Defect controlled ferromagnetism in $Ga_{1-x}Mn_xAs$

Peter Schiffer

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Why do we want a ferromagnetic semiconductor?

• Semiconductors allow us to do wonderful things (circuits)

• Ferromagnets allow us to do wonderful things (GMR, memory, etc.)

• A ferromagnetic semiconductor would combine polarization of carriers with the flexibility of a semiconductor: "semiconductor spintronics"

• Spins polarized in metallic ferromagnets do not transfer easily to semiconductors: hard to do spin injection

$Ga_{1-x}Mn_xAs$: The Canonical FM Semiconductor

H. Ohno *et al.*, APL 1996

(Ga,Mn)As: A new diluted magnetic semiconductor based on GaAs

H. Ohno[a)]
Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan, and Research Development Corporation of Japan (JRDC)

A. Shen and F. Matsukura
Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan

A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye
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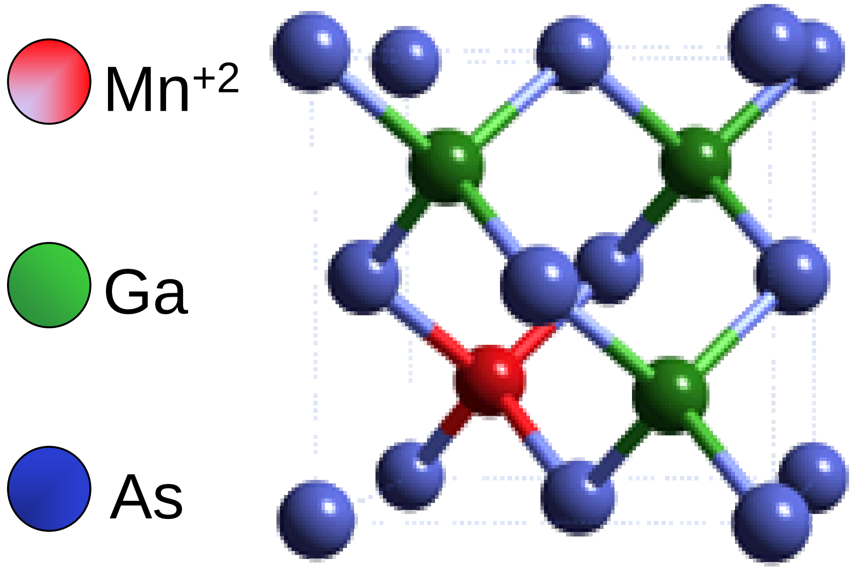
(Received 2 February 1996; accepted for publication 10 May 1996)

A new GaAs-based diluted magnetic semiconductor, (Ga,Mn)As, was prepared by molecular beam epitaxy. The lattice constant of (Ga,Mn)As films was determined by x-ray diffraction and shown to increase with the increase of Mn composition, *x*. Well-aligned in-plane ferromagnetic order was observed by magnetization measurements. Magnetotransport measurements revealed the occurrence of anomalous Hall effect in the (Ga,Mn)As layer.
[S0003-6951(96)04129-0]

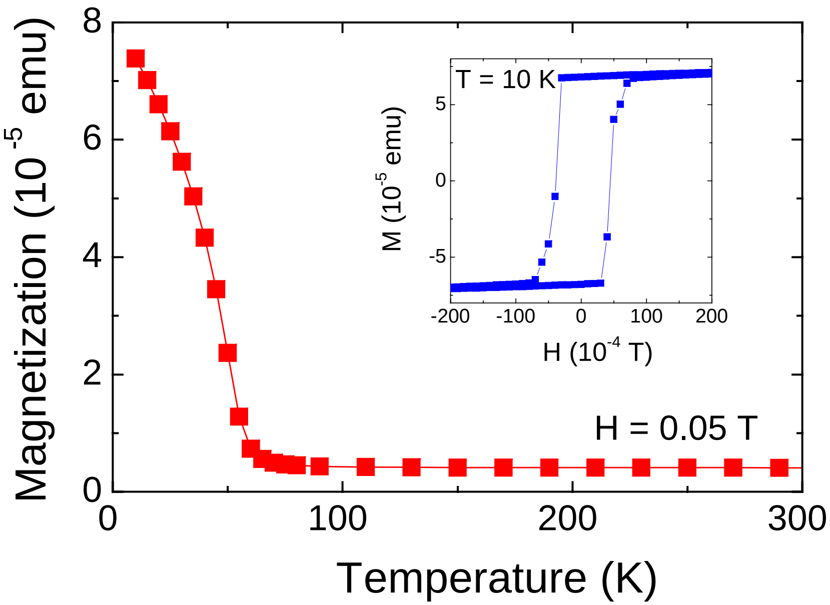
Generic $Ga_{1-x}Mn_xAs$ properties

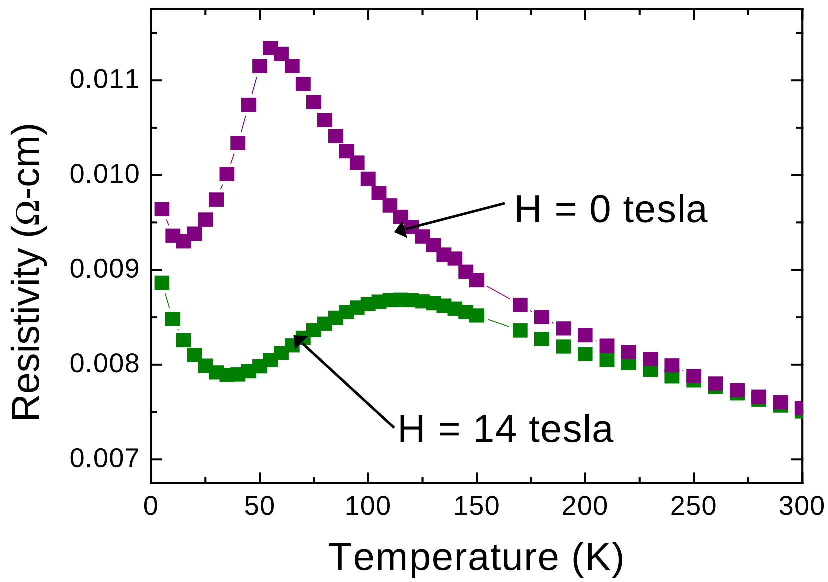
- **Mn substitutes for the Ga: serves as both acceptor and spin (S = 5/2)**
- **Grown by Low-Temp MBE with $x \leq 0.10$**
- **Variety of defects (As antisites, Mn interstitials, Ga vacancies…).**
- **Defects can compensate holes so <u>carrier concentration is not equivalent to Mn concentration</u>**



How do defects affect the physics? Usually very important for semiconductors…

Characteristic Behavior

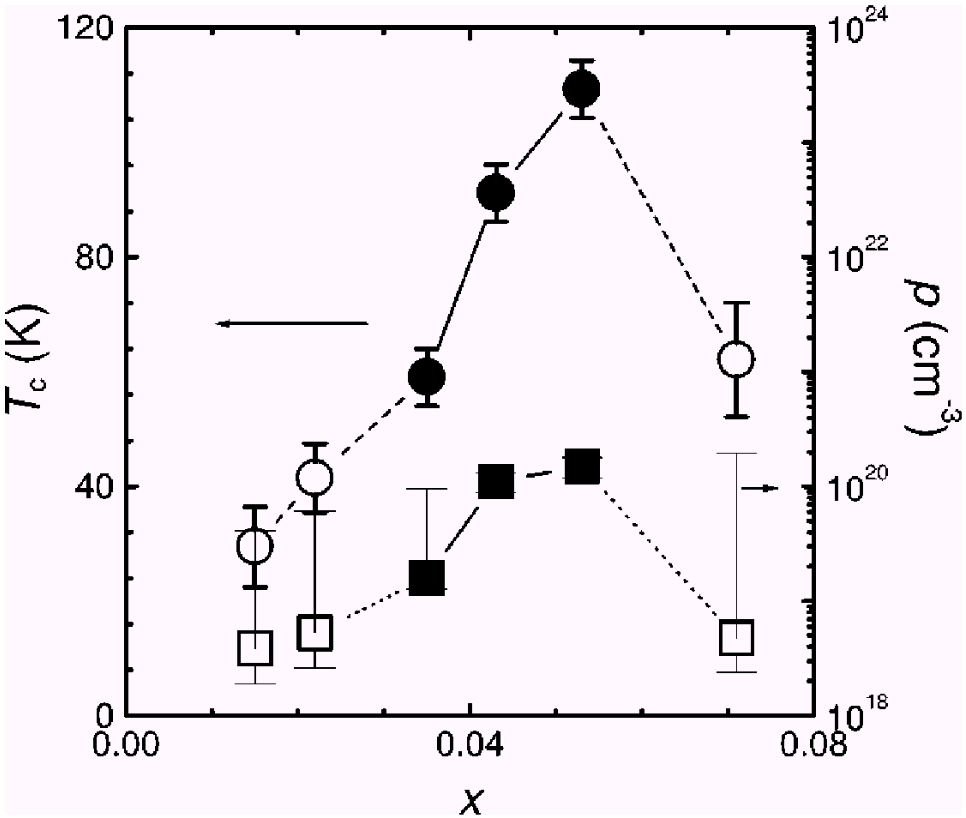




Ferromagnetism accompanied by transition from semiconducting → metallic conduction

Early $Ga_{1-x}Mn_xAs$ phase diagram

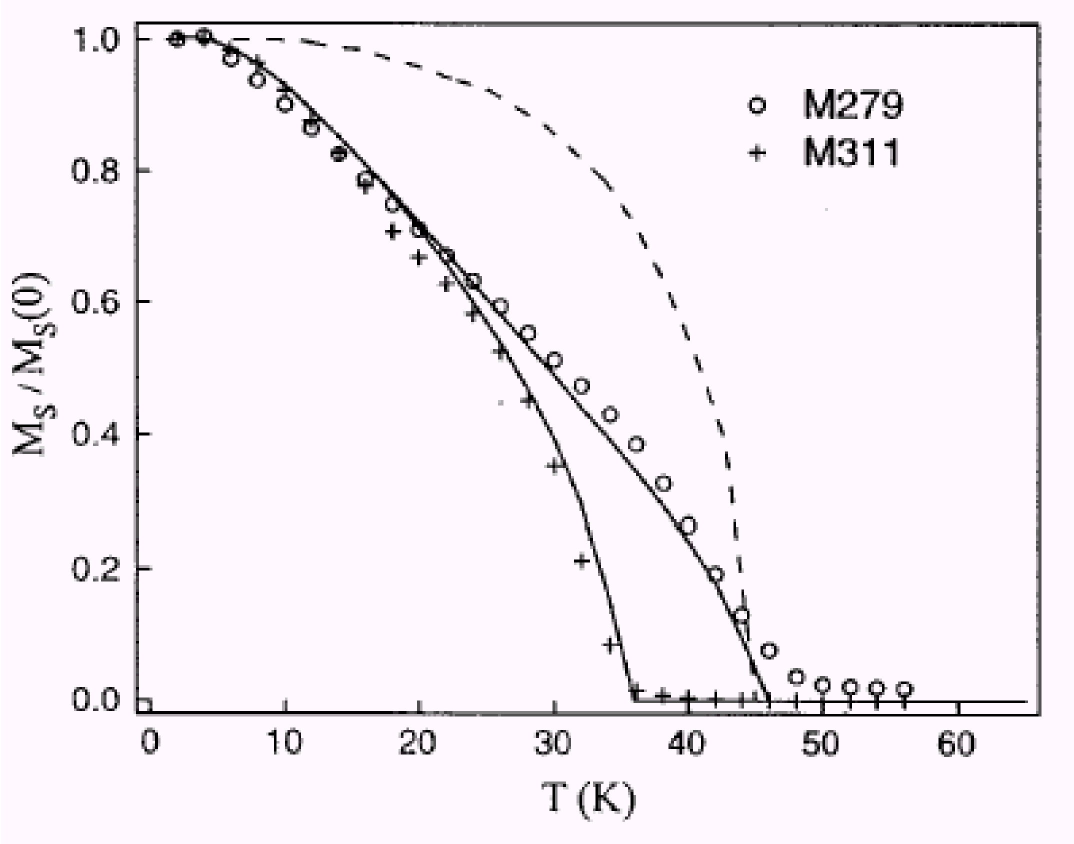
Ferromagnetism is mediated by holes
Carrier concentration and T_c are correlated



Matsukara *et al.*
PRB 1998

FIG. 2. Mn composition dependence of ferromagnetic transition temperature T_c and hole concentration p. Samples on the metal side of the metal insulator transition are shown by the closed symbols (see also Fig. 3).

Characteristic Magnetic Behavior of as-grown $Ga_{1-x}Mn_xAs$



As-grown magnetization does not behave like a standard ferromagnet

Van Esch *et al.* PRB 1997

- **Multiple exchange processes? (Van Esch *et al.*, PRB 1997)**
- **Carrier concentration gradient? (Koeder *et al.*, APL 2003)**
- **Result of magnetic polaron percolation? (Das Sarma *et al.*, PRB 2003)**

Physical properties depend strongly on preparation and annealing

Low temperature growth results in defects → hard to grow samples with reproducible properties

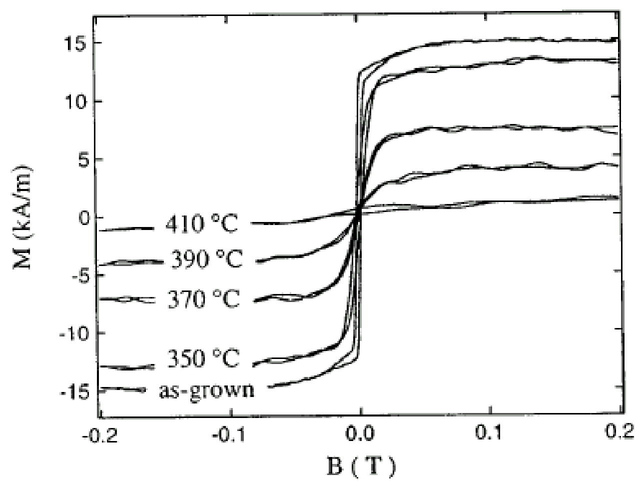


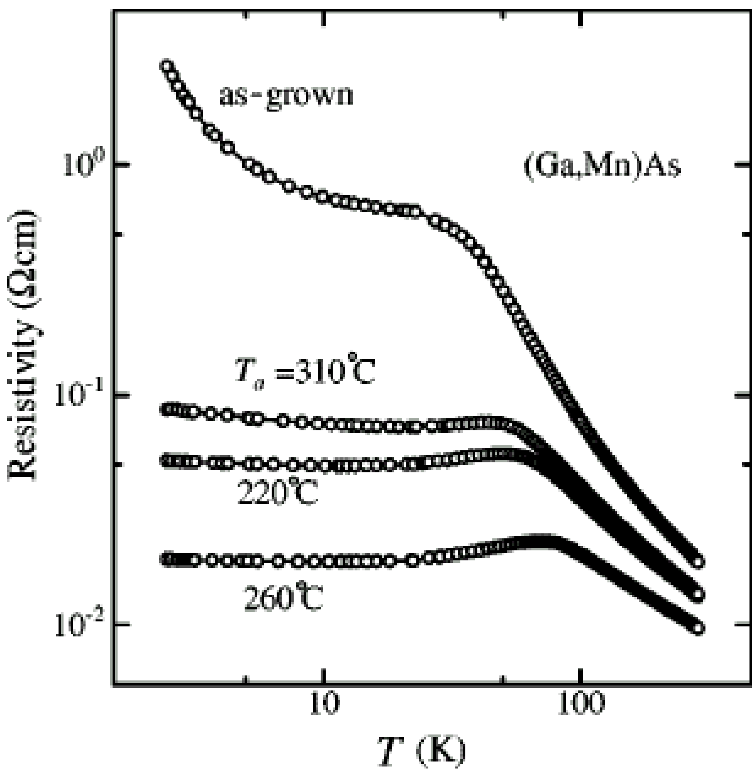
FIG. 5. Magnetization measurements at $T = 10$ K on $Ga_{0.913}Mn_{0.087}As$ (M311) show a decrease in saturation magnetization after low-temperature annealing. The annealing temperatures are indicated in the figure.

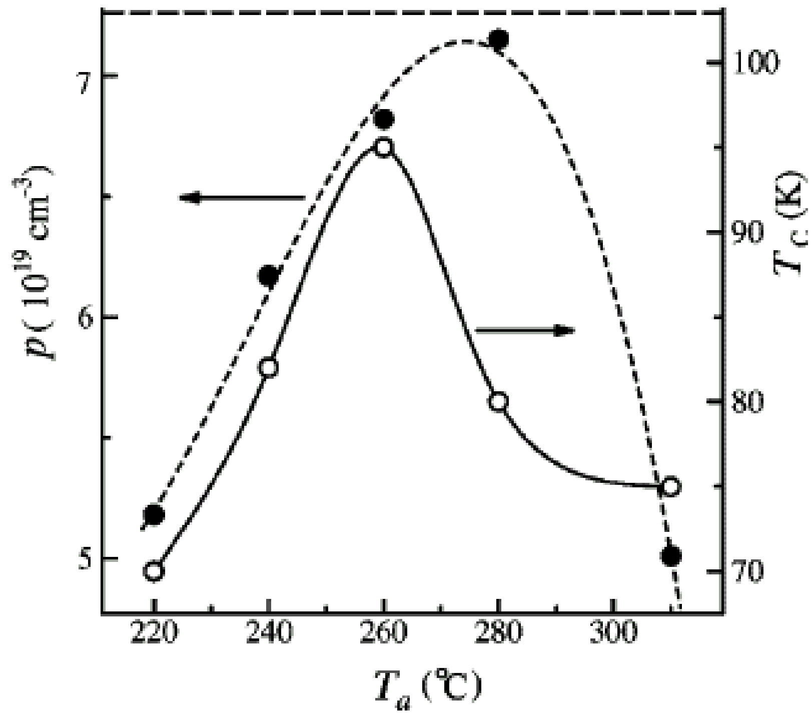
Van Esch *et al.* 1997

Theory predicts disorder should strongly affect physics
Sanvito and Hill, Berciu and Bhatt, and many others

Even low-temperature anneals can drastically affect properties

Hayashi *et al.* (APL 2001) **15 minute anneals in N_2 gas at temperatures close to growth temperature**



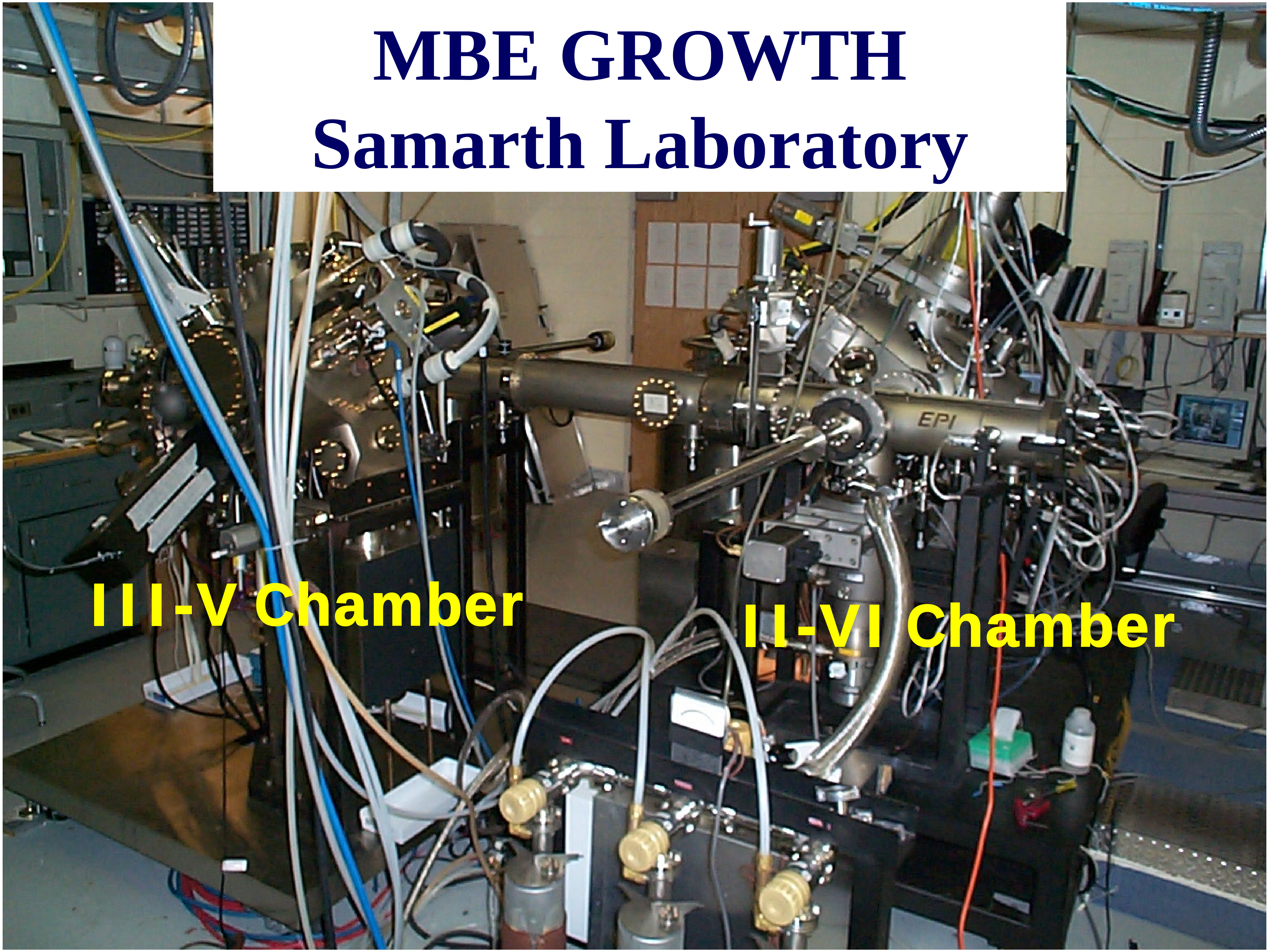


Penn State Annealing Studies

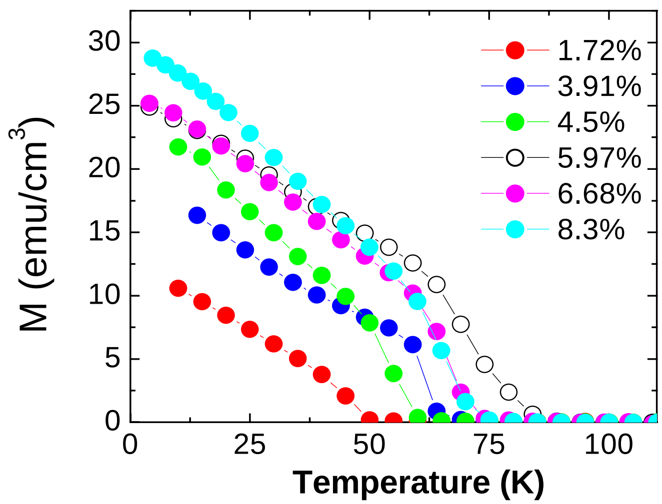
Potashnik *et al.* APL 79 1495 (2001)

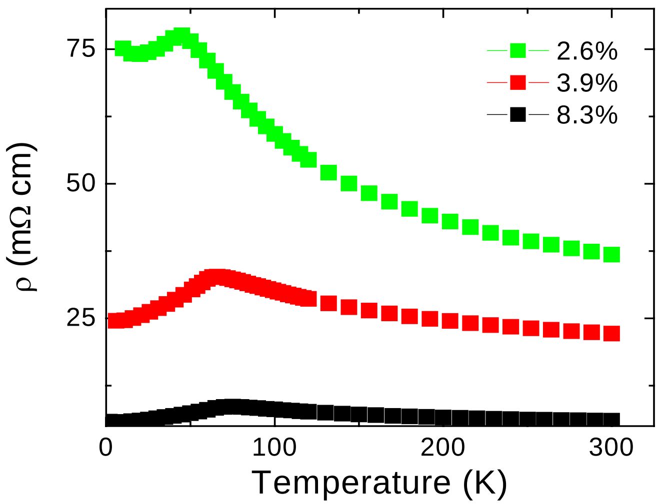
- Anneal at 250 °C in flowing N_2 gas, varying the annealing time (t_{anneal})
- Measure magnetization, magnetotransport, x-ray diffraction as a function of annealing time
- Determine Mn content directly through electron microprobe analysis (EMPA)

MBE GROWTH
Samarth Laboratory



As-grown samples are typical

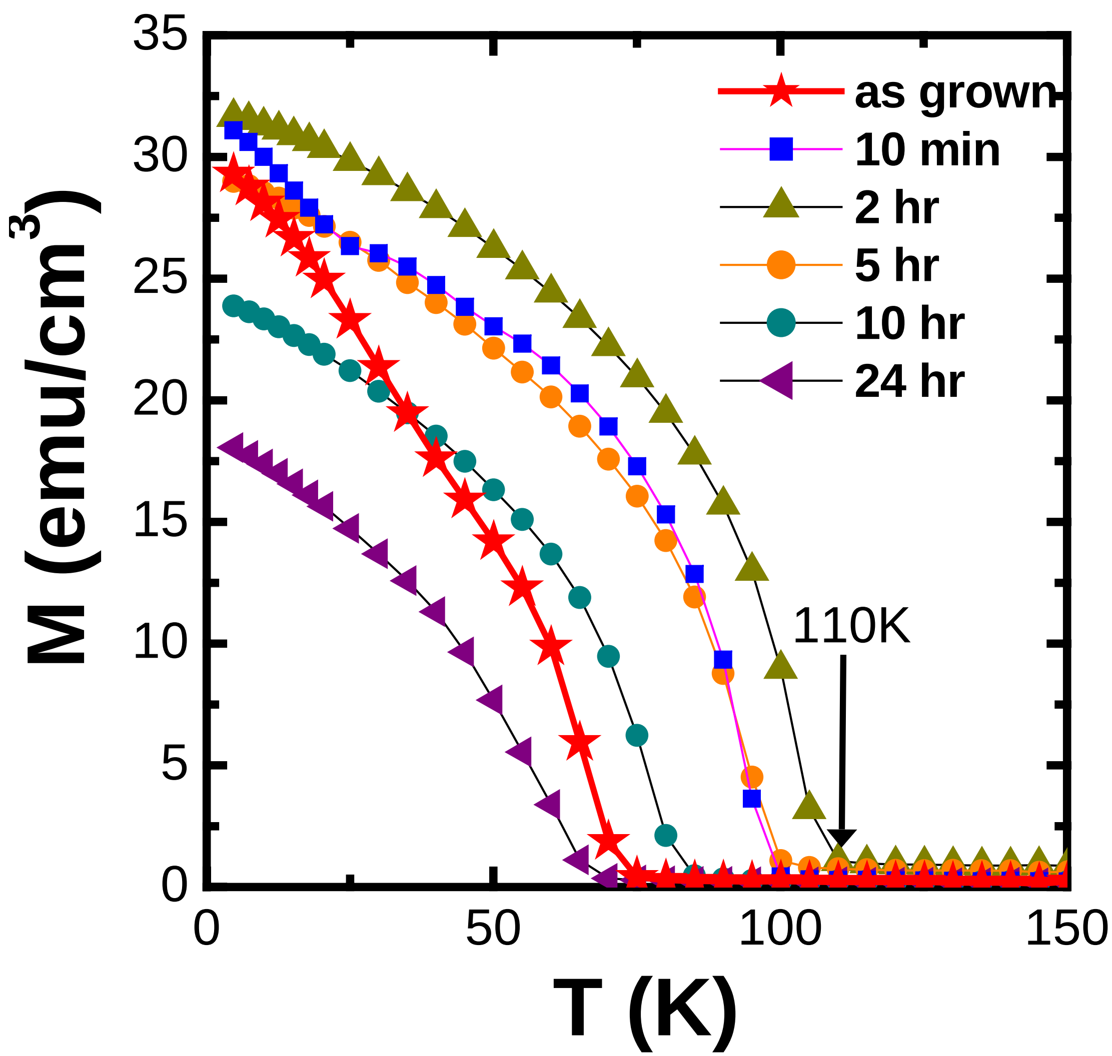




- M(T) has typical as-grown behavior (i.e. ugly)

- Higher Mn concentrations increase saturation moment and decrease resistivity

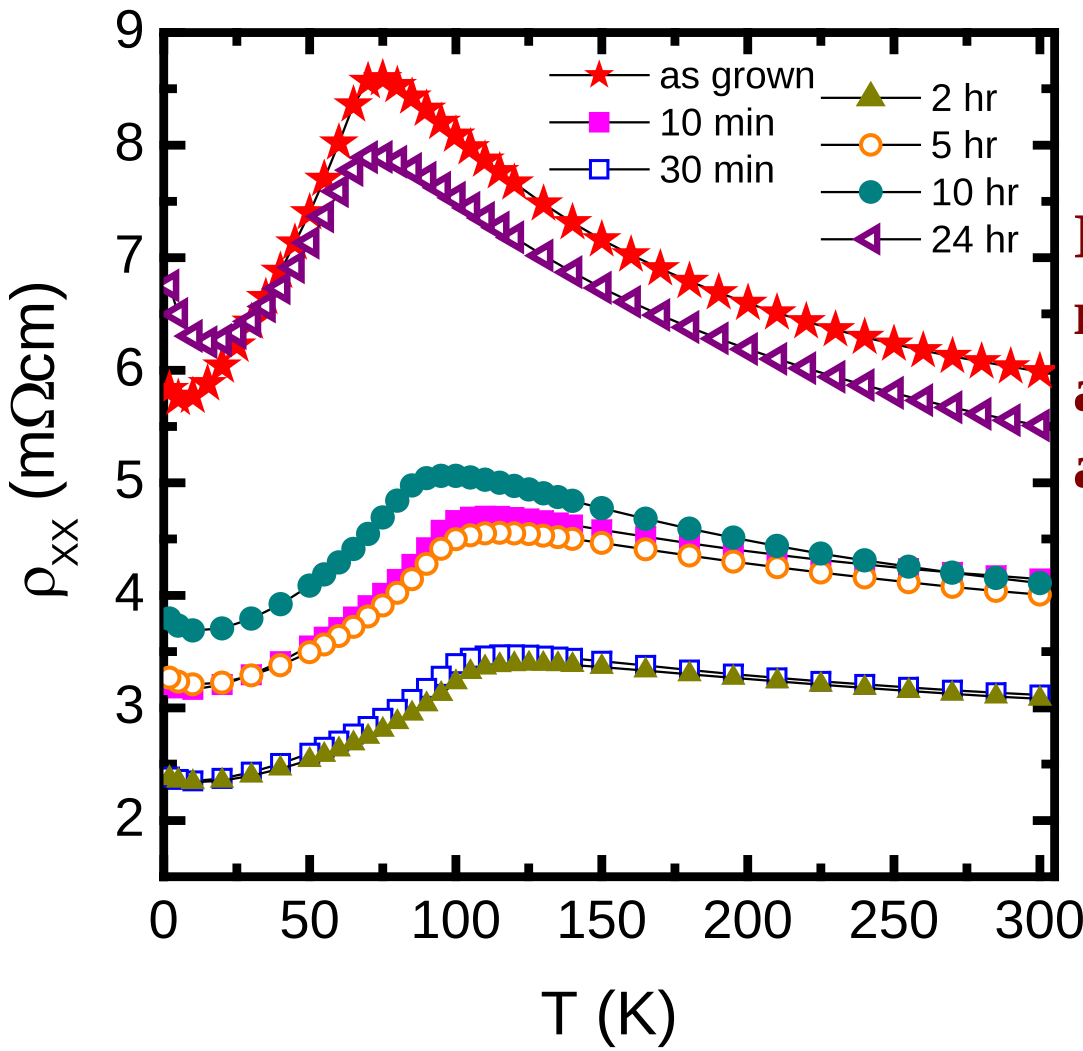
Annealing completely changes magnetism



Annealing changes both T_c and the saturation moment

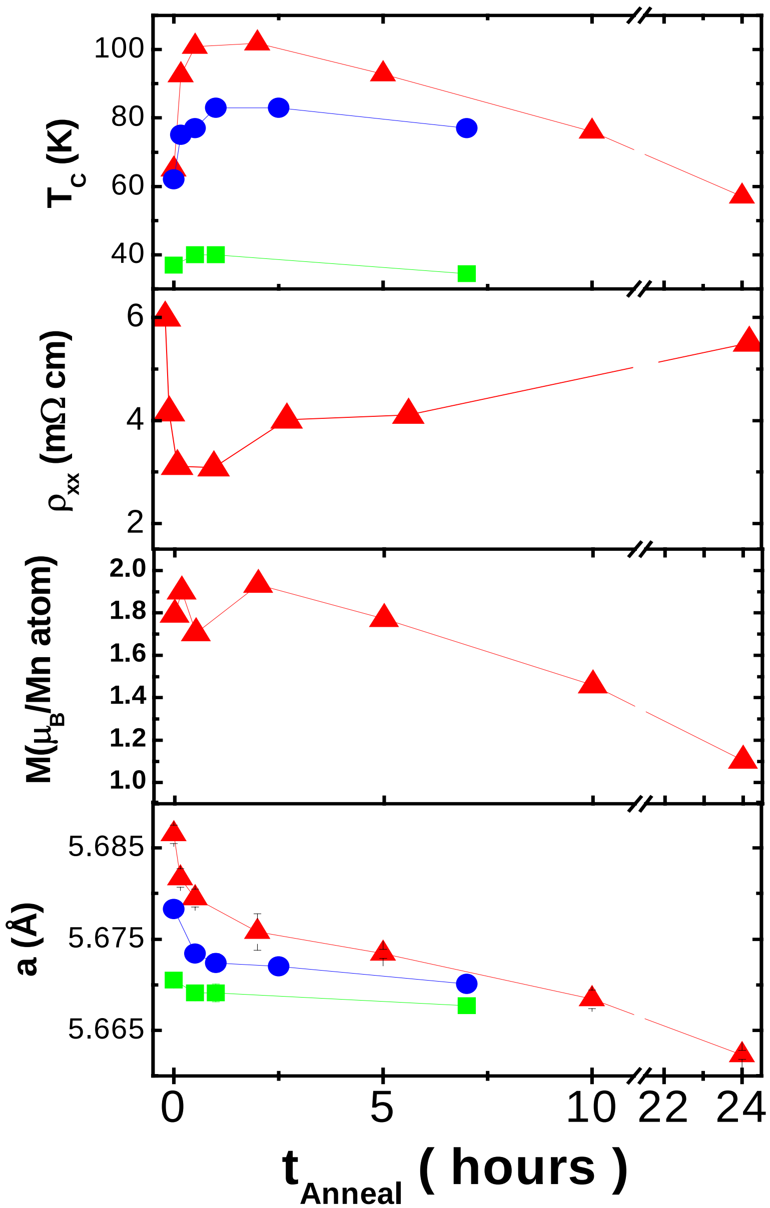
Also changes qualitative character of M(T)

Annealing also affects transport



Initial annealing reduces resistivity while longer anneals cause it to increase again

Annealing Time Dependence Summary



Two regimes in annealing time:

t_{anneal} < 2 hours enhances ferromagnetism and metallicity

t_{anneal} > 2 hours suppresses ferromagnetism and metallicity

Annealing of covered samples gives same results (effects not associated with changes in stoichiometry)

Must involve at least two different processes for reordering of defects

Defects crucial to Physics!

PIXE and RBS Measurements show complex defect motion as result of annealing

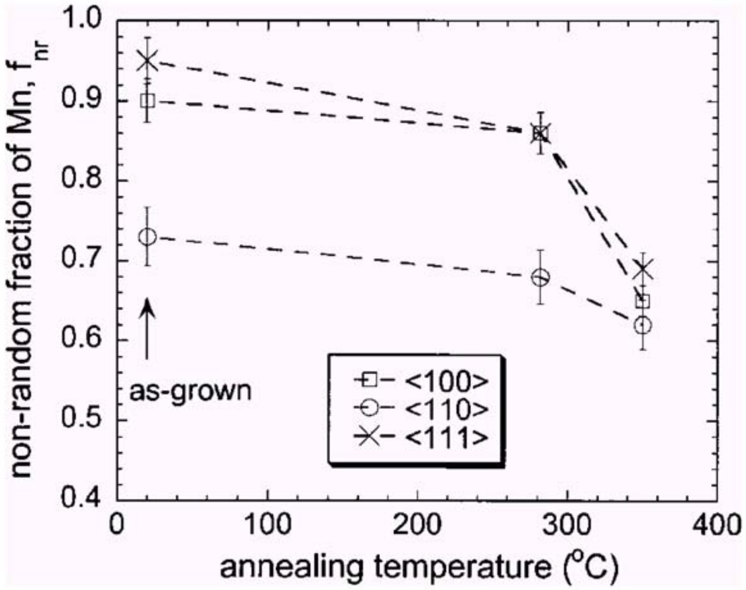


FIG. 2. The nonrandom fractions of Mn for the three different $Ga_{1-x}Mn_xAs$ films as calculated from the values of χ_{GaAs} and χ_{Mn} in the different channel projections.

Yu *et al.* (PRB 2002)

Annealing removes interstitial Mn ions and thus decreases compensation

Annealing also removes substitutional Mn ions

Concentration dependent studies of $Ga_{1-x}Mn_xAs$

Potashnik *et al.* PRB <u>66</u> 012408 (2002)

Probe the fundamental physics governing ferromagnetism

We examine the ferromagnetic properties as a function of Mn content (x) in a series of consecutively grown $Ga_{1-x}Mn_xAs$ samples.

Annealed 90 minutes @ 250 C

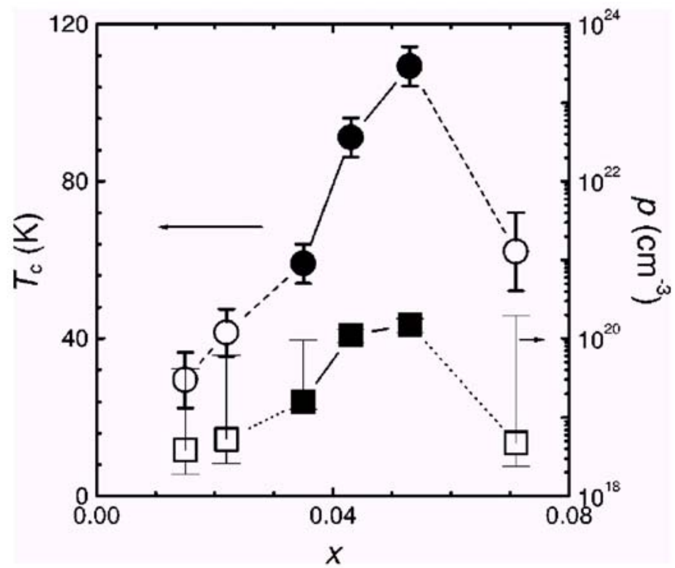


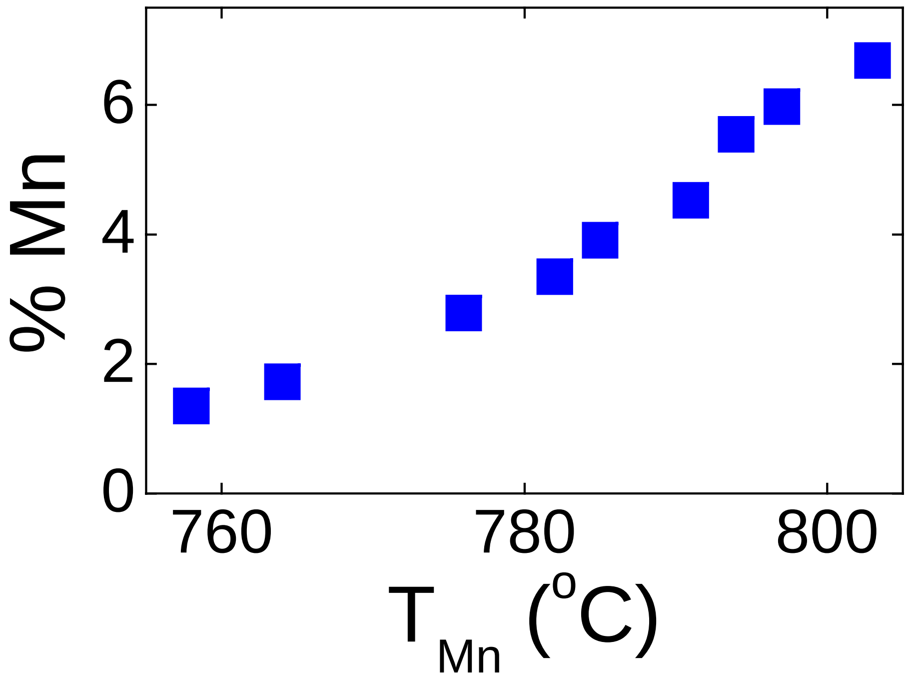
FIG. 2. Mn composition dependence of ferromagnetic transition temperature T_c and hole concentration p. Samples on the metal side of the metal insulator transition are shown by the closed symbols (see also Fig. 3).

Matsukara *et al.*, PRB 1998

Mn concentration measured by EMPA

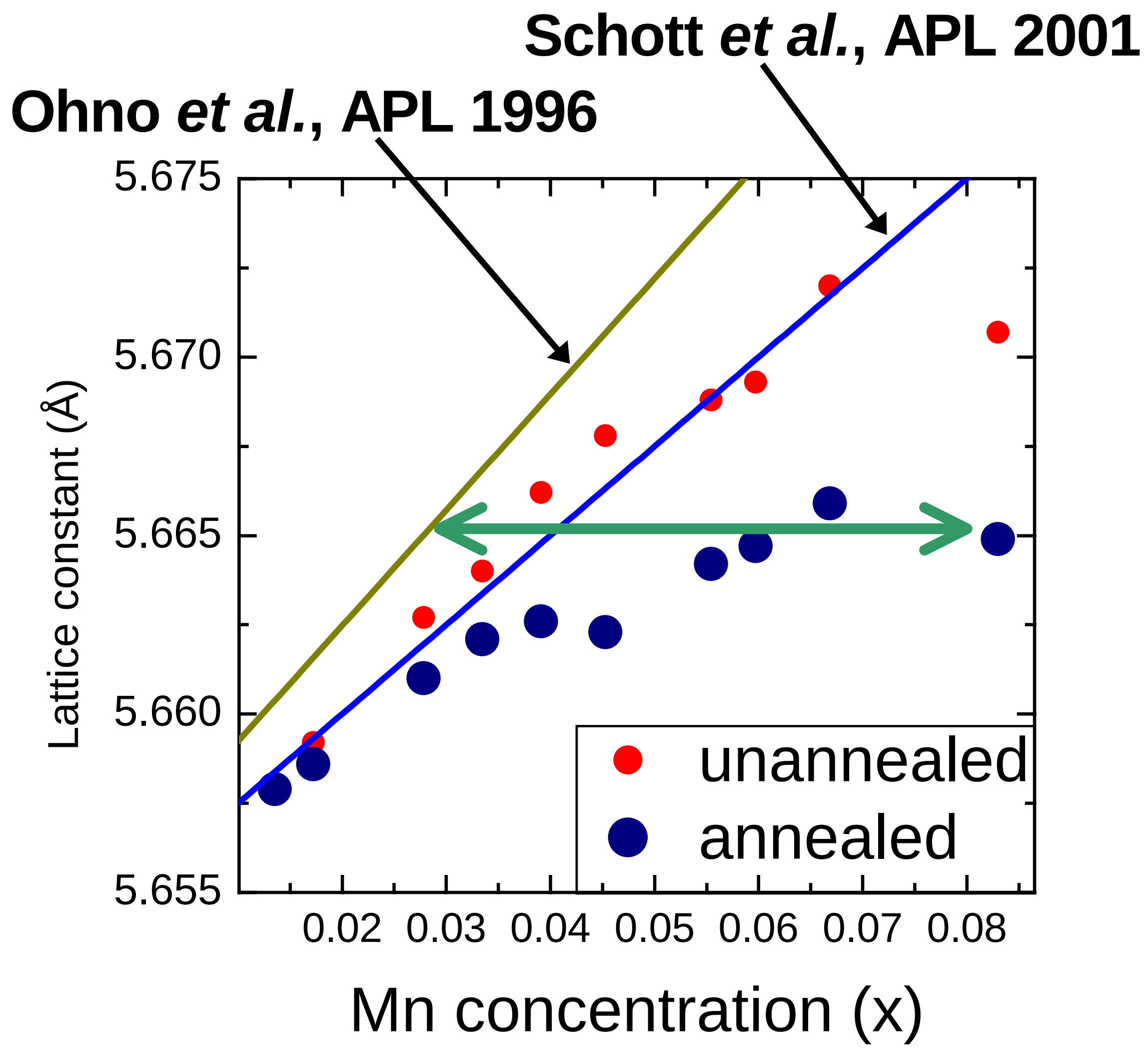
Series of samples with 0.0135 < x < 0.083

All samples except x = 0.083 grown in same MBE run

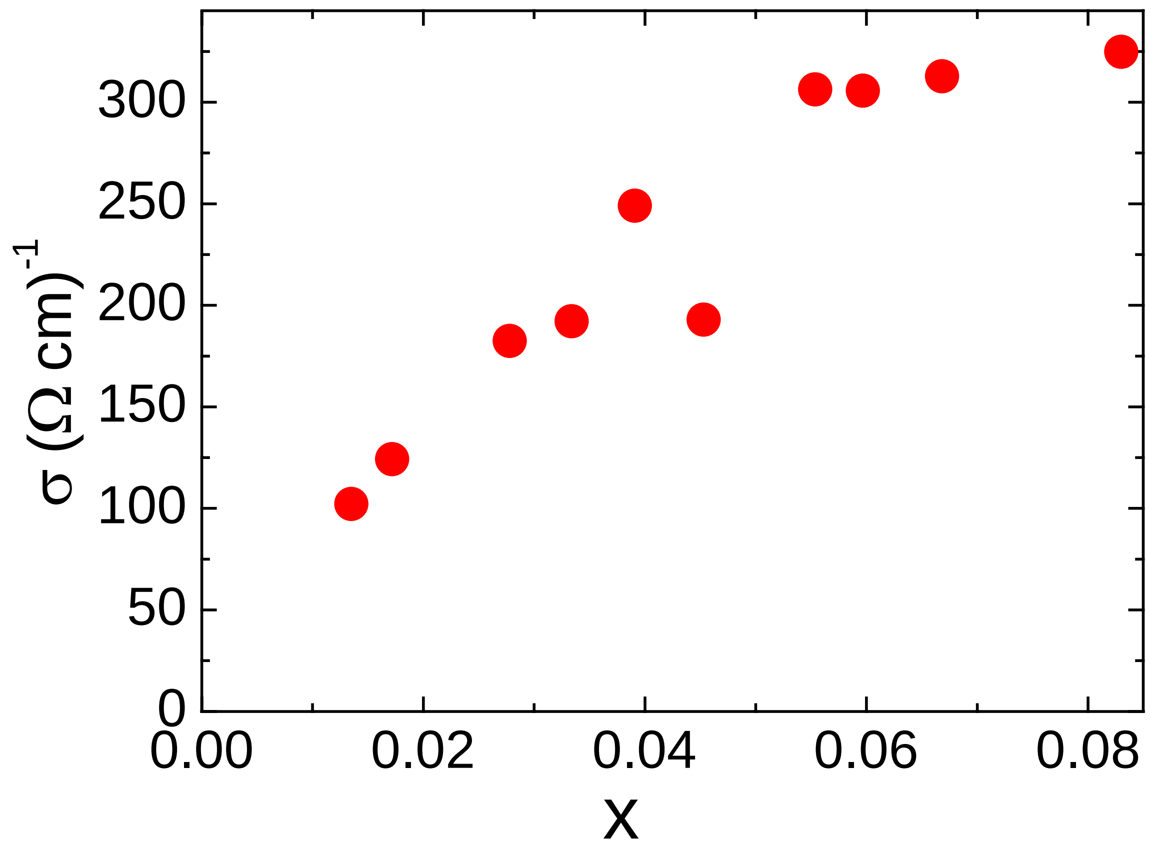


All values of x determined directly through EMPA measurements -- follow expected trend of Mn cell temperature

Lattice constant reflects Mn concentration but not uniquely



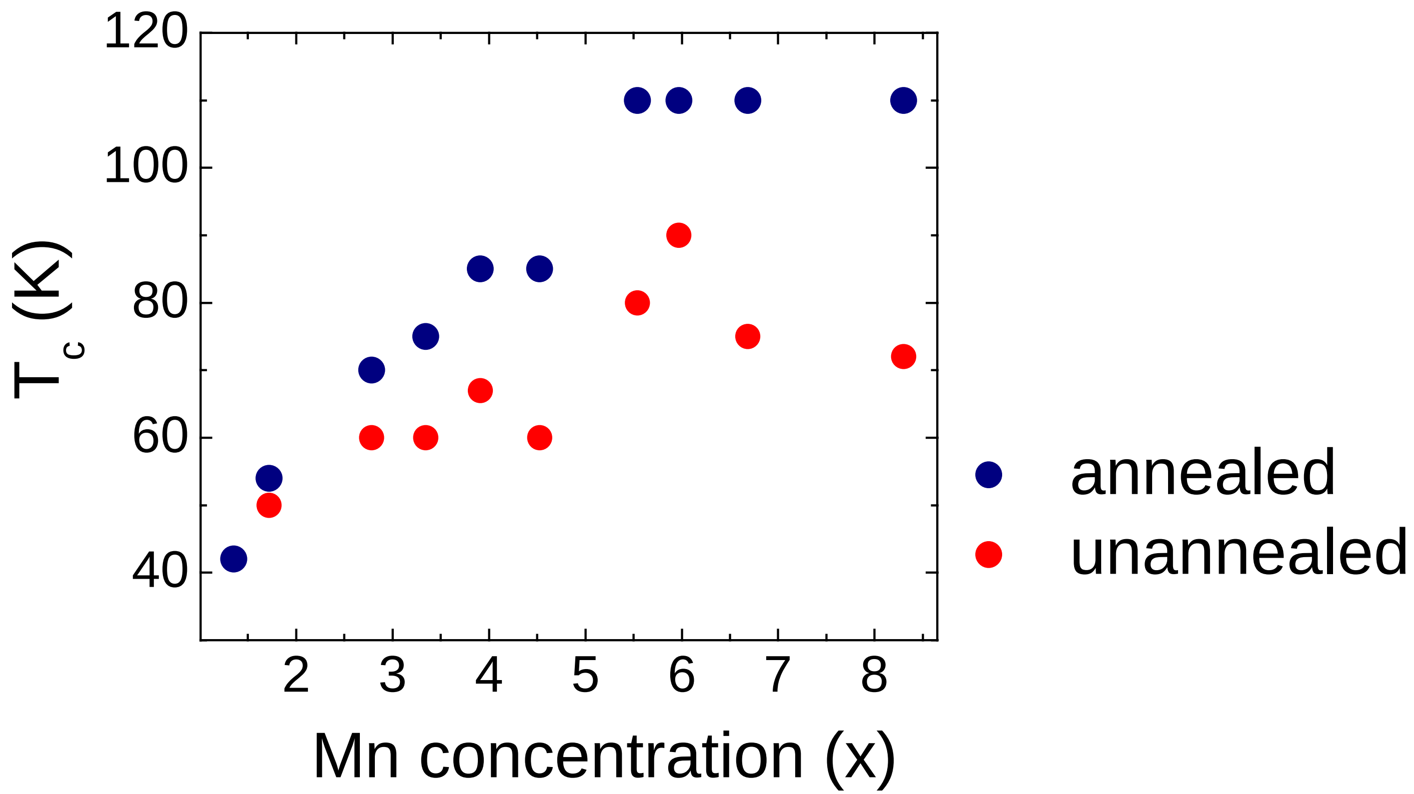
Mn concentration and conductivity



Conductivity increases with x as expected, but no evidence of re-entrant insulating state

T_c saturates above x = 0.05

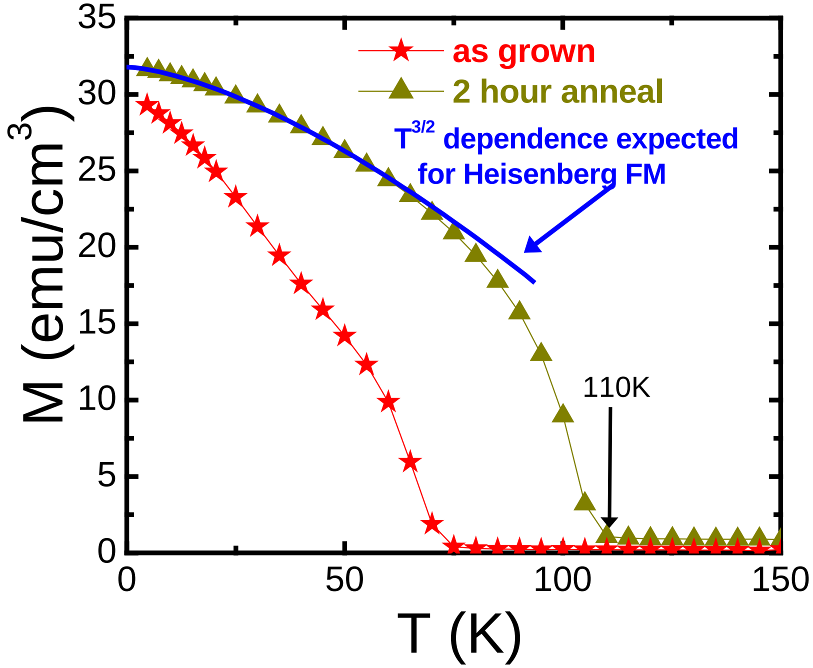
Consistent with Edmonds *et al.*, APL 2002

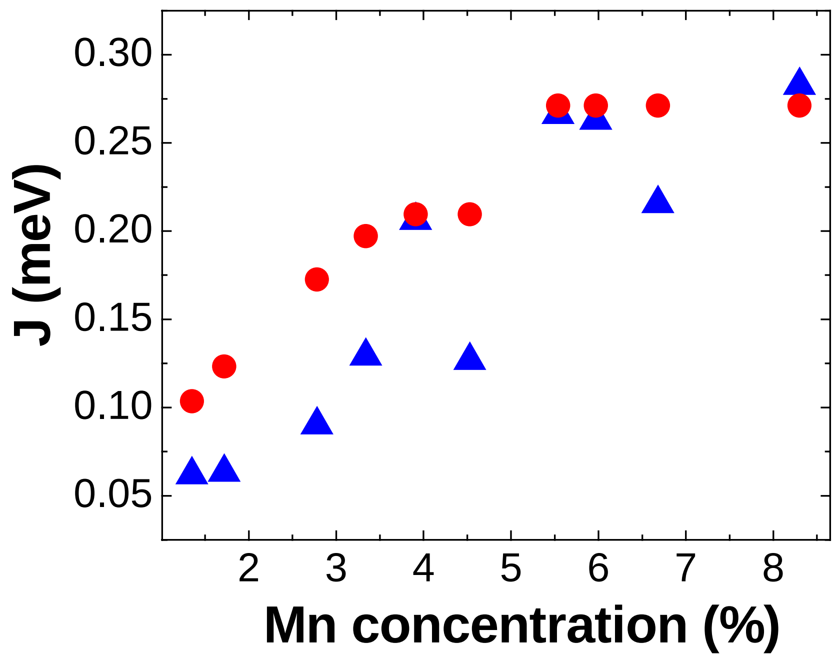


T_c ~ 110 K for x > 0.05 in annealed samples

Possibility raised of 110 K being fundamental limit on T_c?

Annealed samples behave like conventional ferromagnets





$$M(T) = M_0 - 0.117\mu_B(k_BT/2SJd^2)^{3/2}$$

from spin wave theory

$$J = 3k_BT_c/[2zS(S+1)]$$

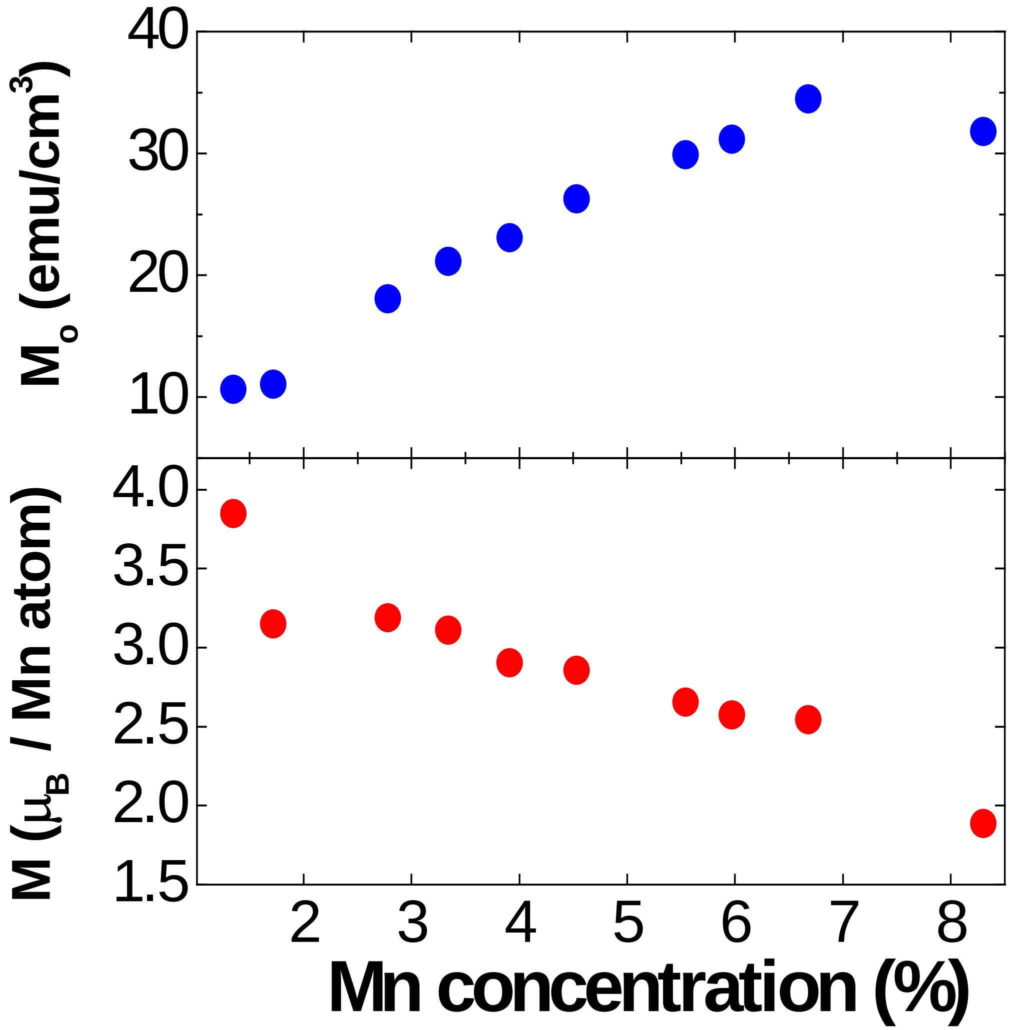
from mean field theory

▲ From spin wave theory

● From T_c (MFT)

Values of *J* are in reasonable agreement with theoretical calculation (König *et al.*, PRB 2001)

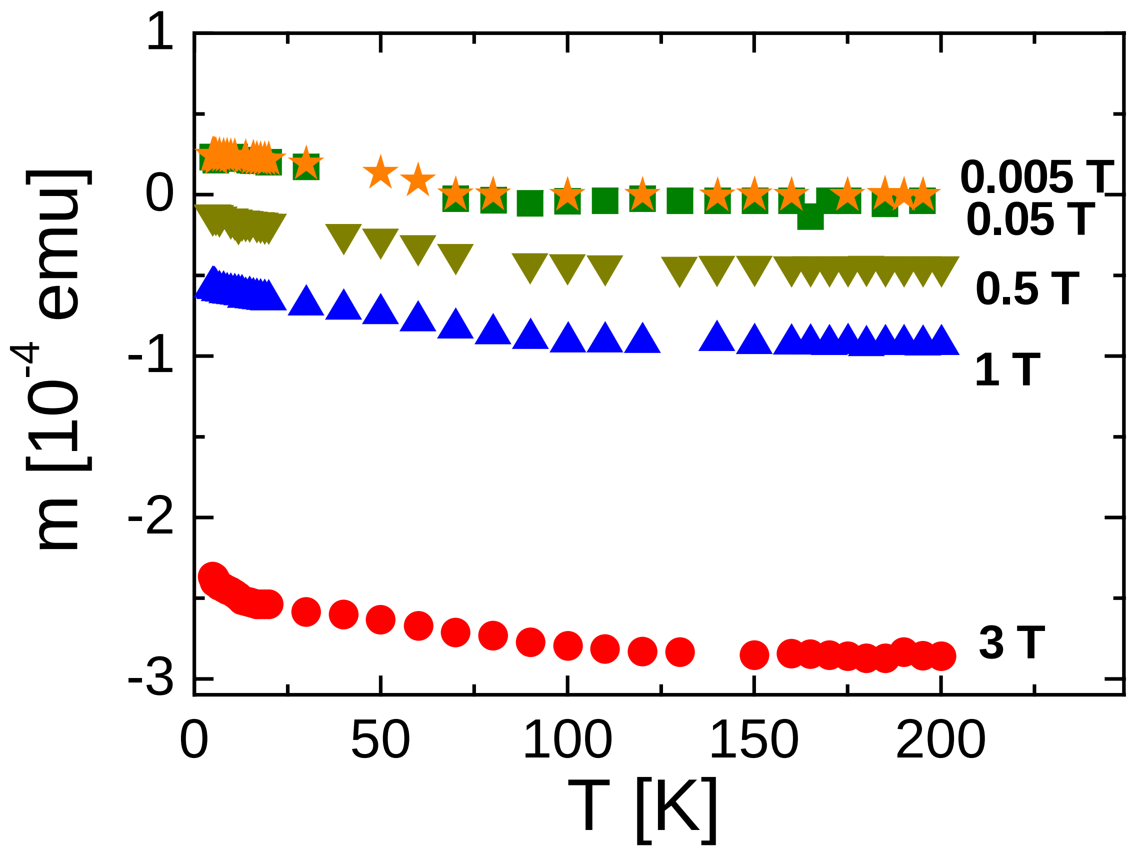
Physical Problem: Magnetization Deficit
(Where are the spins?)



Low temperature moment increases with Mn concentration

Smaller percentage of Mn ions contributing at higher concentrations

Can we recover the FM moment in a big field?

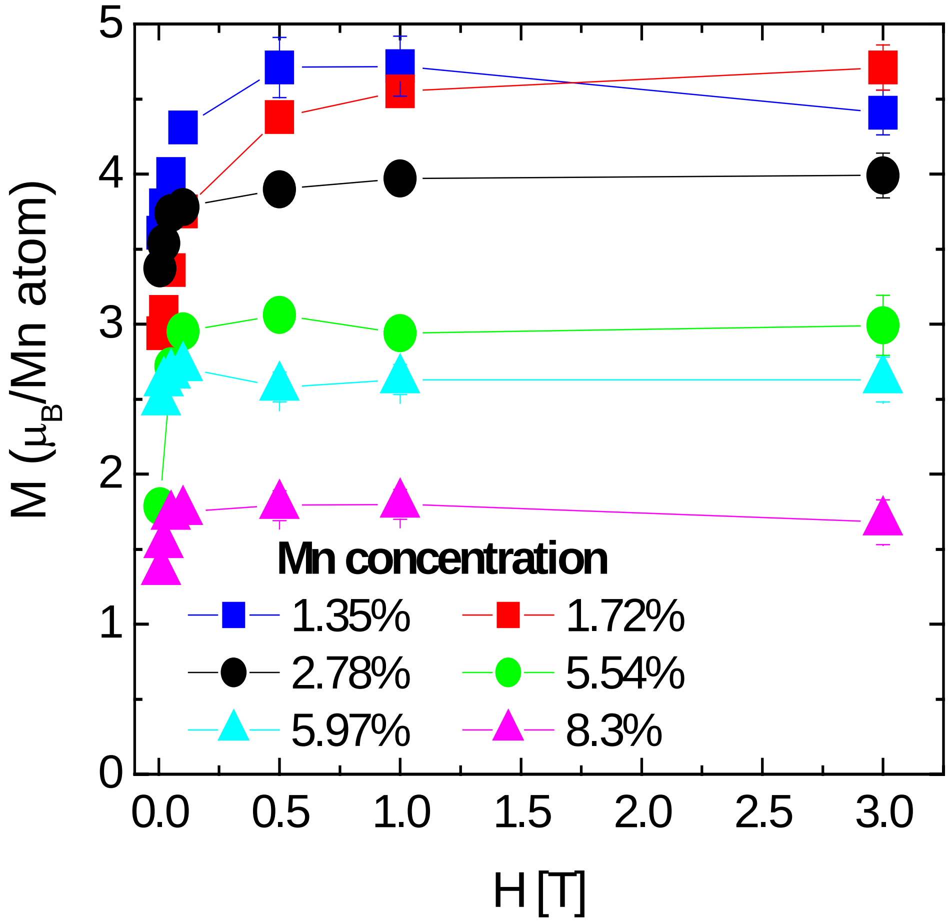


Potashnik *et al.*,
J. Appl. Phys 93 6784 (2003)

Hard to measure high field magnetization
diamagnetic substrate background gets in the way

High Field Magnetization

After careful subtraction of substrate magnetization



- No significant increase in magnetization up to 3T.

- Non ferromagnetic spins are not easily polarized (AFM coupling > 15K)

Magnetization Deficit: How to explain?

- Dipolar effects (Jankó and Zaránd, PRL 2002)
- Non-collinear ferromagnetism (Schliemann and MacDonald, PRL 2002)
- Direct antiferromagnetic coupling (das Sarma *et al.*, PRB 2003)
- Antiferromagnetic coupling due to As antisites (Korzhavyi *et al.*, PRL 2002)
- Antiferromagnetic coupling to interstitial Mn (Yu *et al.*, PRB 2002)
  Strong AFM coupling predicted (Blinkowski and Kacman, PRB 2003)

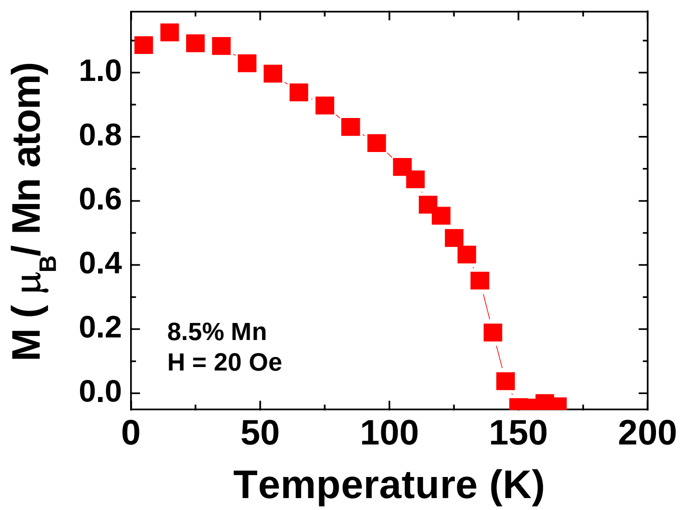
Or are the missing Mn ions just phase separated from the rest of the material?

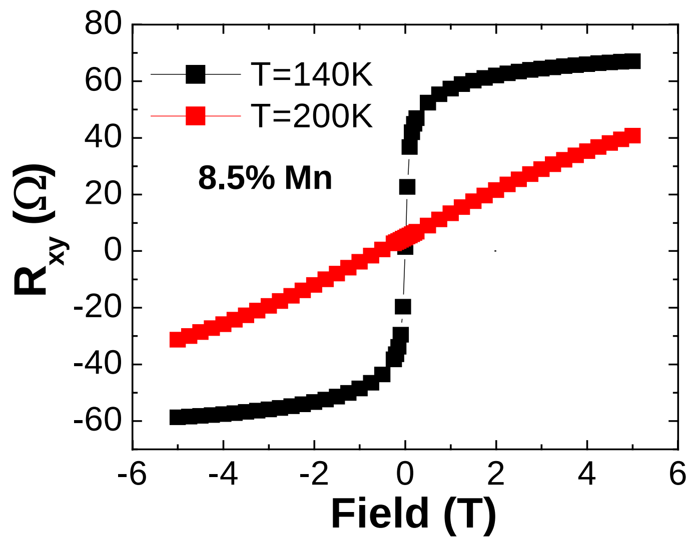
More recently raise T_c (up to 150 K)

Ku *et al.* APL <u>82</u>, 2302 (2003) in collaboration with:

M. J. Seong & A. Mascarenhas (NREL)

E. Johnston-Halperin, R.C. Myers, A.C. Gossard and D.D. Awschalom (UCSB)



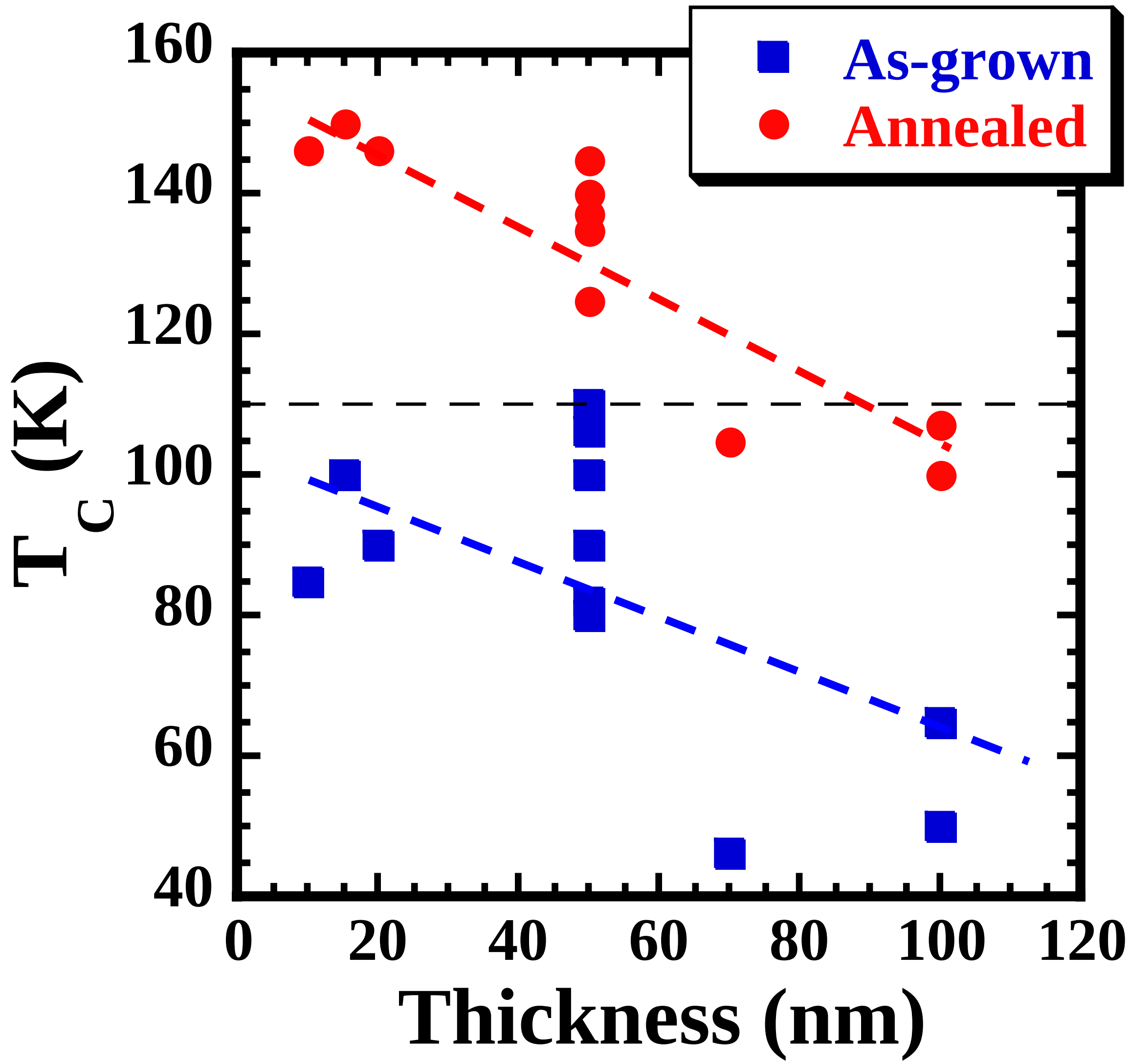


Magnetization, Hall Effect, MCD all confirm that higher T_c is intrinsic to bulk of material

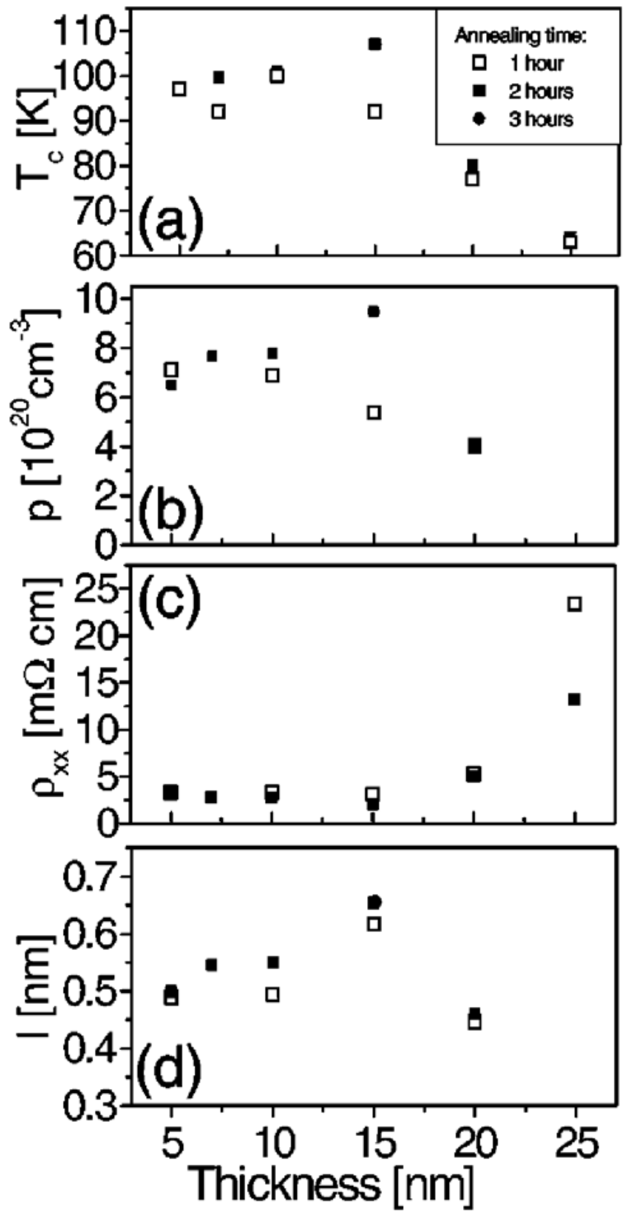
Thin samples are needed for higher T_c

T_c increases with decreasing thickness!

never above 110K with 100 nm thick samples

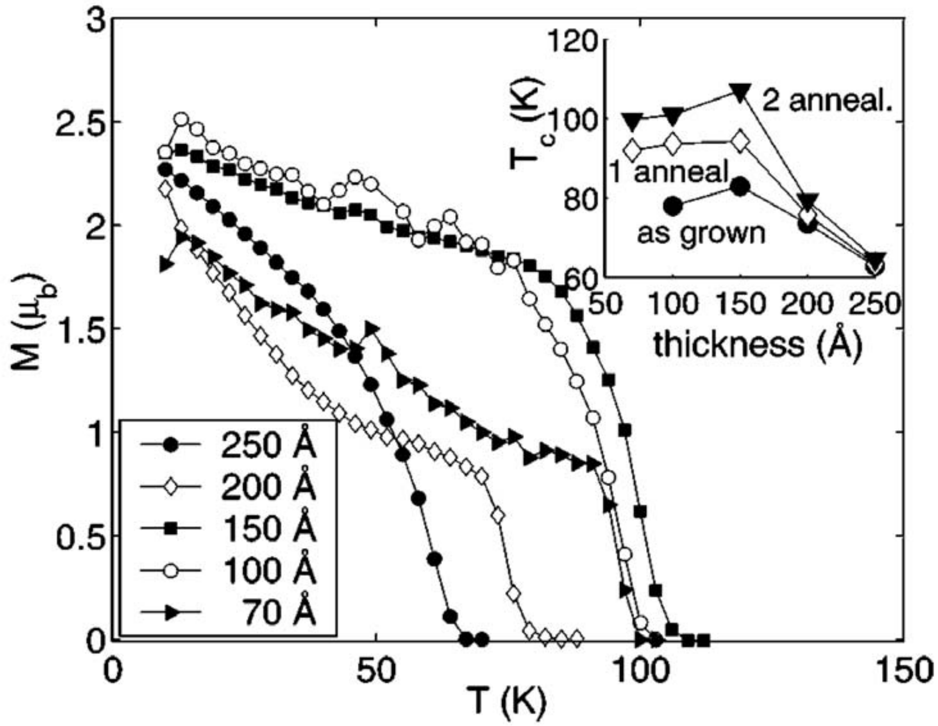


Thickness dependence also seen by other groups



Thinner samples have more carriers and higher T_c

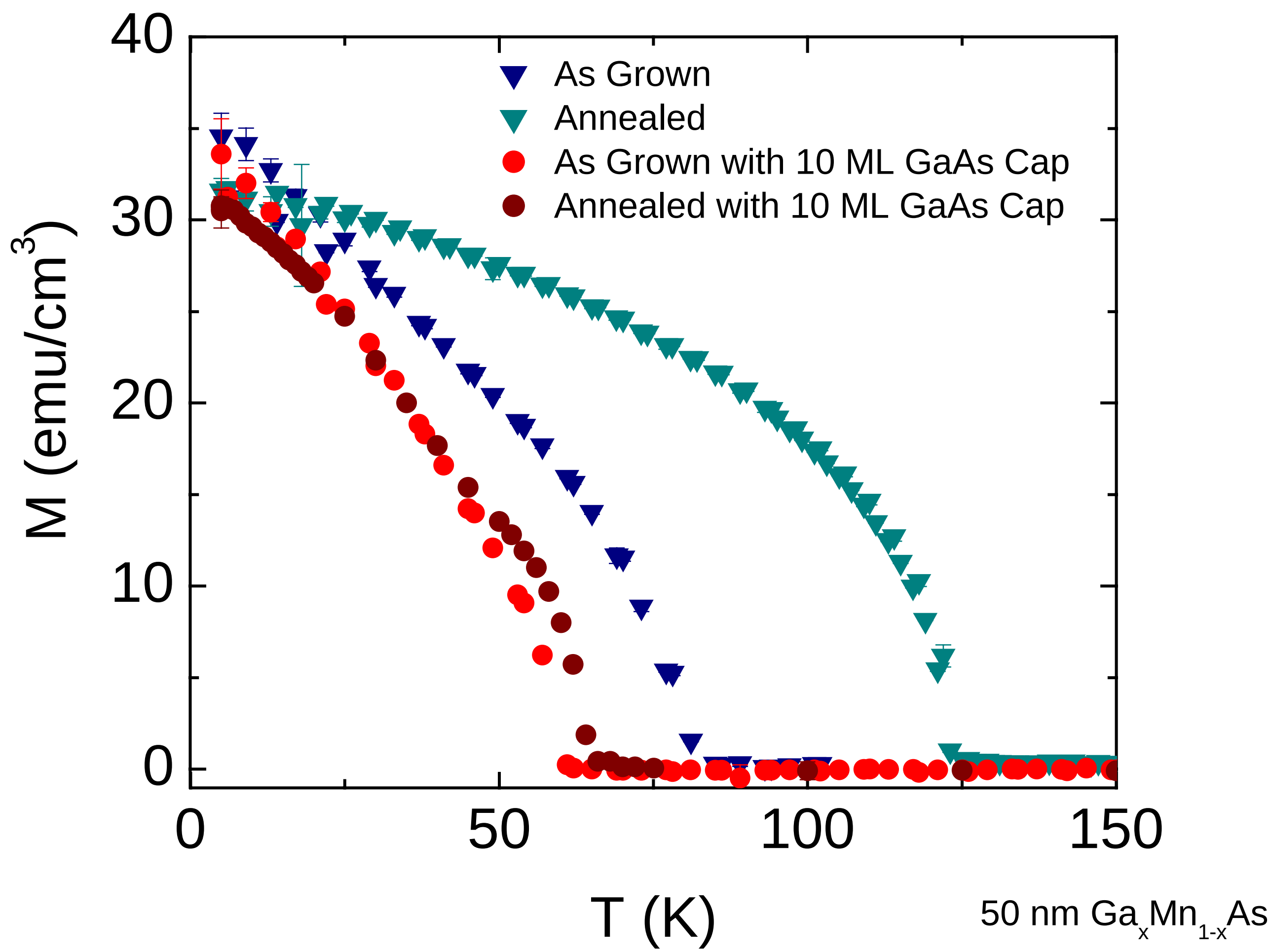
Sørensen *et al.* APL 2003
Mathieu *et al.* PRB 2003



Free surface seems to be important

Study samples with thin capping layer of GaAs

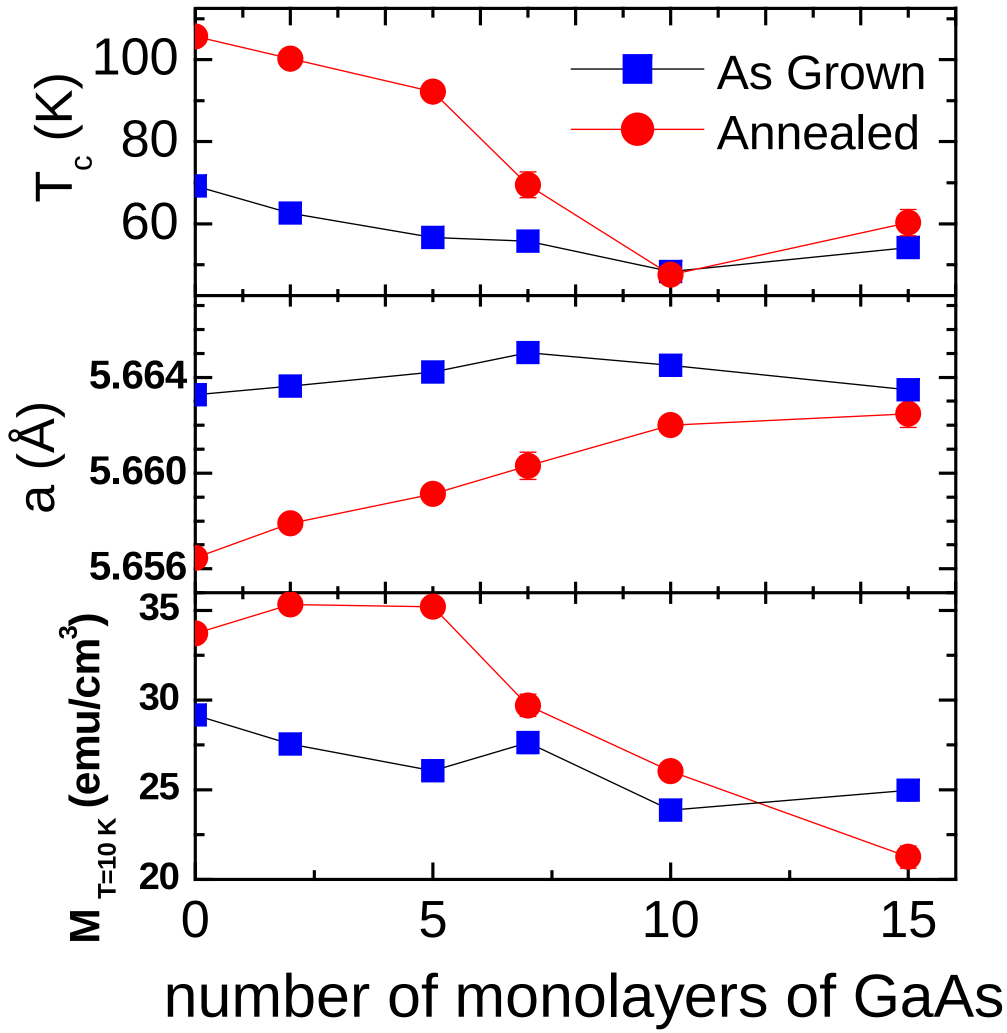
Stone *et al.* APL 2003



Free surface is changing physics?

Erwin and Petukhov, PRL 2002

Capping layer changes annealing effect on thin layers



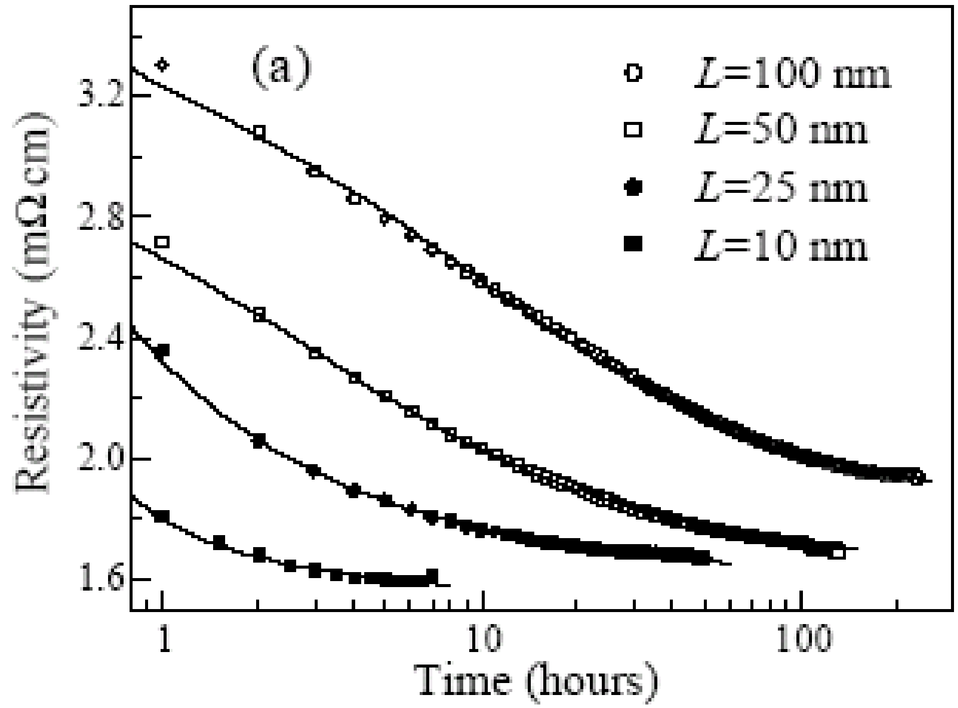
$Ga_{1-x}Mn_xAs$ (50 nm)

Similar results from D. Chiba *et al.*, Appl. Phys. Lett. 82, 3020 (2003)

Very recent: Annealing improvement of properties seems to be the result of diffusion process

Long anneals while monitoring the resistance – show time dependence consistent with diffusion of Mn interstitials

Edmonds *et al.*, PRL 2004



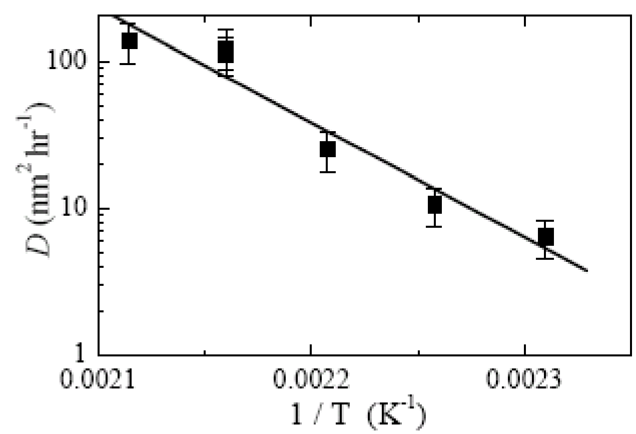
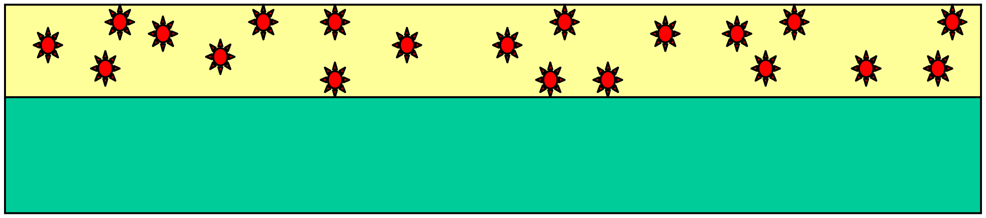
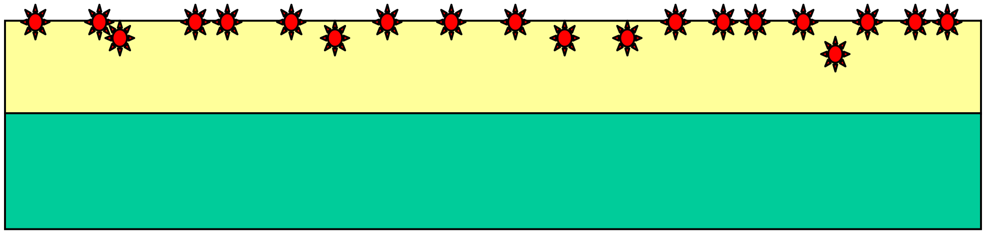


Figure 2. Diffusion coefficient for 25nm thick $Ga_{0.933}Mn_{0.067}As$ films versus 1/T, for temperature

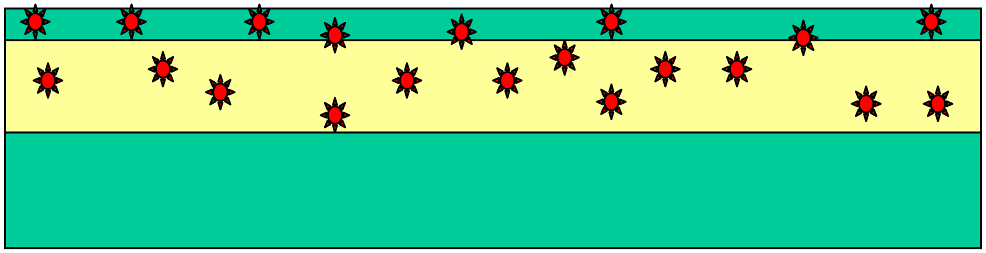
How to understand the effects of annealing and capping: Mn interstitials trying to go to surface



In unannealed samples, the Mn interstitials compensate holes



Annealing thin samples allows Mn interstitials to diffuse to the surface



Capping layer will become n-doped with interstitials – prevents all from diffusing out

Other groups also raising T_c

- **Long slow anneals at really low temperatures → T_c = 140-160 K (Edmonds *et al.* APL 2002, PRL 2004)**

- **Annealed trilayers where top layer has T_c ~ 160 K (Chiba, Takamura, Matsukara, and Ohno, APL 2003)**

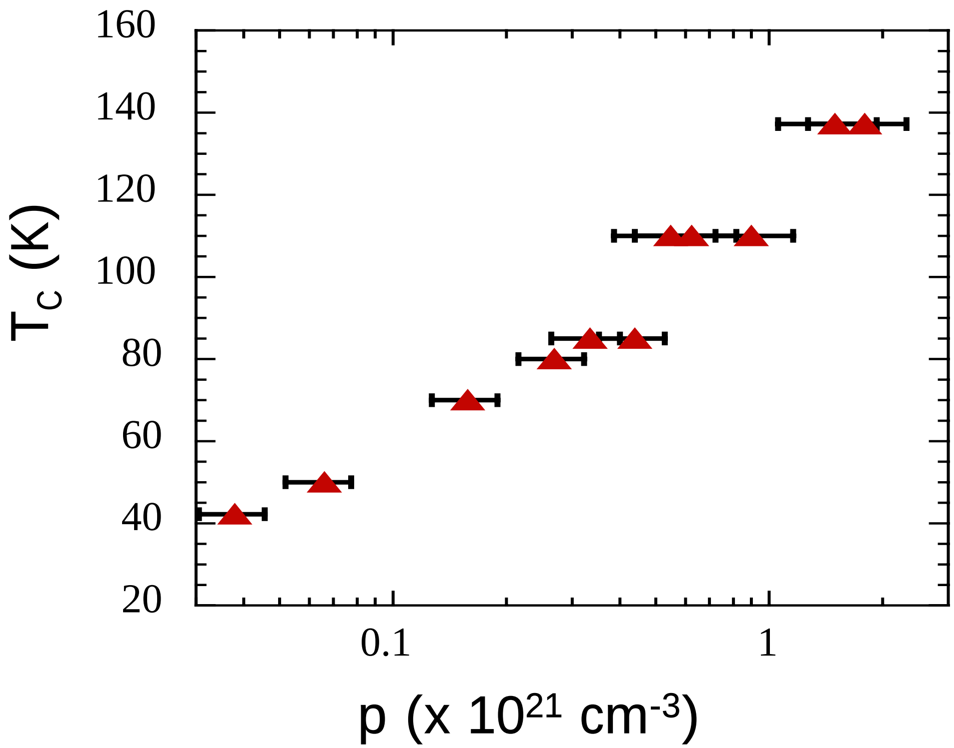
- **δ-doped heterostructure → T_c = 172 K (Nazmul, Sugahara, and Tanaka, PRB 2003)**

What controls T_c in $Ga_{1-x}Mn_xAs$?

Lots of theory:

Dietl *et al.* (Science, 2000) **$T_c \sim xp^{1/3}$**

Also MacDonald, Das Sarma, and many others…



Need to increase p by an order of magnitude for room temperature ferromagnetism?

What is next for $Ga_{1-x}Mn_xAs$?

- T_c will be very hard to raise to above room temperature

- Continue to serve as basis for prototypical semiconductor spintronic devices

- Continue to serve as model materials system for ferromagnetism in a semiconductor

  potentially lots of new physics

$Ga_{1-x}Mn_xAs$ is already the basis for semiconductor spintronic prototype devices

letters to nature

Electric-field control of ferromagnetism

H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl*, Y. Ohno & K. Ohtani

Electrical spin injection in a ferromagnetic semiconductor heterostructure

Y. Ohno*, D. K. Young†, B. Beschoten†, F. Matsukura*, H. Ohno* & D. D. Awschalom†

VOLUME 87, NUMBER 2 PHYSICAL REVIEW LETTERS 9 JULY 2001

Large Tunneling Magnetoresistance in GaMnAs/AlAs/GaMnAs Ferromagnetic Semiconductor Tunnel Junctions

VOLUME 89, NUMBER 10 PHYSICAL REVIEW LETTERS 2 SEPTEMBER 2002

Resonant Enhancement of Tunneling Magnetoresistance in Double-Barrier Magnetic Heterostructures

VOLUME 90, NUMBER 10 PHYSICAL REVIEW LETTERS week ending 14 MARCH 2003

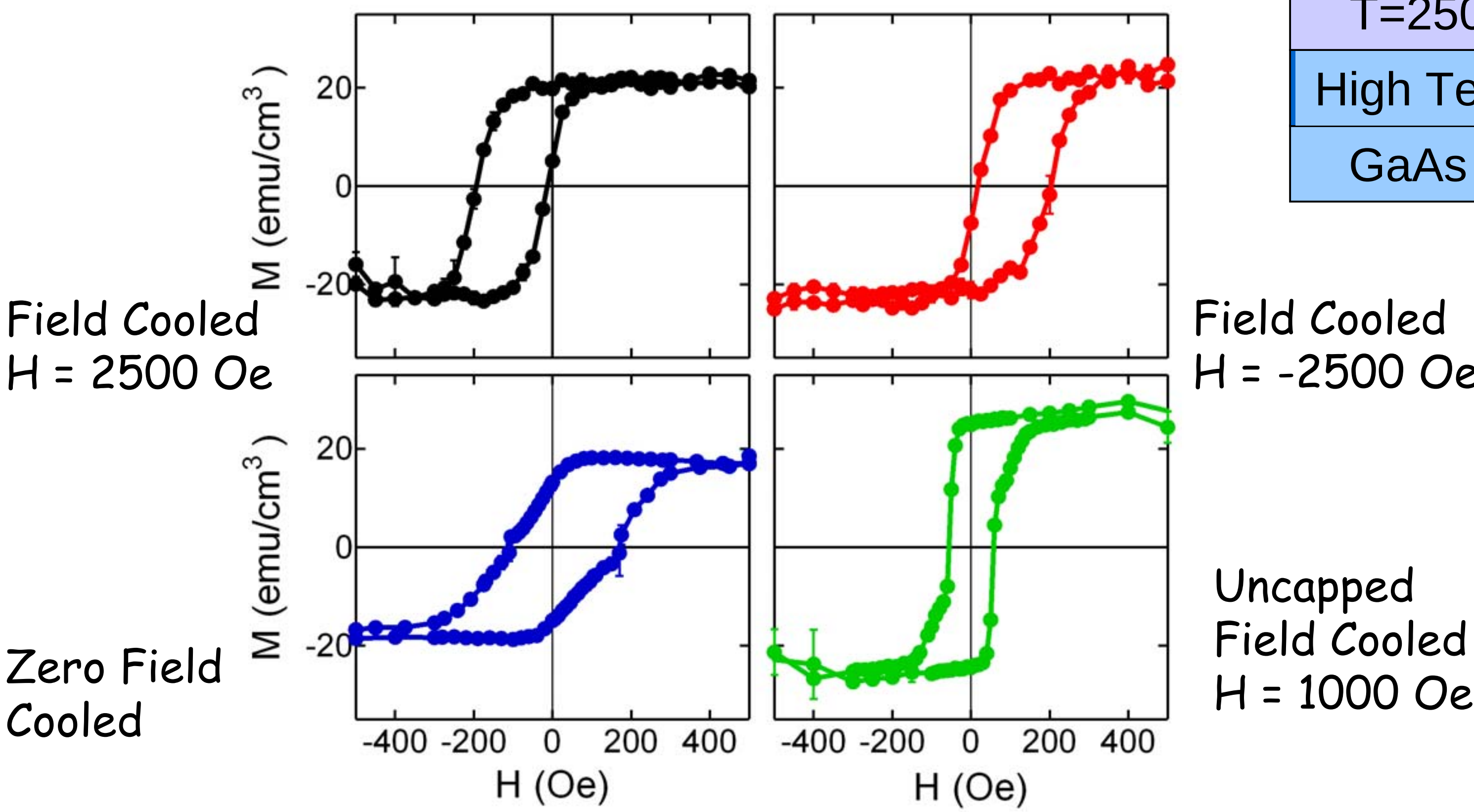
Giant Planar Hall Effect in Epitaxial (Ga,Mn)As Devices

H. X. Tang,[1] R. K. Kawakami,[2] D. D. Awschalom,[2] and M. L. Roukes[1]
[1]*Condensed Matter Physics 114-36, California Institute of Technology, Pasadena, California 91125*
[2]*Department of Physics, University of California, Santa Barbara, California 93106*

Example of new results and hurdles – exchange biasing

Eid *et al.* cond-mat 0312259

AFM	~4 nm Mn
FM	10 nm $Ga_{1-x}Mn_xAs$
	T=250 C GaAs buffer
	High Temp GaAs buffer
	GaAs (001) substrate



Associated with oxidized Mn overlayer -- clearly a lot of materials physics to be studied

Conclusions

Physics of ferromagnetism in $Ga_{1-x}Mn_xAs$ is complex, but we are making progress

- **Low temperature anneals substantially alter physical properties**
  defects are crucial to physics and neighboring layers matter

- **In annealed samples, magnetic behavior looks very conventional,**
  but many Mn not contributing to FM state

- **Provides a model system for studying physics and prototype devices**
  but not clear can enhance T_C to room temperature and above
  Need to look to other materials systems….