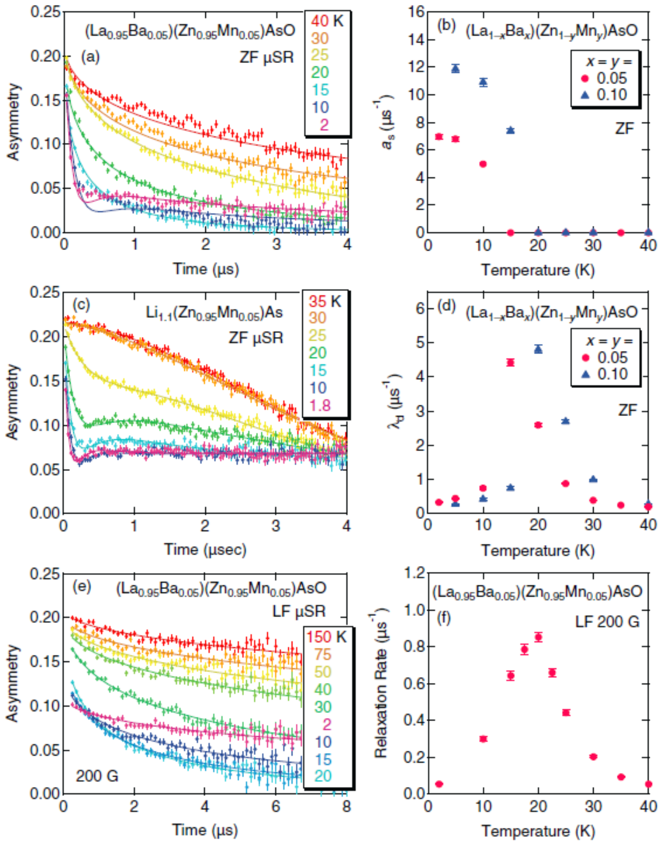
$$G_z^{\mathrm{L}}(T) = \frac{1}{3} + \frac{2}{3}(1-at)\exp(-at),$$

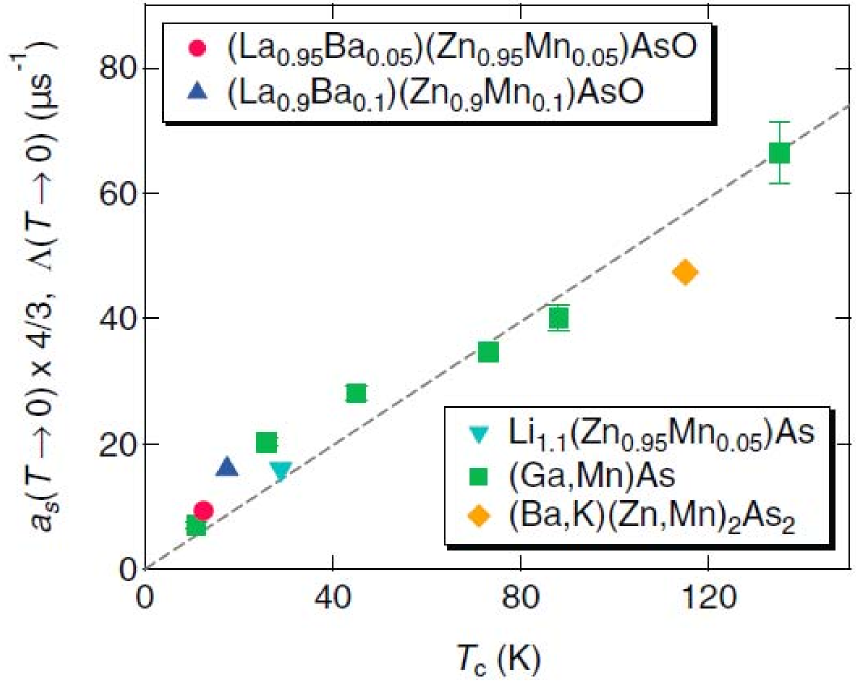
a_s --- relaxation rate (static local field amplitude)

$(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ (T_C ~180 K)

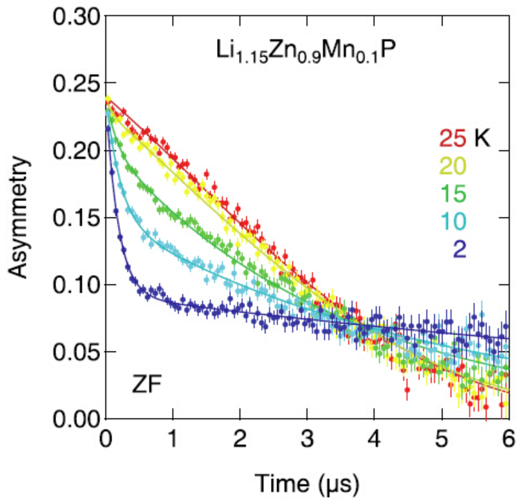


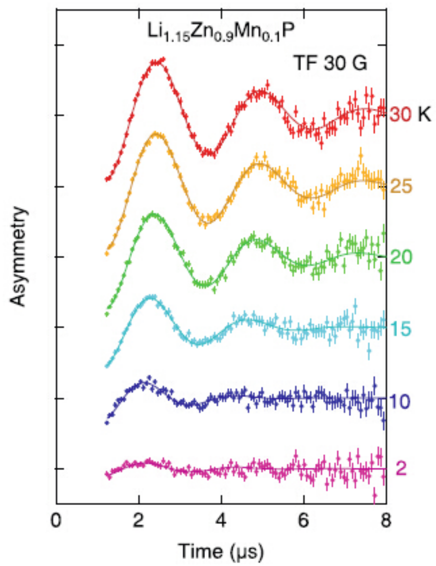
$(La_{1-x}Ba_x)(Zn_{1-x}Mn_x)AsO$ T_C ~ 40K

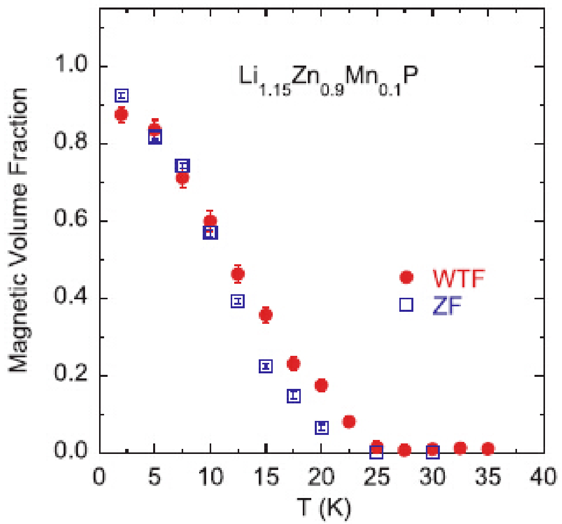




$Li_{1.15}(Zn_{0.9}Mn_{0.1})P$: $T_C \sim 22$ K

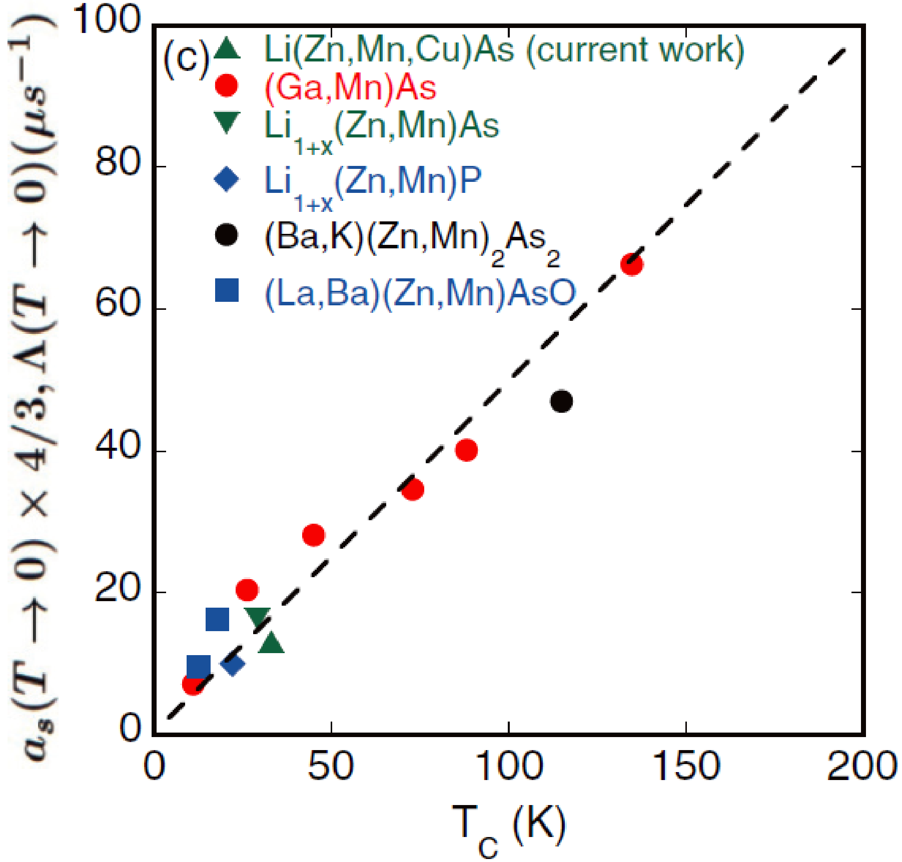






F.L. Ning et al, PRB 90,085123 (2014)

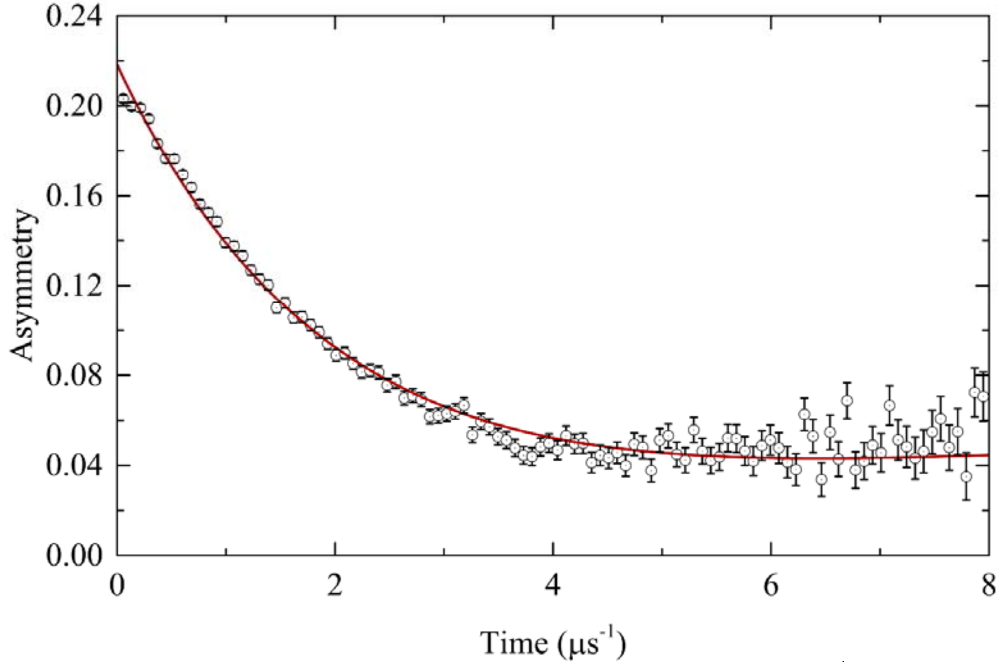
Static local field amplitude a_s: which is proportional to the individual ordered moment size multiplied by the moment concentration



S. Dunsiger, Nature Material, 2009
C. Ding, Physical Review B, 2013
K. Zhao, Nature Communications, 2013
Z. Deng, Nature Communications, 2011
F.L. Ning, Physical Review B, 2014

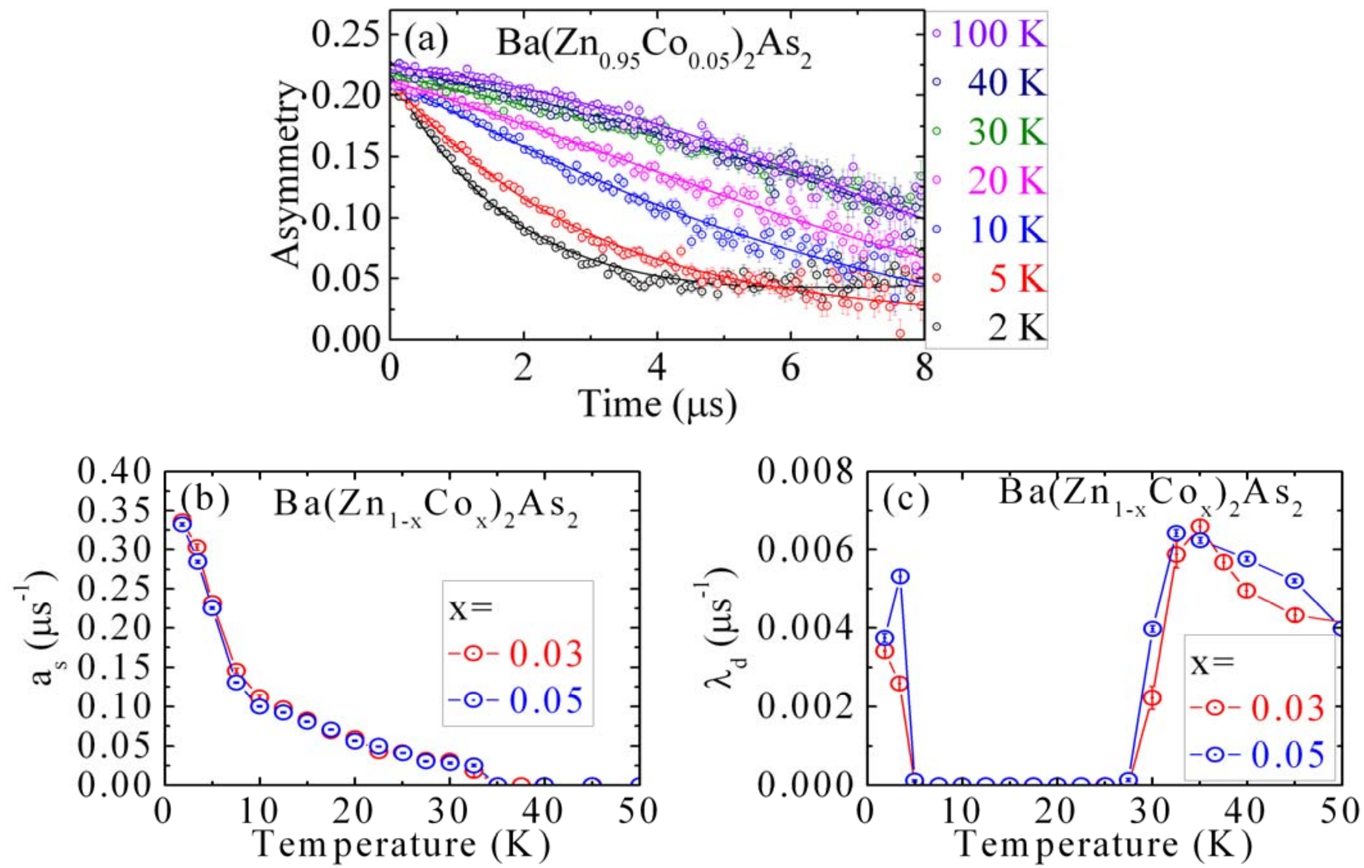
T_C: which is a measure of the effective average ferromagnetic interaction

Zero field (ZF-) MuSR asymmetry spectra of $Ba(Zn_{0.95}Co_{0.05})_2As_2$ at 2 K



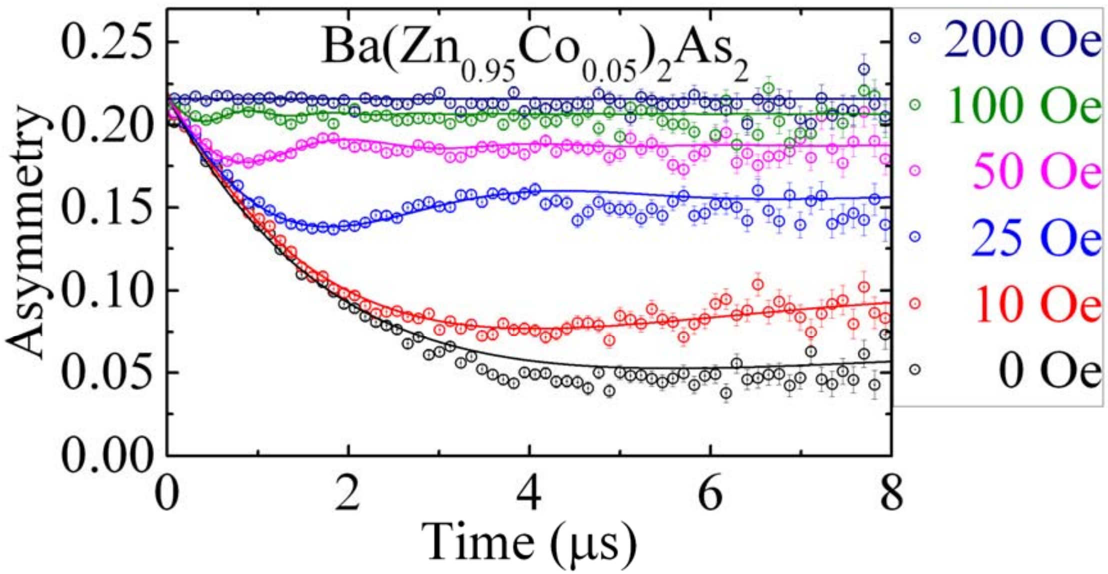
Fitting Function for dilute spin systems: $G_z(t) \times g_z^G(t)$, $G_z(t) = \frac{1}{3} exp\left(-(\lambda_d t)^{\frac{1}{2}}\right) + \frac{2}{3}\left[1 - \frac{a_s^2 t^2}{(\lambda_d t + a_s^2 t^2)^{\frac{1}{2}}}\right] exp\left[-(\lambda_d t + a_s^2 t^2)^{\frac{1}{2}}\right]$, $g_z^G(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta_0^2 t^2) exp\left(-\frac{1}{2}\Delta_0^2 t^2\right)$. Uemura*et al.*Phy. Rev. B **31**, 546 (1985).

ZF-MuSR results for $Ba(Zn_{1-x}Co_x)_2As_2$



Static field arises below T_C

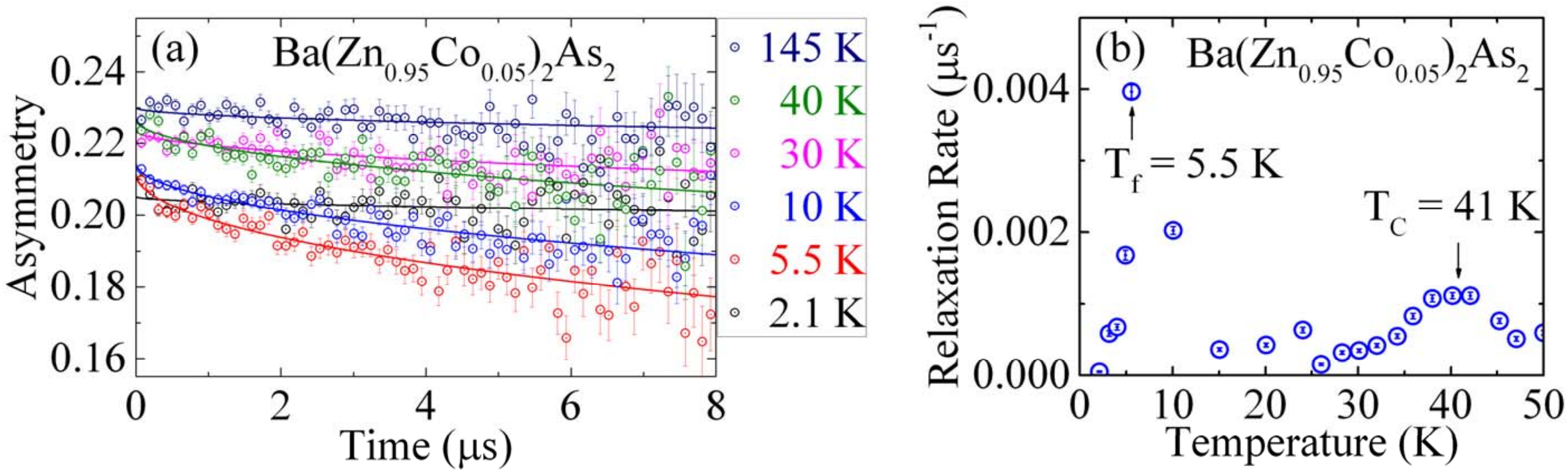
Longitudinal field (LF-) MuSR results for $Ba(Zn_{1-x}Co_x)_2As_2$ at 2 K

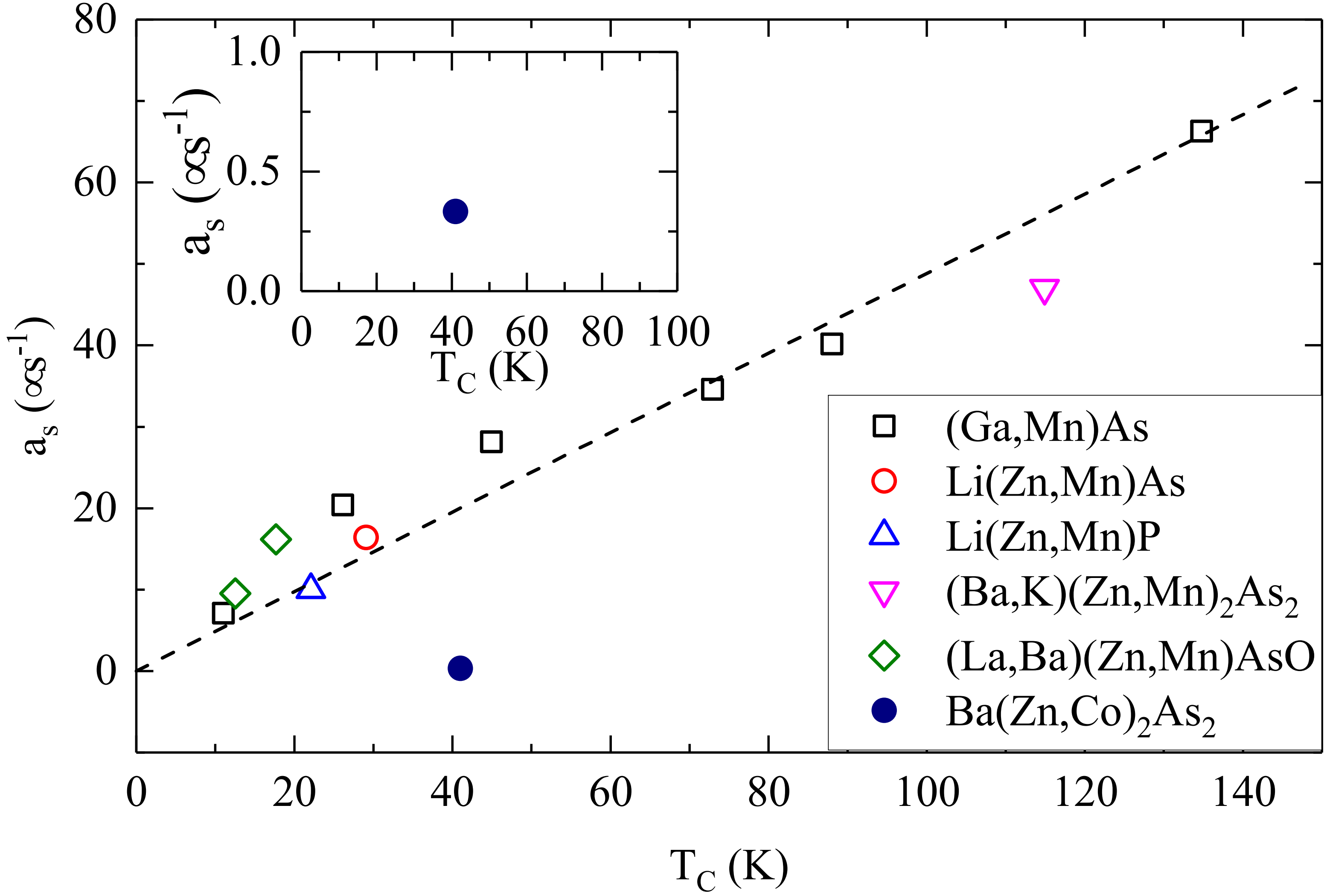


The asymmetry is fully decoupled at ~ 100 Oe.

Conclusion: the internal field at 2 K muon suffered is fully static and magnitude is ~ 10 Oe.

Temperature scan 100 Oe LF-MuSR results for $Ba(Zn_{1-x}Co_x)_2As_2$





Ferromagnetic exchange coupling is much larger in this system compared these other p-type systems.

Outline

a. Introduction of some newly fabricated DMSs

"111", 122","1111", "42622","32522"

----- **$Li_{1+y}(Zn_{1-x}Mn_x)P$**

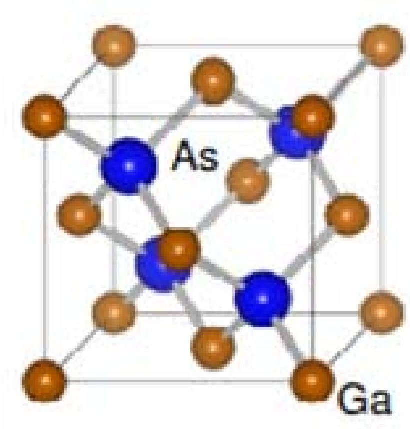
----- n-type **$Ba(Zn_{1-2x}Co_xMn_x)_2As_2$**

b. Microscopic characterization

----- μSR on $Li_{1.15}(Zn_{1-x}Mn_x)P$

-----NMR results on $Li_{1.1}(Cd_{1-x}Mn_x)P$ and $Li_{1.15}(Zn_{1-x}Mn_x)P$

“III-V” versus “I-II-V” semiconductors



GaAs (1.42ev)

LiZnAs (1.6ev)
LiZnP (2.04ev)
LiCdP (1.30ev)

$Li_{1.1}(Cd^{+2}_{0.9}Mn^{+2}_{0.1})P$ and $Li_{1.15}(Zn^{+2}_{0.9}Mn^{+2}_{0.1})P$

decouple spins and carriers

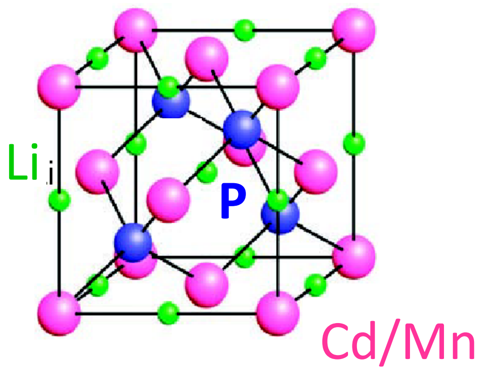
- Mn doping induces local moments
- Li extra or deficiencies create itinerant or localized carriers

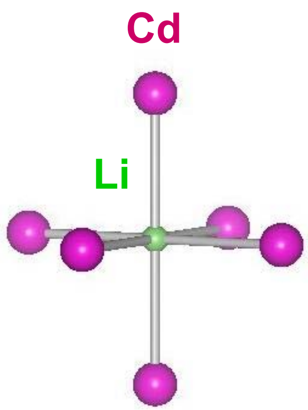
----- use Li to control the type of carriers

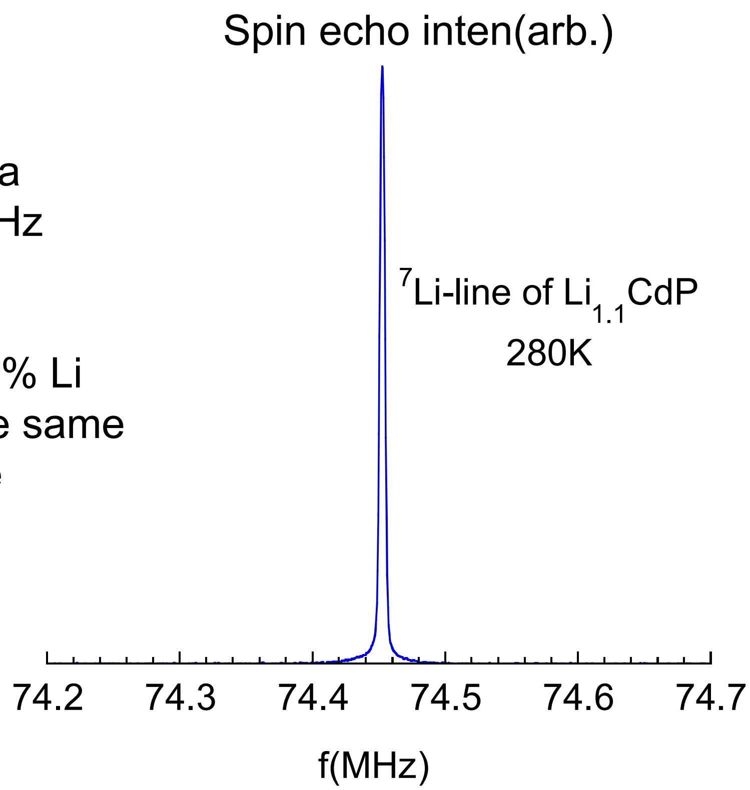
^{7}Li NMR line shape ---- $Li_{1.1}CdP$

For ^{7}Li:
- Nuclear spin = 3/2
- Gyromagnetic ratio = 16.546MHz/Tesla
- B_{ext} = 4.5 Tesla → $f_{resonance}$ = 74.457MHz

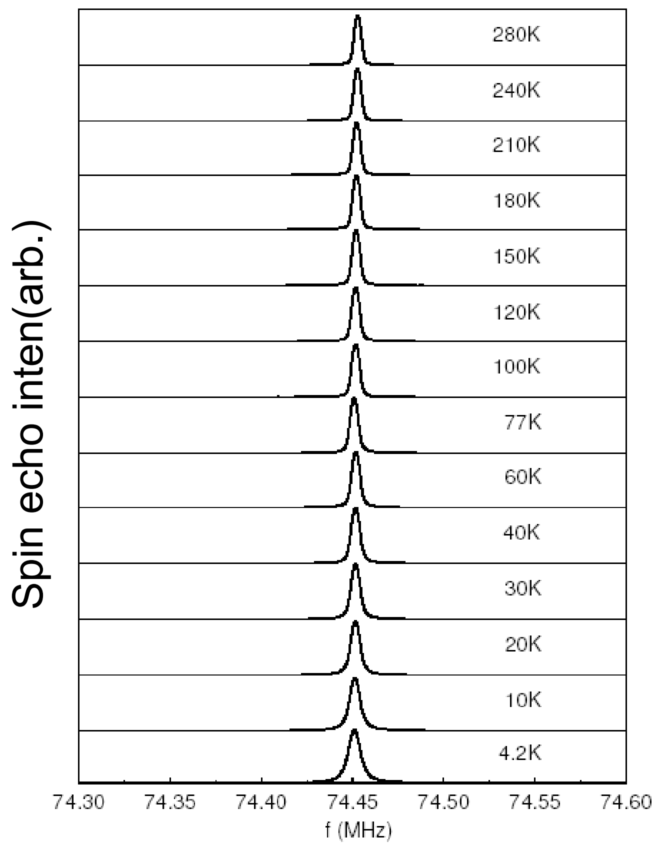
- Single line with line width = 4KHz
- No additional Li line found for extra 10% Li
- 6 Cd atoms at N.N. site, all Li have the same environment -----define it as Li(0) site

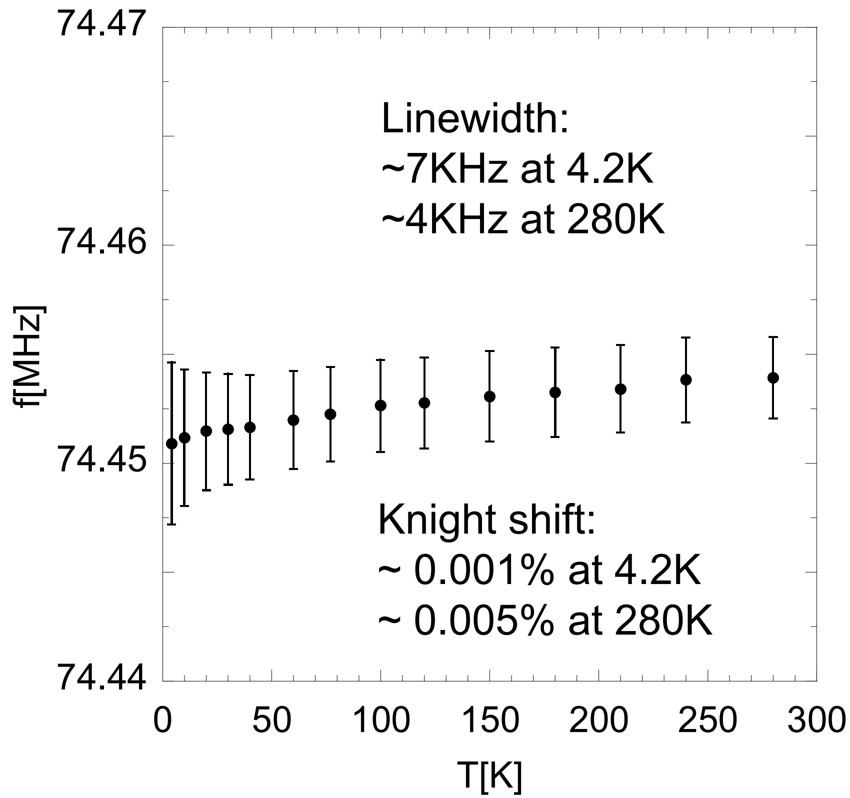






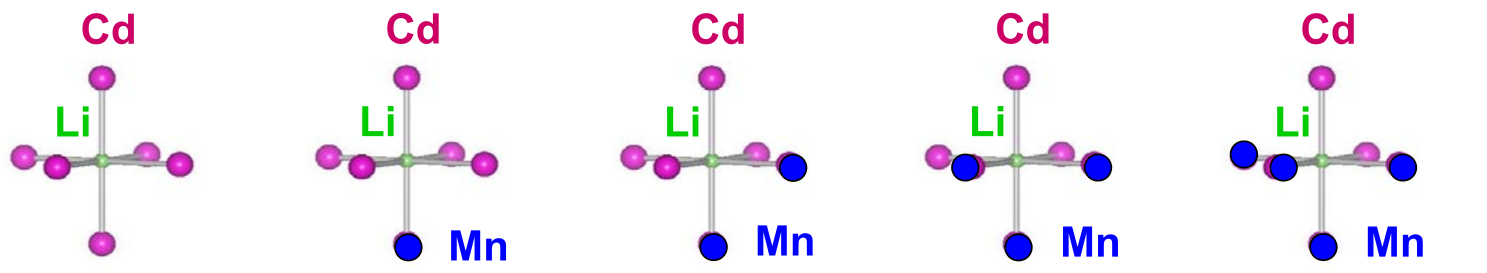
^{7}Li NMR line shape ---- $Li_{1.1}CdP$





^{7}Li NMR line shape ---- $Li_{1.1}Cd_{0.9}Mn_{0.1}P$

10% Mn doped into Cd sites, the probability to find n = 0, 1, 2, 3, 4, 5, 6 Mn atoms at N.N. sites are $P(n) = C_6^n(0.1)^n(0.9)^{6-n}$



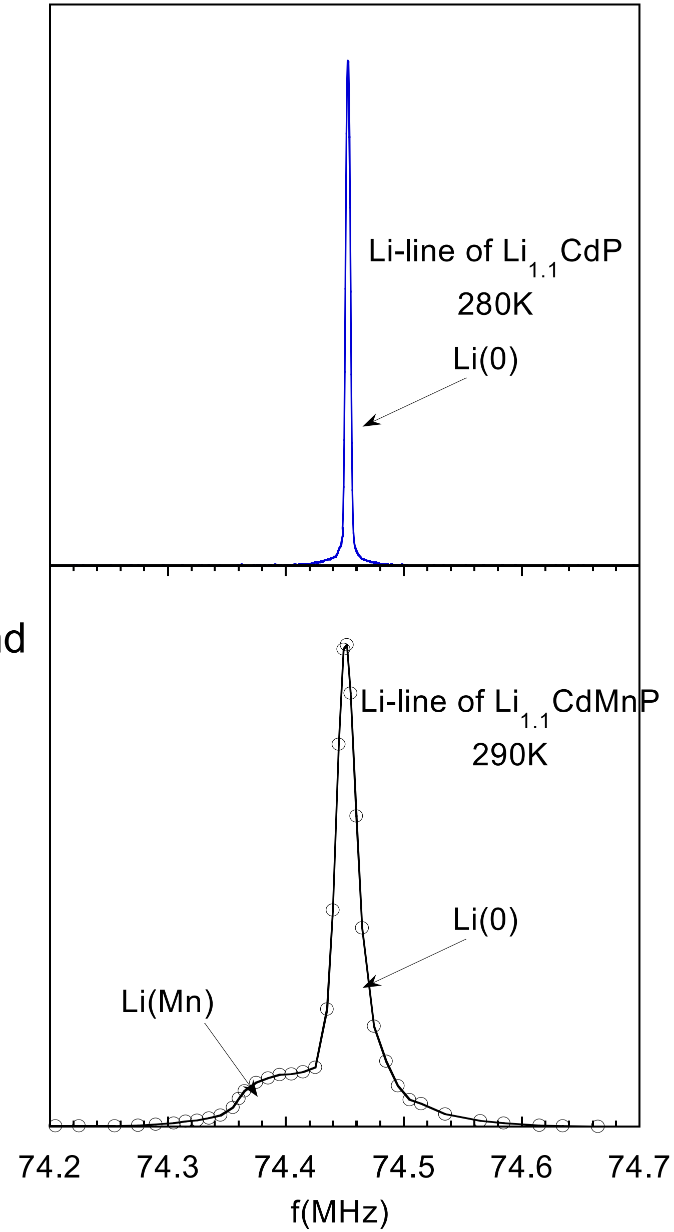
Li(0): 53% Li(1): 35% Li(2): 10% Li(3): 1.5% Li(4): 0.1%

Li(0):Li(Mn) ~ 50%:50%

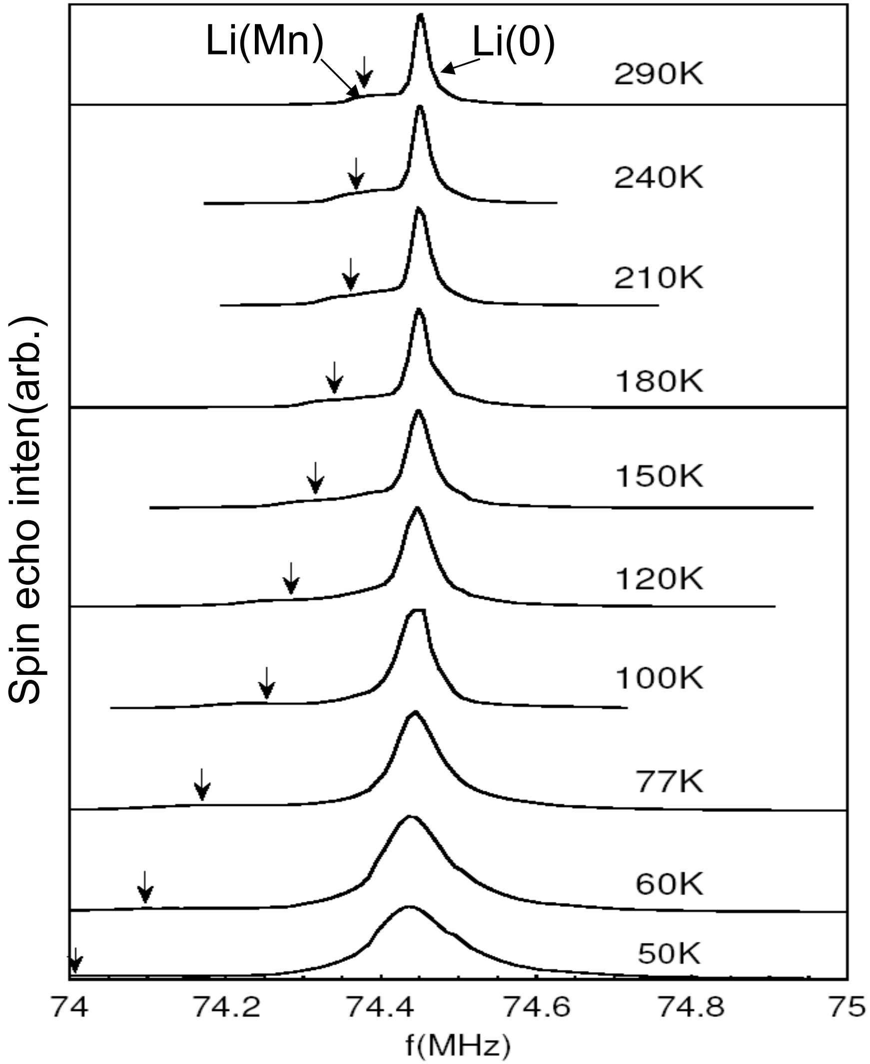
^{7}Li NMR line shape
---- $Li_{1.1}Cd_{0.9}Mn_{0.1}P$

Key features:

- Li(0) line preserve but broaden
- Li(Mn) line appears, broad peak at left hand
- Li(Mn) line has a large negative shift
- Integrated area, Li(Mn):Li(0) = 50:50



^{7}Li NMR line shape ---- $Li_{1.1}Cd_{0.9}Mn_{0.1}P$



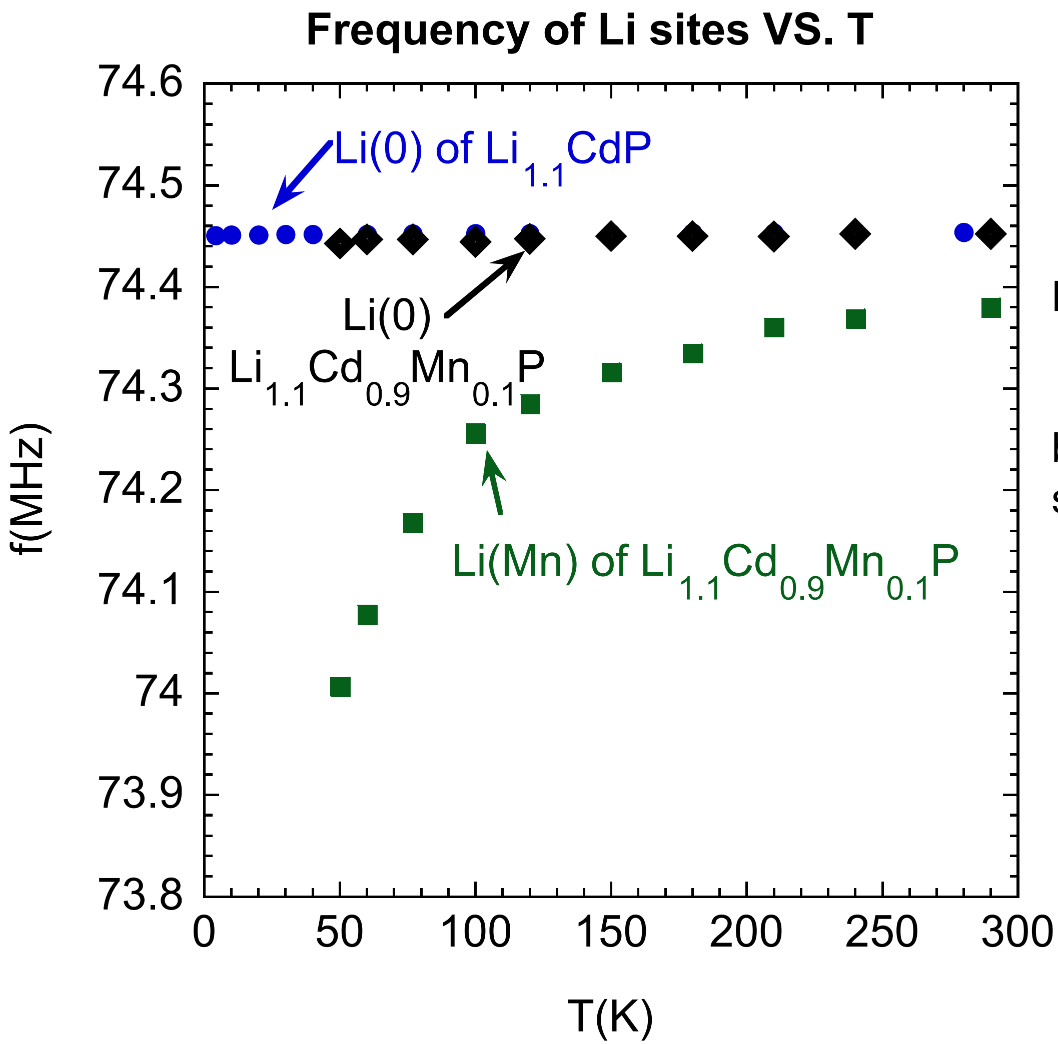
Key features:

• Frequency shifts of Li(Mn) follows a Curie-Weiss law

• Li(0) continuously broaden from 20KHz (at 290K) to 240KHz (at 4.2K) ~ 10 times broadening. Line width follow a Curie-Weiss law

• For Li(0) site in the parent compound $Li_{1.1}CdP$, only increase from 4KHz (at 280K) to 7KHz (at 4.2K).

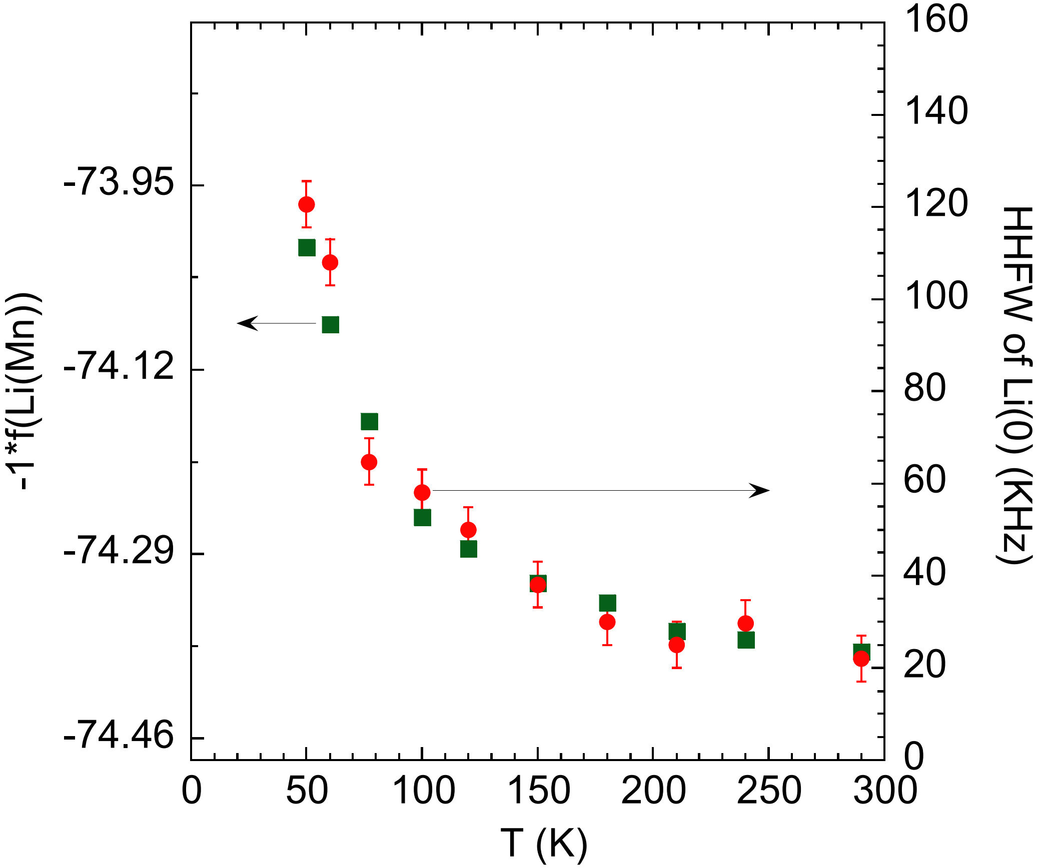
Frequency VS. Temperature



Negative frequency shift:

---hyperfine coupling constant between ^{7}Li nuclear spin and surrounding electrons is negative

$Li_{1.1}Cd_{0.9}Mn_{0.1}P$

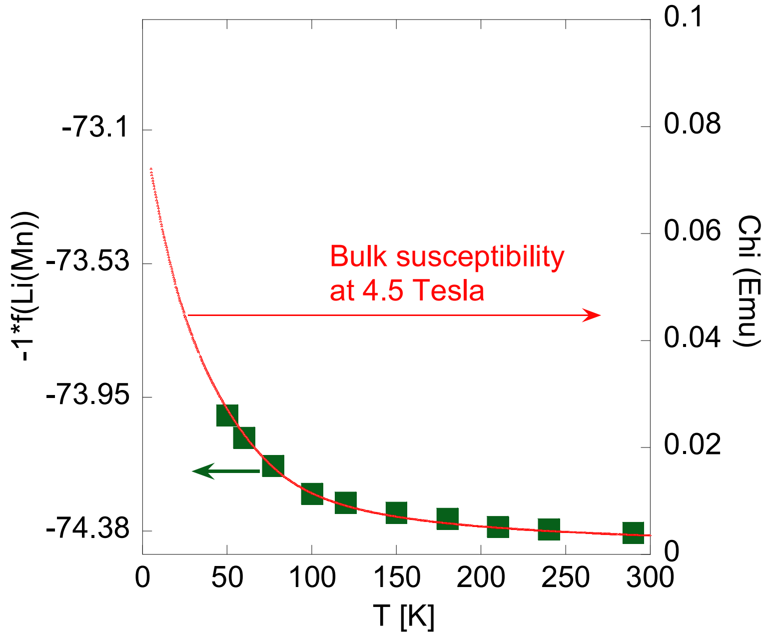


The line broadening of Li(0) which do not have Mn at N.N. is the same as the frequency shifts of Li(Mn).

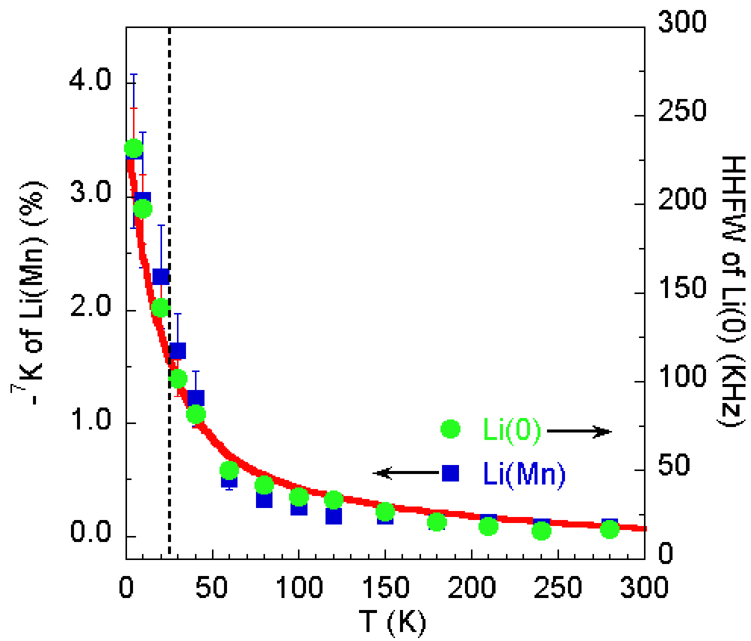
→

Li(0) and Li(Mn) sites are electronically coupled!

$Li_{1.1}Cd_{0.9}Mn_{0.1}P$



$Li_{1.15}Zn_{0.9}Mn_{0.1}P$

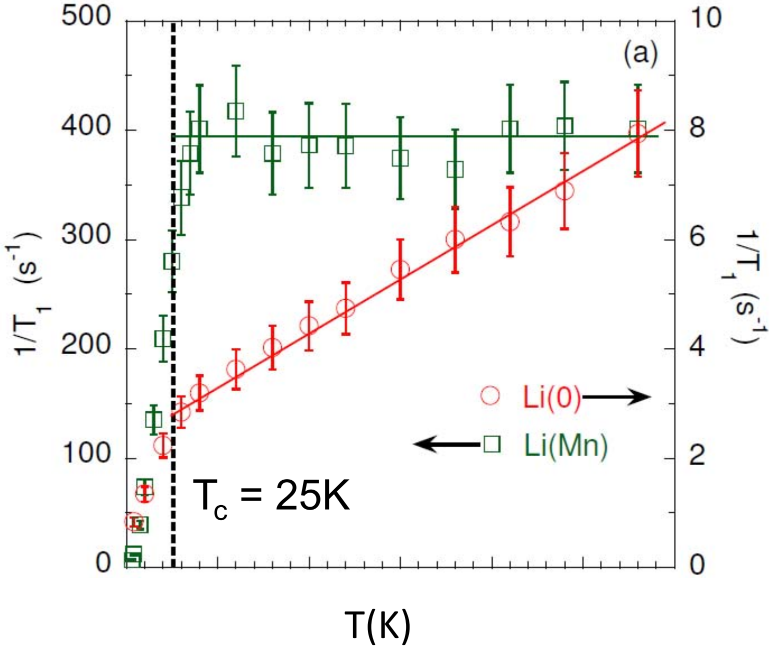


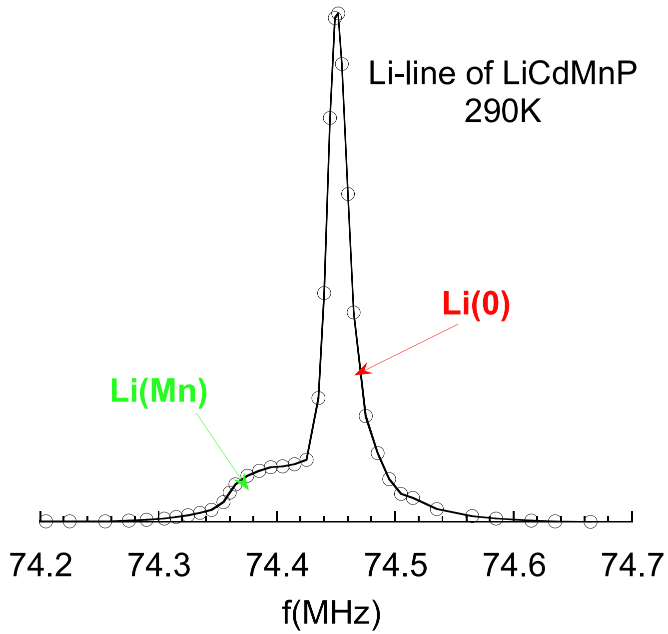
Mn atoms are homogenously distributed in the compound, and no Mn clusters exist.

Consistent with 100% magnetic ordered volume from μSR experiment.

The ferromangetic ordering is intrinsic, from the Mn atoms in the ionic sites in I-II-V DMS! It is NOT from spurious phase.

Spin dynamics----$Li_{1.15}Zn_{0.9}Mn_{0.1}P$ and $Li_{1.1}Cd_{0.9}Mn_{0.1}P$



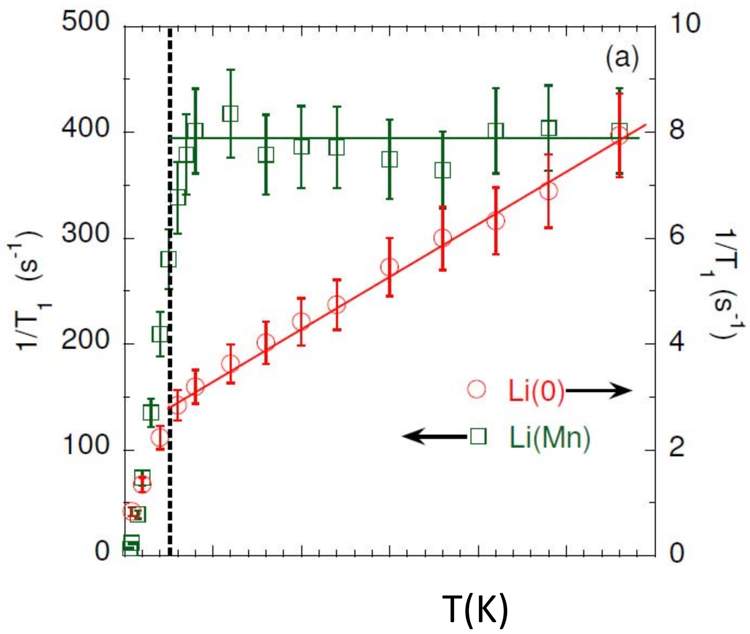


T_1 of Li(Mn) is 50 times shorter than T_1 of Li(0)

Below T_c, for both Li(Mn) and Li(0) sites, T_1 decrease

C. Ding et al., Physics Review B 88, 041108 (R) (2013).

Spin dynamics----$Li_{1.15}Zn_{0.9}Mn_{0.1}P$



For Li(Mn) site, $1/T_1$ ~ constant
Spin fluctuations are locked
at T range ~100 K, J~ 100K

For Li(0) site, $1/T_1$ ~ a +bT
Korringa relation,
Related to information of carriers

Li(Mn) represent "spins"
Li(0) represent "carries"

Carrier mediated ferromagnetism!

$$\frac{1}{T_1} = \sqrt{2\pi}\,\frac{S(S+1)}{3\omega_e}\left(\frac{A_0}{\hbar}\right)^2 \sim 400\ \mathrm{s}^{-1}$$

Moriya's exchange narrowed regime

$$\omega_e \sim 1.1 \times 10^{15}\ \mathrm{rad/s}$$

Characteristic frequency of the Mn spin fluctuations

$$\omega_e^2 = \frac{2}{3} z S(S+1)\left(\frac{J}{\hbar}\right)^2$$

Moriya's Gaussian approximation for the spin-spin correlation function

Z~ 10^3 is the number of Mn sites within the range of Mn-Mn interactions

Summary

• **Series of bulk DMSs with (highest T_C = 230 K) have been fabricated, and these DMSs have common mechanism with (Ga,Mn)As, and can serve as model systems to study the ferromagnetism in DMS**

• **A n-type DMS $Ba(Zn_{1-x}Co_x)_2As_2$ (T_C = 45K) have been successfully synthesized**

• **NMR and μSR: Mn atoms are homogenously doped, the ferromagnetic ordering is from Mn in the ionic Zn site**

• **NMR results are consistent with a carrier mediated ferromagnetism picture.**

• **Now with the same 122 tetragonal structure,** junctions could be made **via As layer between following materials:**

N-type DMS $Ba(Zn_{1-x}Co_x)_2As_2$ (T_C = 45K)
P-type DMS $(Ba_{1-y}K_y)(Zn_{1-x}Mn_x)_2As_2$ (T_C=230K)
Superconductor $Ba(Fe_{1-x}Cox)_2As_2$ (T_c=25K)
Antiferromagnet $BaMn_2As_2$ (T_N=625K)
Paramagnetic $BaCo_2As_2$

Thank you for your attention!