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Advanced Workshop on

Recent Developments in Nanomaterials

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Synthesis & Properties of Nanoscale Transition Metal Pnictides: Novel Magnetic Materials

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ICMR-ICTP Advanced Workshop on Recent Developments in Nanomaterials

Why Nano? Size-Dependent Phenomena

- Structural stability
  - *Non-thermodynamic structures can be accessed*
- Melting and phase transformation temperature and pressure
  - *Melting point depression*
  - *Solid-solid phase transformation pressure elevation*
- Catalytic
  - *Increased activity due to large surface to volume ratio*
- Optical/electronic
  - *Quantum confinement effect in semiconductors*
  - *Surface plasmon resonance in metals*
- Magnetic
  - *Coercive effect in ferromagnets*
  - *Magnetoresistive effect in nanocomposites*

Grand Challenges for Nanotechnology

Nanoparticle

components

I: New chemistry to expand the range of properties available to components

- ternary, quaternary compositions
- unique architectures (core:shell)
- size and shape modulation

II: Development of versatile nanoparticle assembly techniques

- integration into devices
- interfacing different properties together for synergy
- maintaining nanoparticle properties in a connected network

State of the Science

Single-phase nanomaterials

Elements/Alloys

Au, Pt

catalytic

Fe, $SmCo_5$

magnetic

Si, Ge

semiconducting

Compounds

Oxides

TiO_2, SnO_2

photocatalytic

Fe_2O_3, MFe_2O_4

magnetic

Chalcogenides and pnictides

ZnS, CdSe

II-VI semiconductors

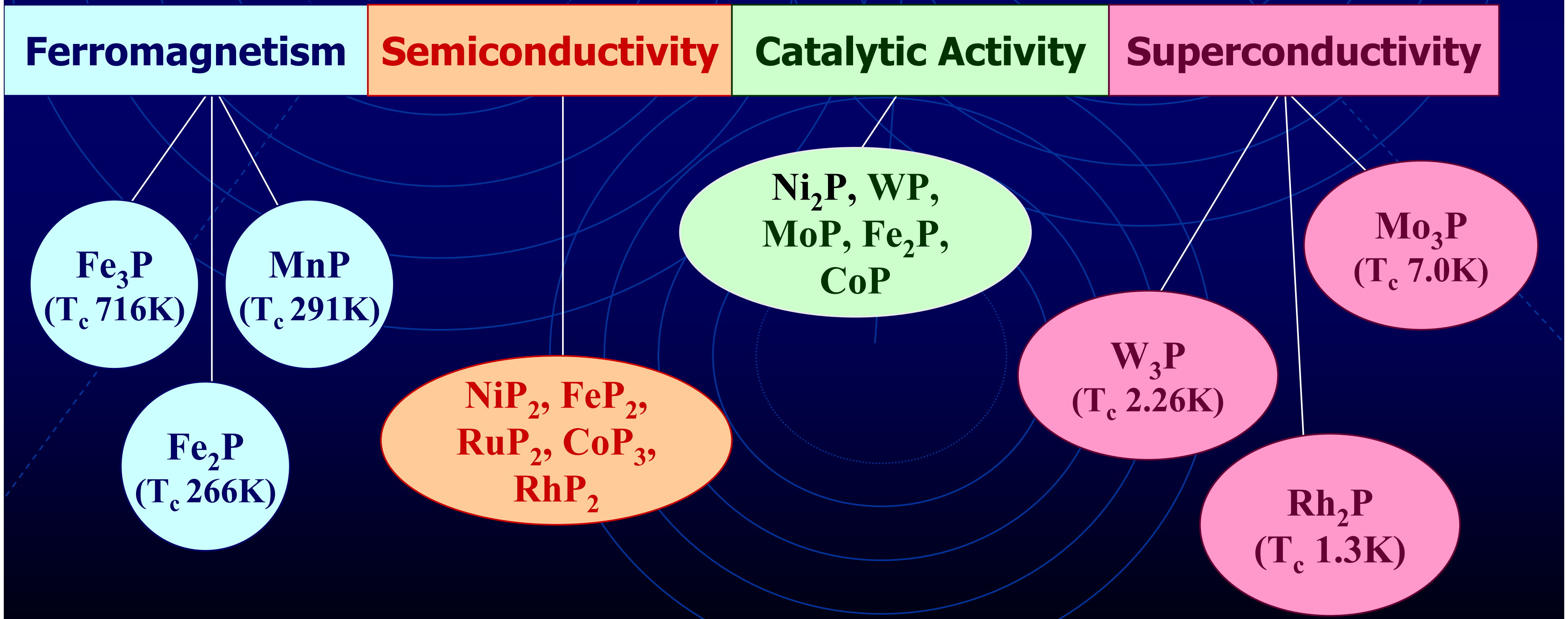
InP, GaAs

III-V semiconductors

Transition Metal Phosphides

Rich class of materials with a wealth of stoichiometries and structures

Wide range of interesting and device-relevant physical properties – *size-dependent properties largely unexplored*



- **Ferromagnetism**
  - Fe_3P (T_c 716K)
  - MnP (T_c 291K)
  - Fe_2P (T_c 266K)
- **Semiconductivity**
  - NiP_2, FeP_2, RuP_2, CoP_3, RhP_2
- **Catalytic Activity**
  - Ni_2P, WP, MoP, Fe_2P, CoP
- **Superconductivity**
  - Mo_3P (T_c 7.0K)
  - W_3P (T_c 2.26K)
  - Rh_2P (T_c 1.3K)

Diluted Magnetic Semiconductors

Spin polarization of conducting electrons by magnetic component

Potential spin-dependent applications:

- Magneto-Electronic, Magneto-Optical devices
  - E.g. High density nonvolatile magnetic memory, magnetic sensors, etc.

Semiconductor: typically II-VI or III-V

Magnetic ion (dopant) of choice: Mn^{2+} d^5

- when coupled to a hole, ferromagnetism can result

Theoretical calculations suggest 5% Mn and 3.5×10^{20} holes/cm^3 are needed to achieve a system with spontaneous room-temperature ferromagnetism in GaN or ZnO*

*Dietl et. al. *Science*, **2000**, *287*, 1019

Phase-Segregation Problems in DMS

In III-V systems, isovalent substitution of Mn^{3+} results in formation of Mn^{2+} with a hole introduced to valence band.

Equilibrium growth of III-V DMS results in phase segregation of MnPn (Pn = P, As), but up to 5.3 % can be incorporated in GaAs:Mn prepared by low-temperature MBE (Tc max = 110 K) and conduction electron spin-polarization has been observed and exploited in a device.

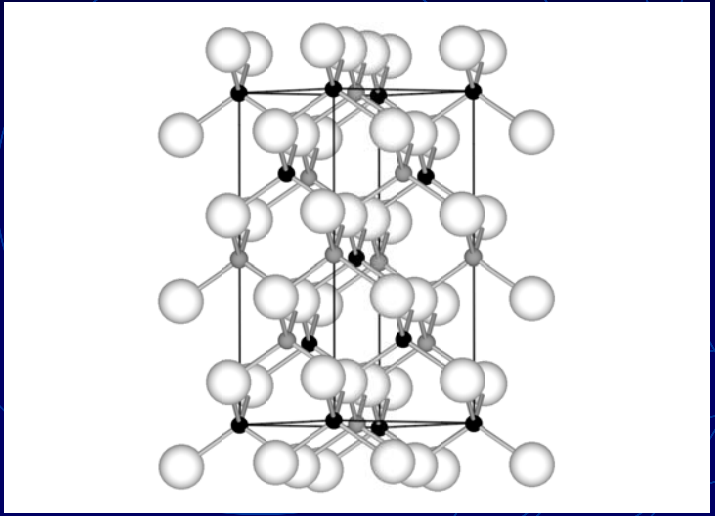
High solubility of Mn in II-VI systems, phase segregation is largely a problem in III-V….but high hole-dopant concentrations are difficult to achieve in II-VI systems

Reports of RT ferromagnetism in II-VI systems including TiO_2:Mn and ZnO:Mn, but no one has shown spin-polarization in these systems

Recent reports suggest magnetism in some systems may be due to phase segregated impurities.

Might the problem of phase-segregation be more wide-spread than we think?

Mn-doped Chalcopyrites: RT Ferromagnetic Semiconductors?



$CdGeP_2$:Mn 310, 320 K

$ZnGeP_2$:Mn 300, 312 K

$ZnSnAs_2$:Mn 329 K

$ZnGeAs_2$:Mn 333 K

Mn deposition on single crystals or polycrystalline powders followed by heating at 500 °C under N_2-flow, or reaction of elements at 1000 °C

Could these properties be due to bulk and/or nanoscale impurities of MnP or MnAs, both of which have bulk T_c transitions at or near RT?

Sato, Medvedkin – Japan-Russia collaboration
Cho, Kim, Choi, Zhao, Gen, Freeman –Northwestern U.-S. Korea-Japan collaboration

Importance of Understanding Magnetic Properties of Nanoscale Magnets for Spintronics

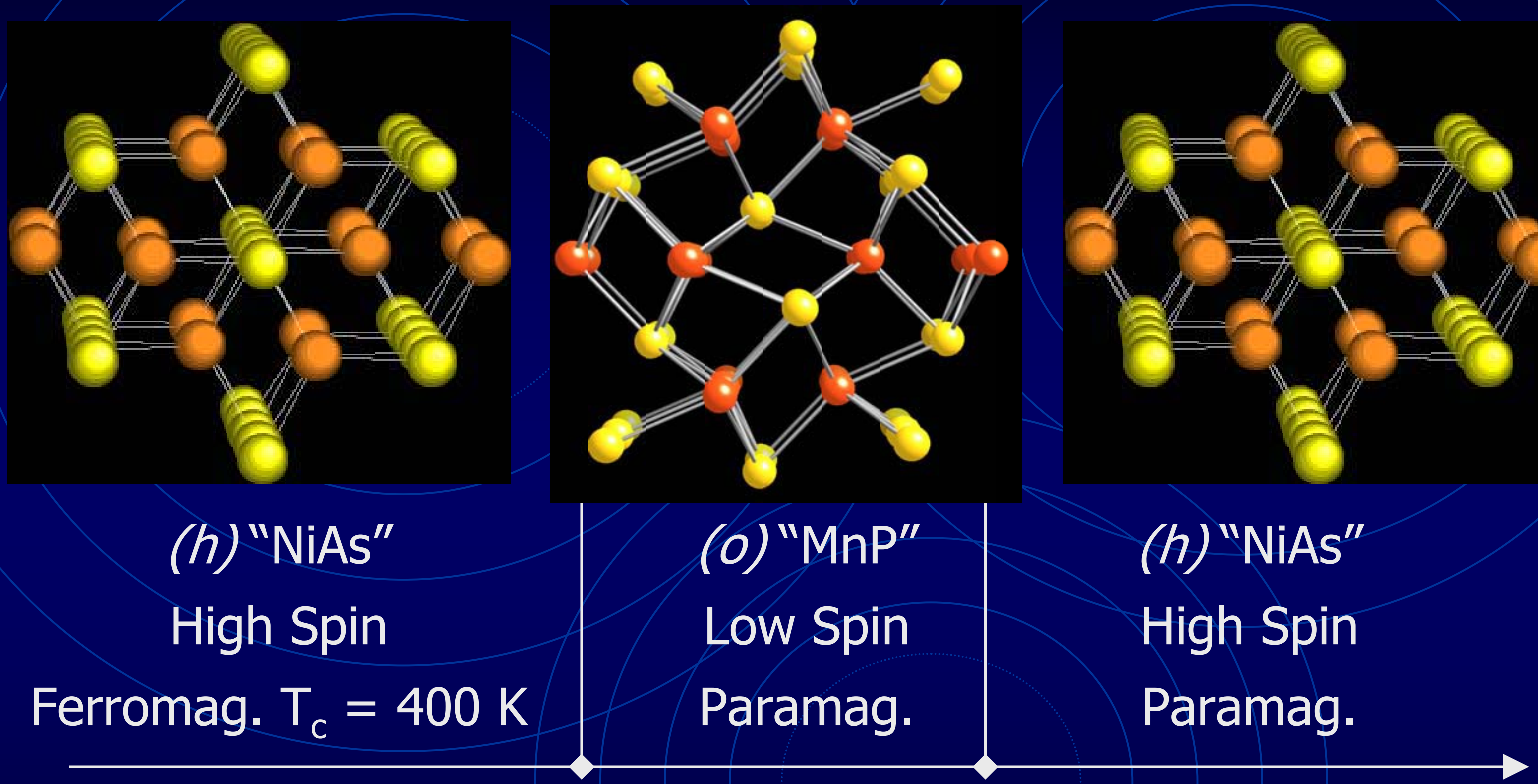
- Magnetic properties are size dependent for size <100 nm
- It can be difficult to isolate/verify occurrence of particles in the semiconductor matrix
- Most “reported” DMS materials have only been analyzed by magnetic susceptibility techniques-few reports of spin-polarization measurements. Will the nanoscale inclusions result in “spintronic” activity?
- Potential to create nanoscale magnetic semiconductors as heterostructures by introducing a semiconductor “shell” to the magnetic “core”. Mimic heterosructure thin-films, e.g., MnAs:GaAs, MnGa:GaAs

Starting points: MnP and MnAs nanoparticles

Bulk MnP: $T_N \sim 50$ K (metamagnetic), $T_C = 291$ K

Bulk MnAs: first order solid-solid phase transition, $T_C = 317$ K

Magnetic Phase Diagram for MnAs*



(h) "NiAs"
High Spin
Ferromag. T_c = 400 K

(o) "MnP"
Low Spin
Paramag.

(h) "NiAs"
High Spin
Paramag.

$T_c\uparrow$ = 317 K
$T_c\downarrow$ = 307 K

T_t ~ 400 K

Temp.

Large magnetostrictive, magnetocaloric, and magnetooptical effects are associated with the phase transition. The temperature and nature of the transition should be tunable by size.

* Goodenough & Kafalas, *Phys. Rev. B*, **1967**, *157*, 389.

How to Make MnP or MnAs Nanoparticles?

Use a soluble source of Pn^{3-}

Perform reaction in coordinating solvent that can passivate surface of resultant particle (arrested precipitation) and confer solubility

$$MX_3 + Pn(SiMe_3)_3 \rightarrow MPn + XSiMe_3$$

M = trivalent TM, Pn = P, As; X = Cl, acac

Advantages:

- non-redox route
- surface of resultant nanoparticles can be modified
- methodology previously developed for main group materials

Synthesis of Metal Phosphide Nanoparticles by Non-redox De-silylation Reactions in Coordinating Solvents

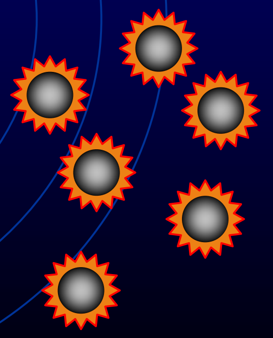
$$MX_3 + P(SiMe_3)_3 \xrightarrow{TOPO} MP + XSiMe_3$$

M = Fe, Mn
X = acetylacetonate (acac), 2,2,6,6,-tetramethyl-3,5-heptanedionate (TMHD)
TOPO = Trioctylphosphine oxide

$$MX_3 + TOPO + DA(MA) \xrightarrow[100\ ^\circ C/12\ h]{} \text{M-TOPO Complex}$$

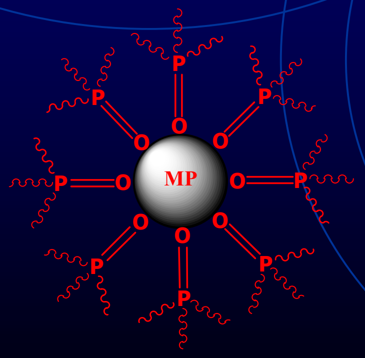
DA = dodecylamine
MA = myristic acid

$$\text{M-TOPO Complex} \xrightarrow[2\text{-}3\ \text{days}]{P(SiMe_3)_3,\ 240\text{-}280\ ^\circ C} \text{TOPO-capped MP}$$



TOPO-capped MP

$$\xleftarrow[\text{Pyridine/Hexane or Toluene/Methanol}]{\text{Isolation}}$$



Synthesis of MnP Nanoparticles by De-silylation

In Trioctylphosphine Oxide (TOPO), T = 265-320 ºC:

$Mn(acac)_3 + P(SiMe_3)_3 \rightarrow$ dark brown solution

No ppt with MeOH!

In CH_3CN, T = 80 ºC:

$Mn(acac)_3 + P(SiMe_3)_3 \rightarrow$ dark brown solution and white ppt

X-ray fluorescence of white ppt reveals Mn, but no P!

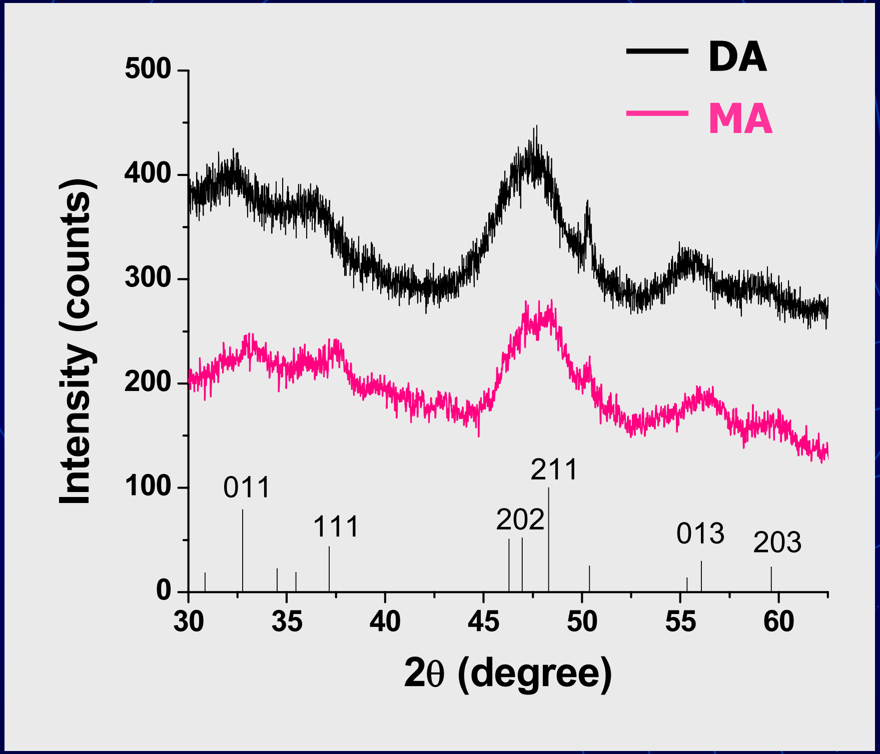
What About Iron?

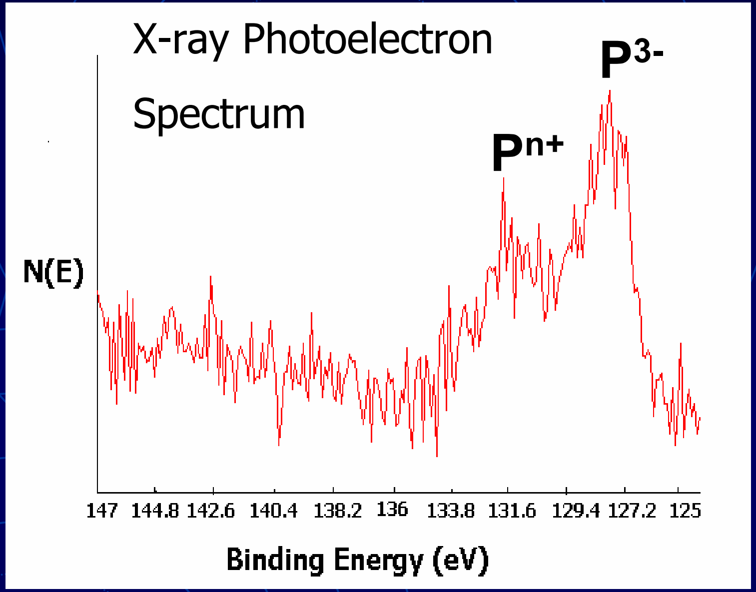
Bulk crystalline materials demonstrate a diverse range of Physical properties

Nanocrystalline Fe_xP phases are implicated in the soft ferromagnetic properties observed in Ferrophos alloys

Fe_3P	Metallic, Ferromagnetic ($T_c = 716$ K)
Fe_2P	Metallic, Ferromagnetic ($T_c = 266$ K)
FeP	Metallic, Helimagnetic ($T_N = 120$ K)
FeP_2	Semiconducting, ($E_g = 0.37$ eV) Paramagnetic

Synthesis of FeP Nanoparticles by De-silylation

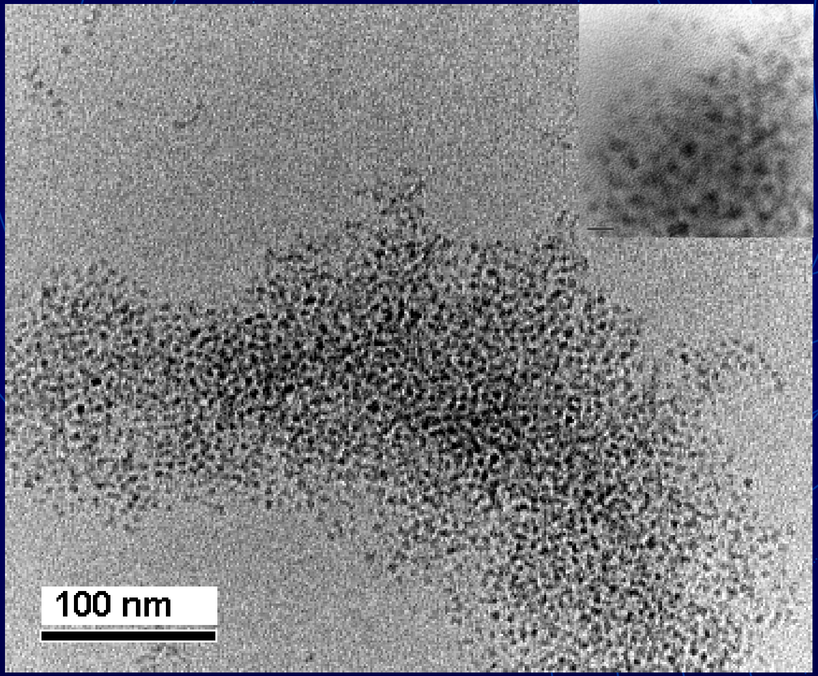


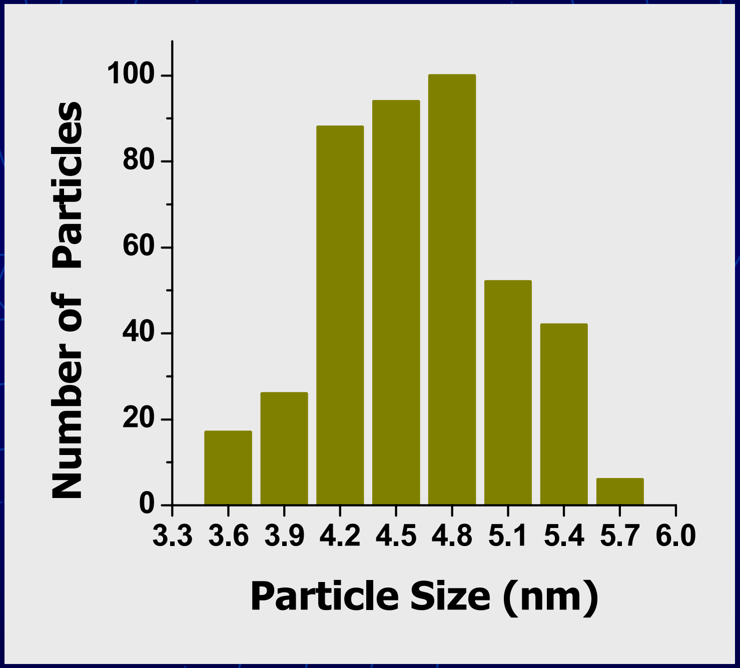


- Peak at 128.3 eV – P from FeP
- Peak at 131.6 eV – P from TOPO and surface oxides

Perera, S. C.; Fodor, P. S.; Tsoi, G. M.; Wenger, L. E.; Brock, S. L. *Chem. Mater.* **2003,** *15*, 4034-4038

TEM Imaging and Particle Size Distribution of FeP Nanoparticles

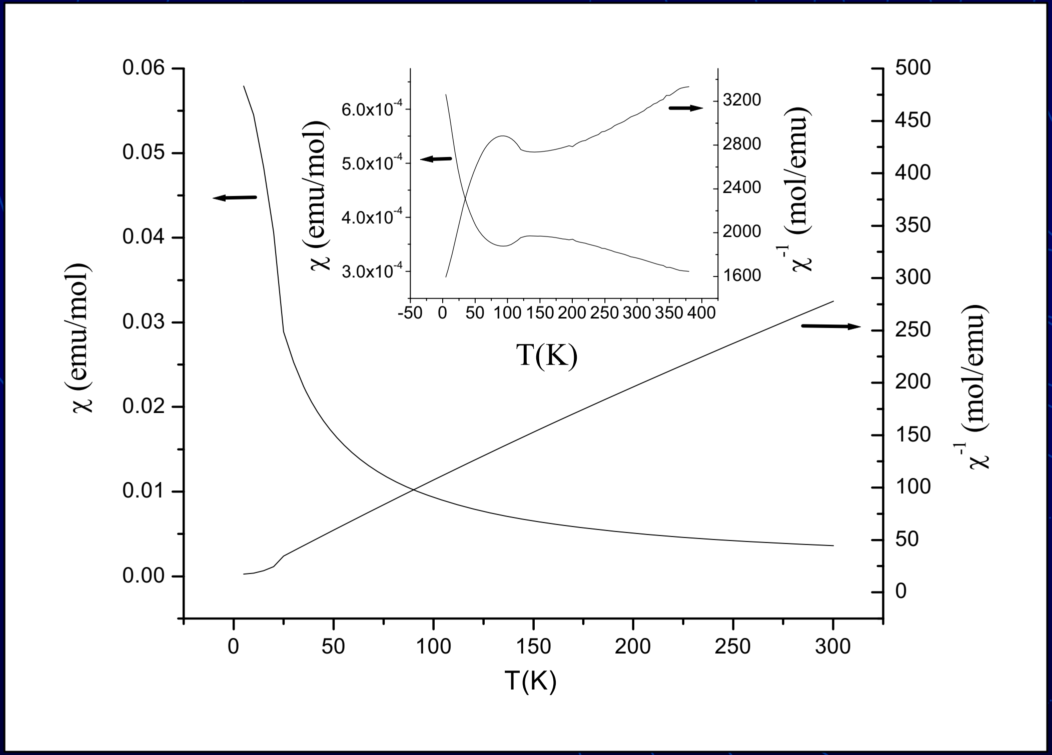




Average particle size 4.65 ± 0.74 nm (~ 16% standard deviation)

Perera, S. C.; Fodor, P. S.; Tsoi, G. M.; Wenger, L. E.; Brock, S. L. *Chem. Mater.* **2003,** *15*, 4034-4038.

Effect of Dimensional Limiting on Magnetic Properties in FeP



Magnetic susceptibility of ~ 5 nm FeP and bulk FeP (inset)

FeP: helimagnetic, T_N ~ 125 K

Spin rotation along *c*, magnetic cell dimension ~2.9 nm

Metamagnetic transition is suppressed!

Targeting Reduced Phosphides

“Redox Neutral” methods do work for FeP. Can we use this methodology to prepare nanoparticles of the reduced iron phosphides Fe_2P and Fe_3P, which *are* ferromagnetic?

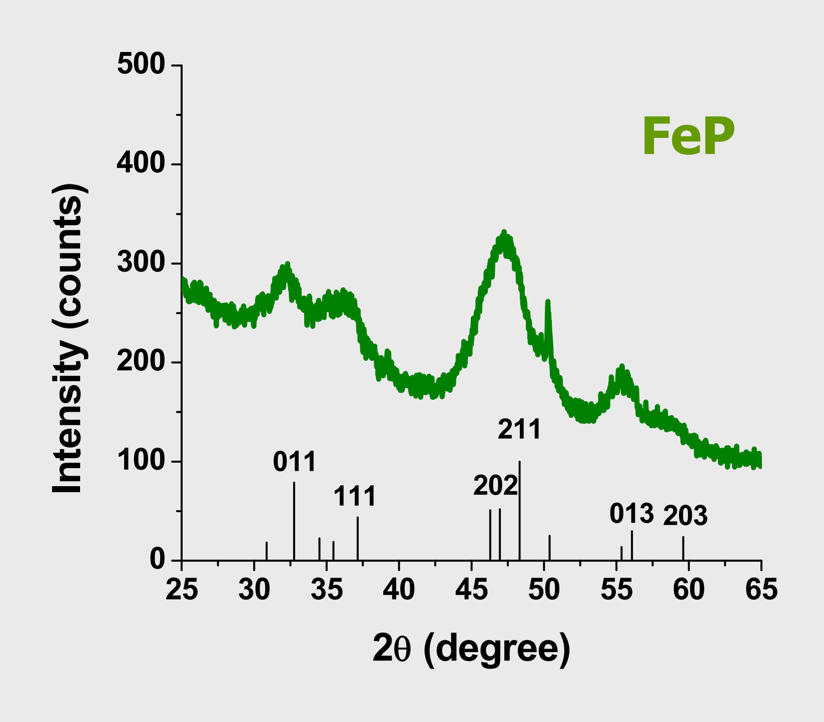
Complexes with the requisite $Fe^{+1.5}$ and Fe^{+1} formal oxidation state for targeting Fe_2P and Fe_3P are rare

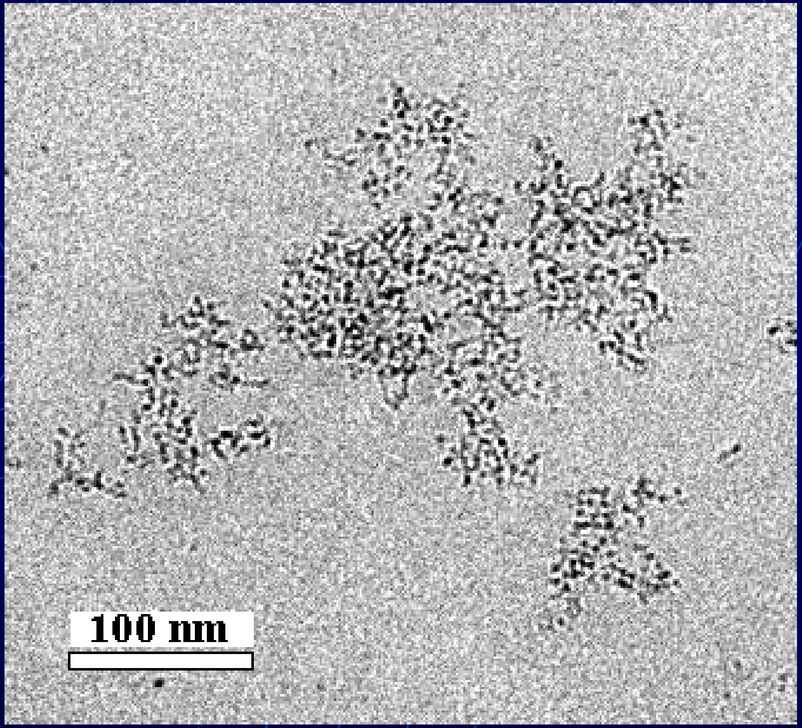
Can we prepare “lower valent” phosphides by mixing oxidation states?

$FeCl_3 + Fe(CO)_5 + P(SiMe_3)_3 \rightarrow \xcancel{Fe_2P?}$ FeP!

Perera, S. C.; Fodor, S. P.; Tsoi, G.; Wenger, L. E.; Brock, S. L. *Chem. Mater.* **2003**, *15*, 4034-4038.

“Control” Reaction of $P(SiMe_3)_3$ with $Fe(CO)_5$ in TOPO (270 °C)

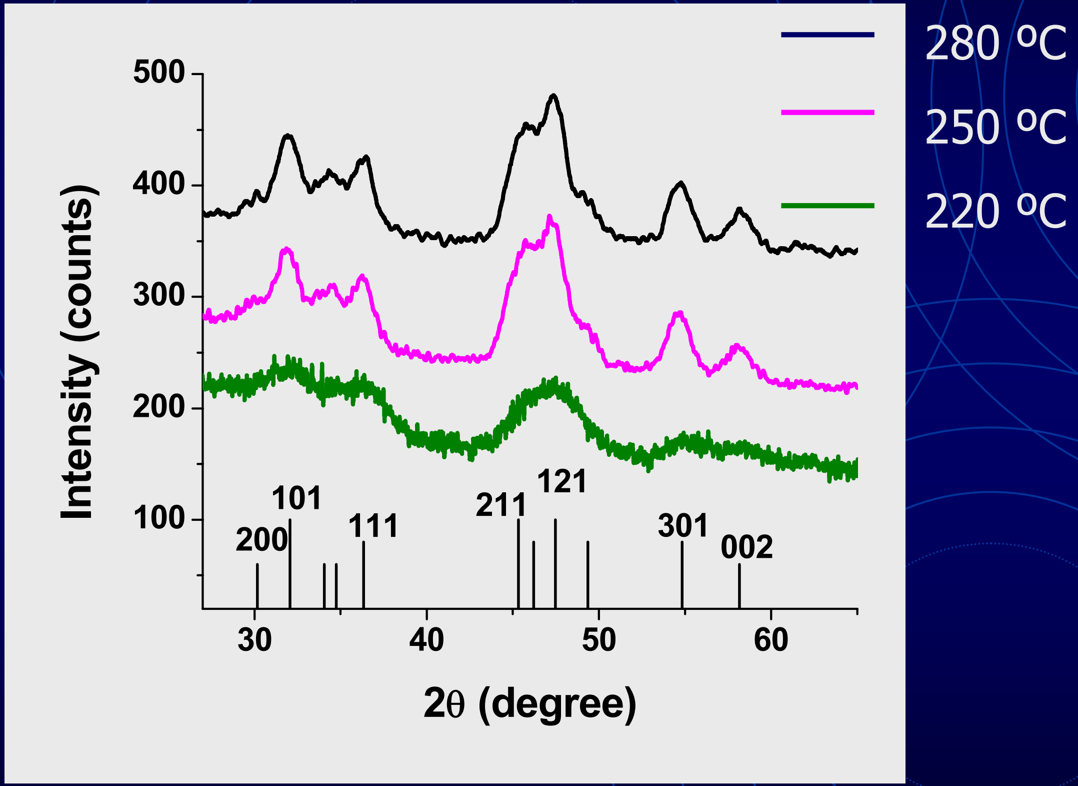




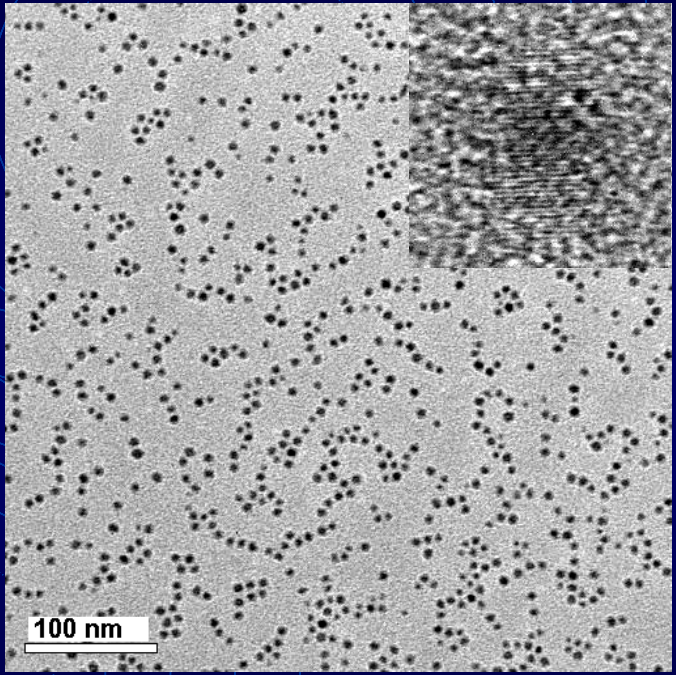
Average particle size 3.16 ± 0.33 nm

Under these conditions, the reactions are not redox innocent

$$Mn_2(CO)_{10} + TOPO \xrightarrow[240\text{-}280\ ^{o}C]{P(SiMe_3)_3} MnP$$ (92%)



The line diagram is for reflections of MnP (PDF # 07-0384)

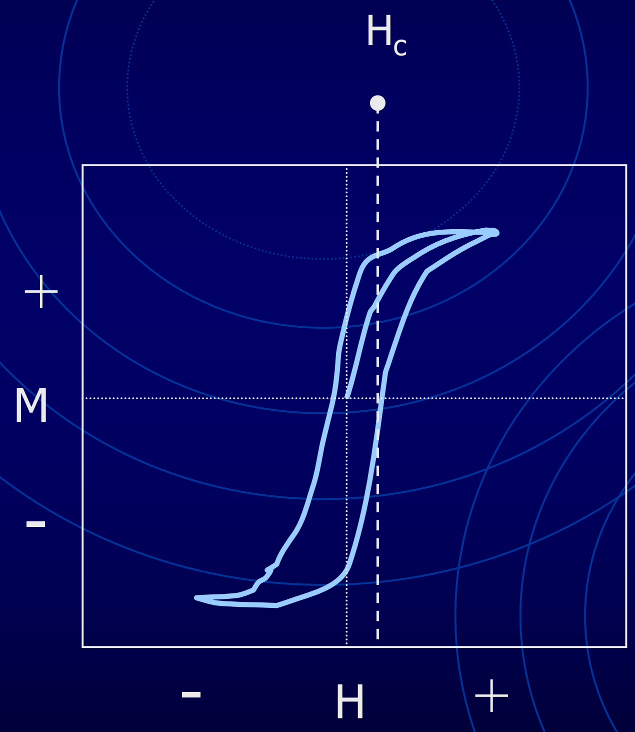


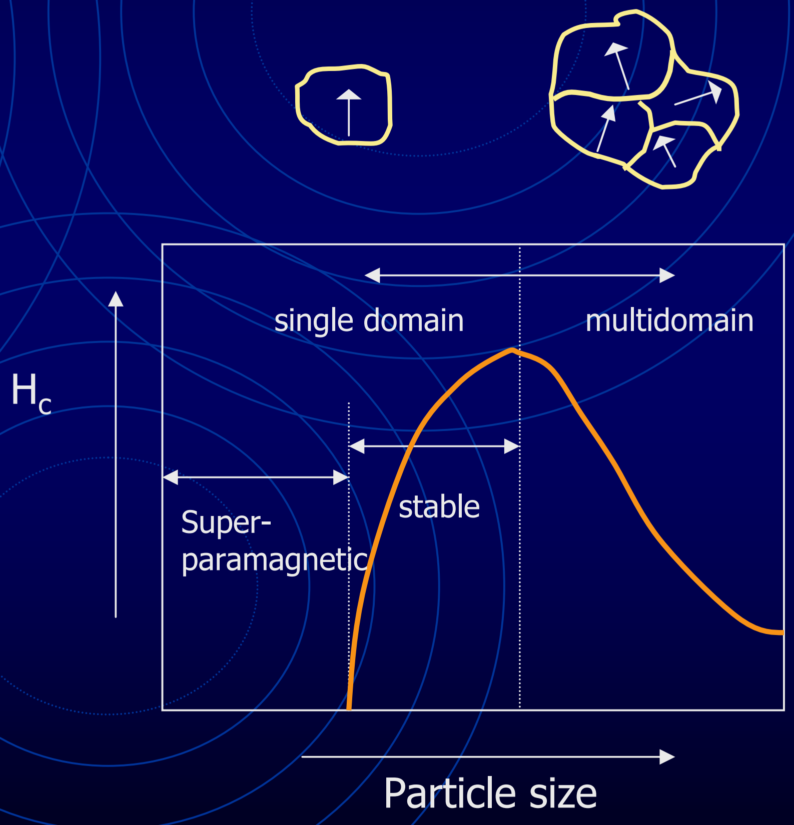
220 °C, 5.11 ± 0.48 nm

250 °C, 6.67 ± 0.33 nm

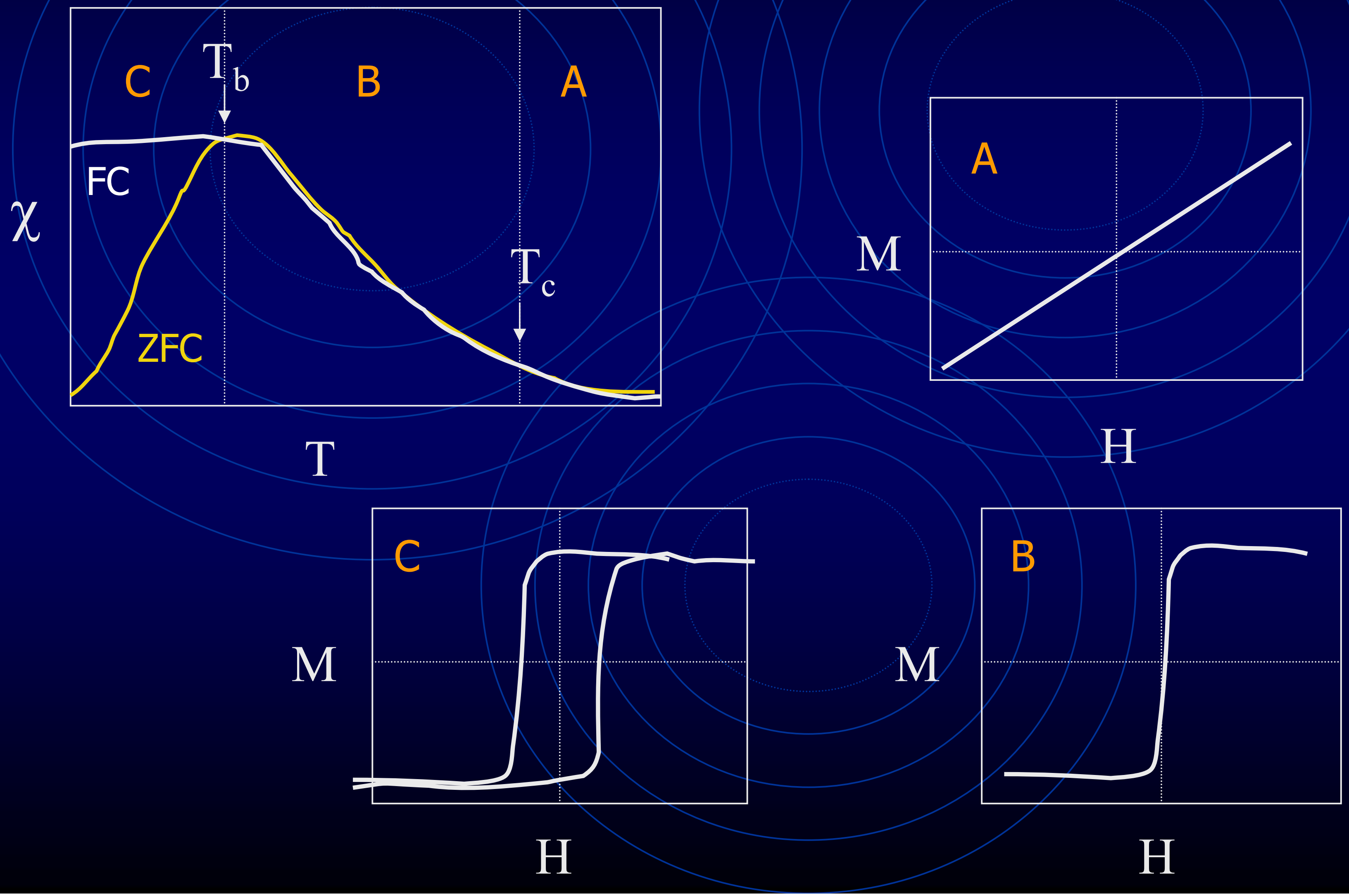
Perera, S. C.; Tsoi, G.; Wenger, L. E.; Brock, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13960-13961.

Effects of Dimensional Reduction on the Coercivity in Ferromagnets



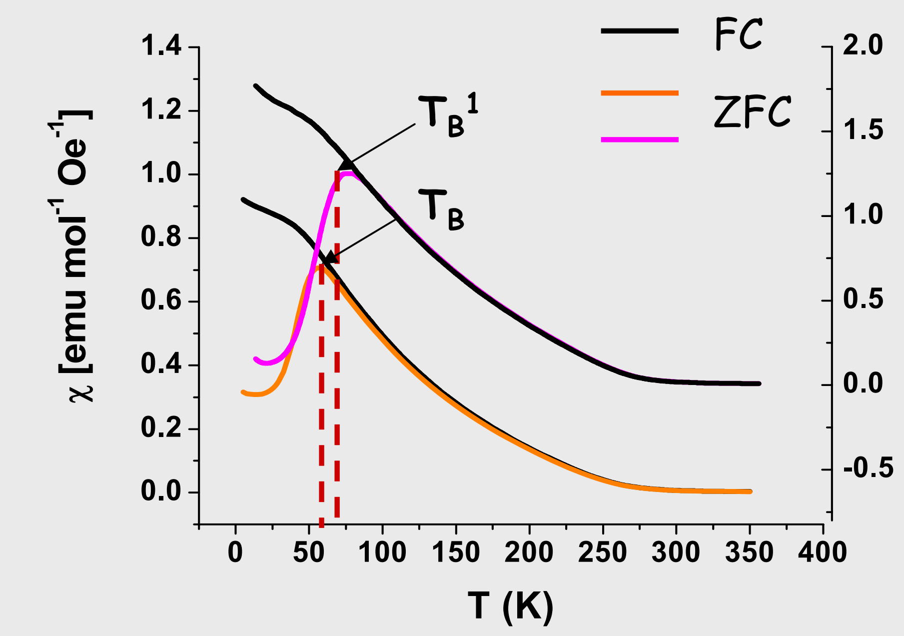


Magnetic Behavior of Nanoscale Ferromagnets

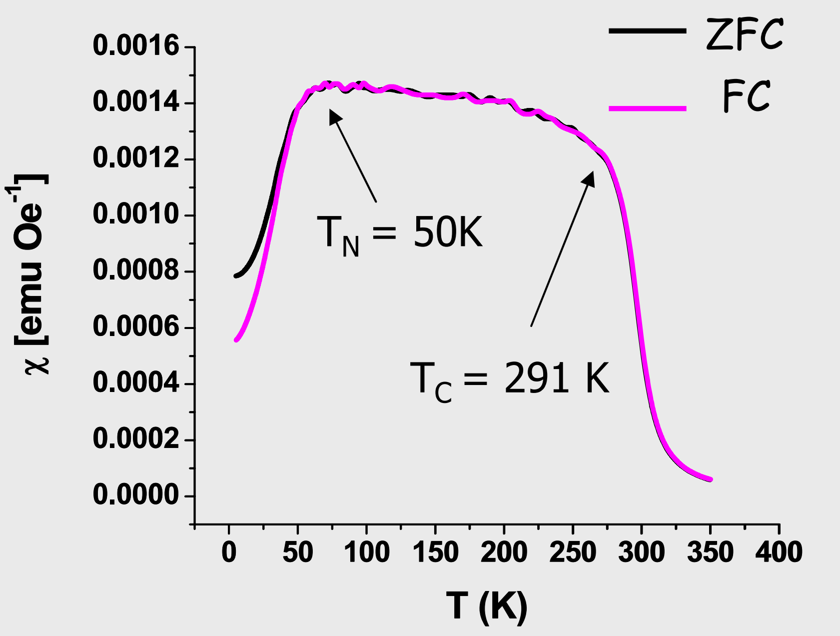


Variation of Magnetic Susceptibility (χ) with Temperature

Nano (H = 500 Oe)



Bulk (H = 5000 Oe)



T_B (60.8 K) = Blocking temp. for 5.1(5) nm

T_B^1 (74.3 K) = Blocking temperature for 6.7(3) nm

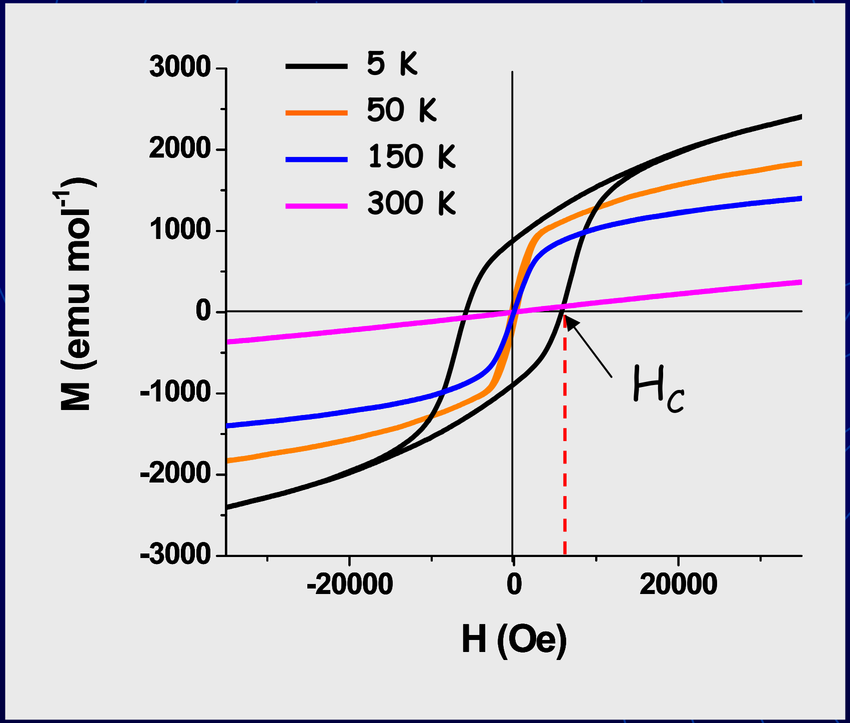
ZFC = Zero Field Cooled

FC = Field Cooled

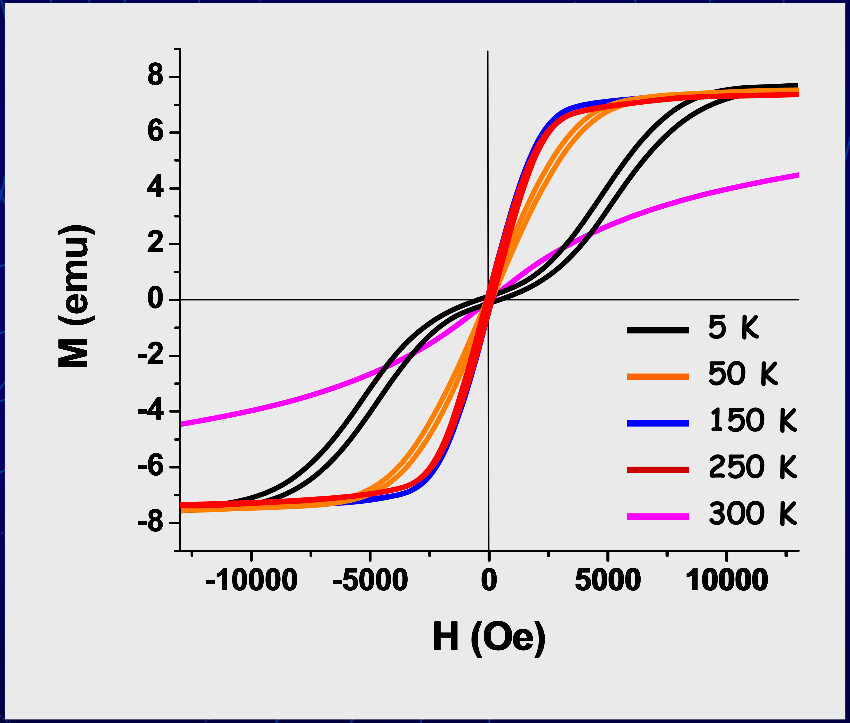
Perera, S. C.; Tsoi, G.; Wenger, L. E.; Brock, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13960-13961.

Variation of Magnetic Moment (M) with Field (H)

Nano= (5.11 nm)



Bulk



5.1(5) nm; H_C = 6000 Oe (at 5 K)

Bulk; H_C = 111 Oe (at 50 K)

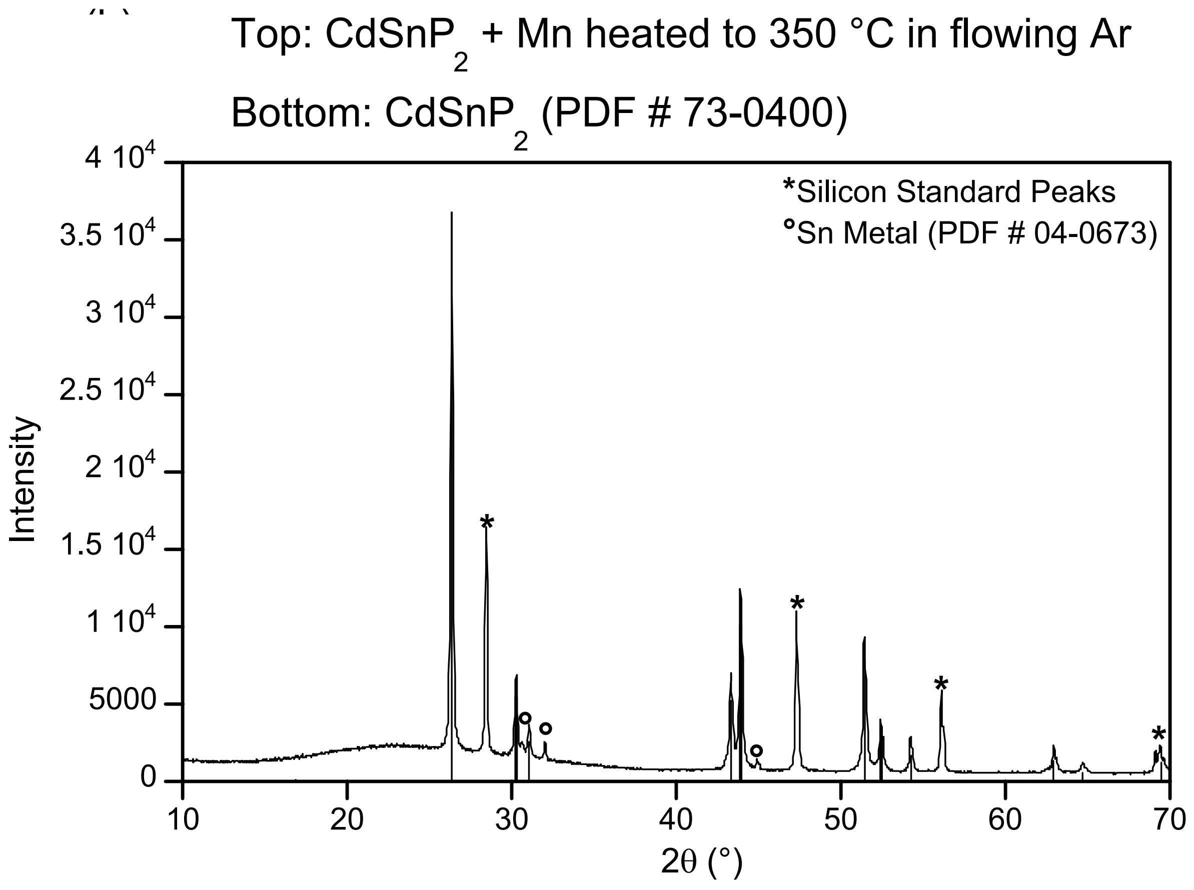
6.7(3) nm; H_C = 4860 Oe (at 5 K)

Perera, S. C.; Tsoi, G.; Wenger, L. E.; Brock, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13960-13961.

Synthesis of “bulk” DMS $CdSnP_2$:Mn

1. Prepare “bulk” $CdSnP_2$ from CdP_2 and Sn in an Sn-flux at 650 °C, dissolve Sn in acid.

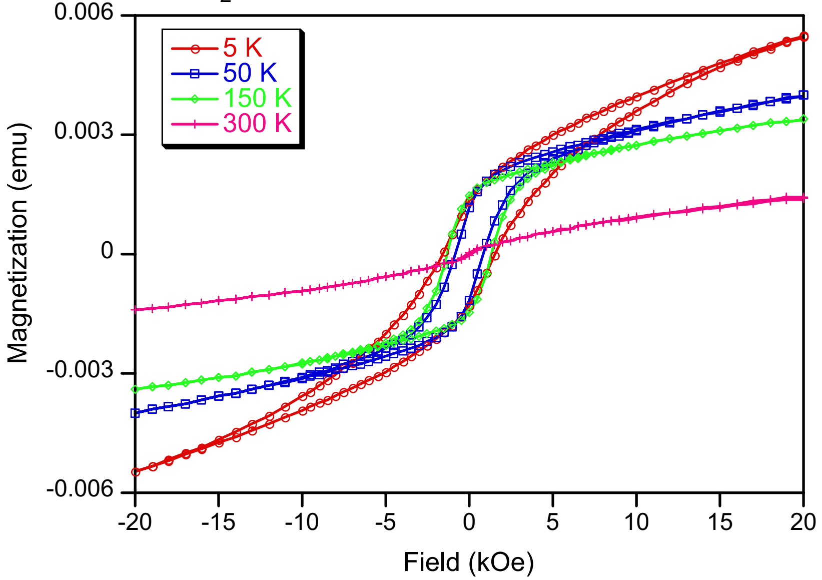
2. Combine $CdSnP_2$ with Mn and heat under flowing Ar at 350 and 500 °C in a tube furnace



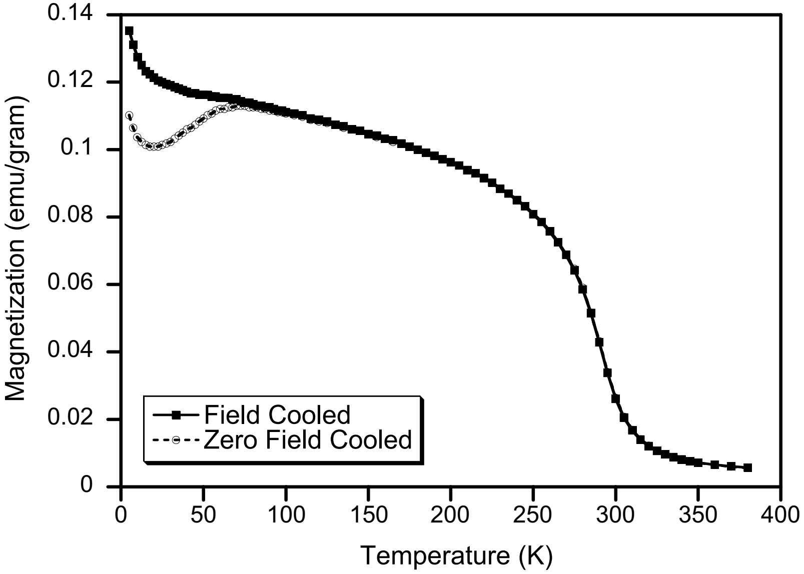
Top: $CdSnP_2$ + Mn heated to 350 °C in flowing Ar

Bottom: $CdSnP_2$ (PDF # 73-0400)

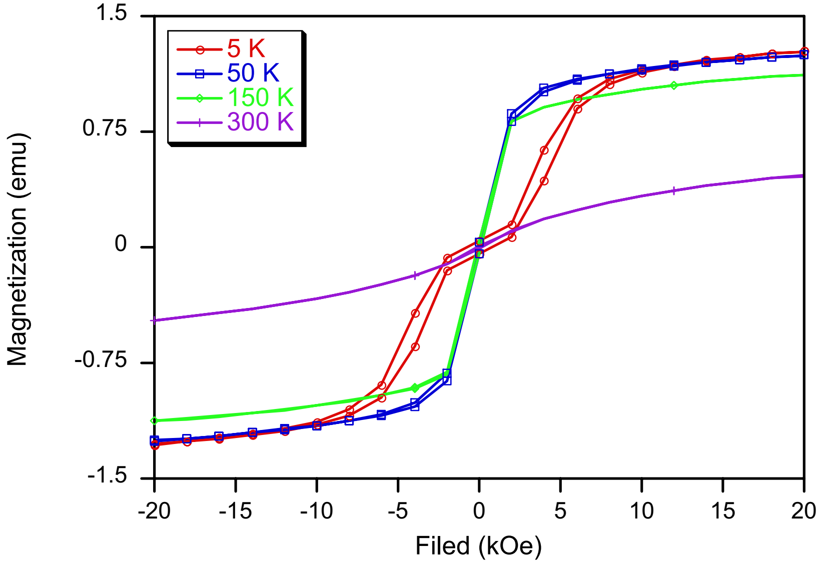
$CdSnP_2$ + Mn heated to 350 °C under flowing Ar



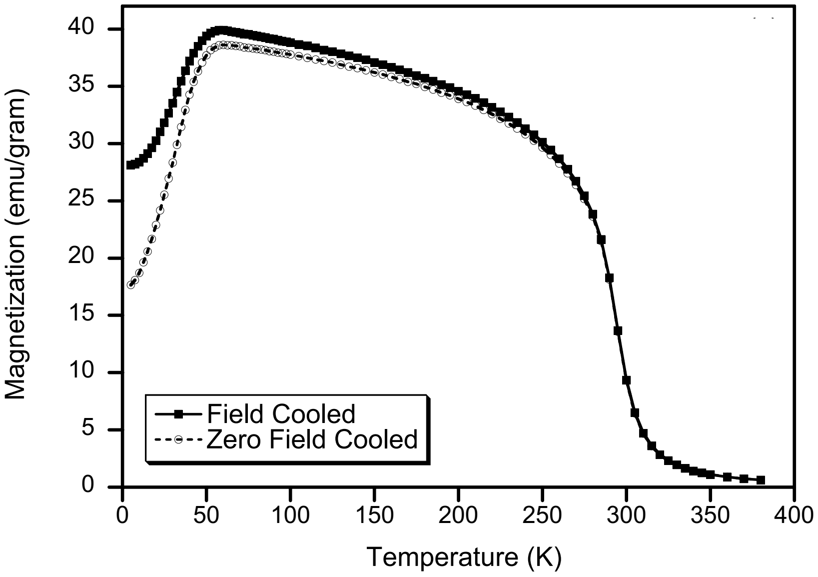
$CdSnP_2$ + Mn heated to 350 ºC under flowing Ar



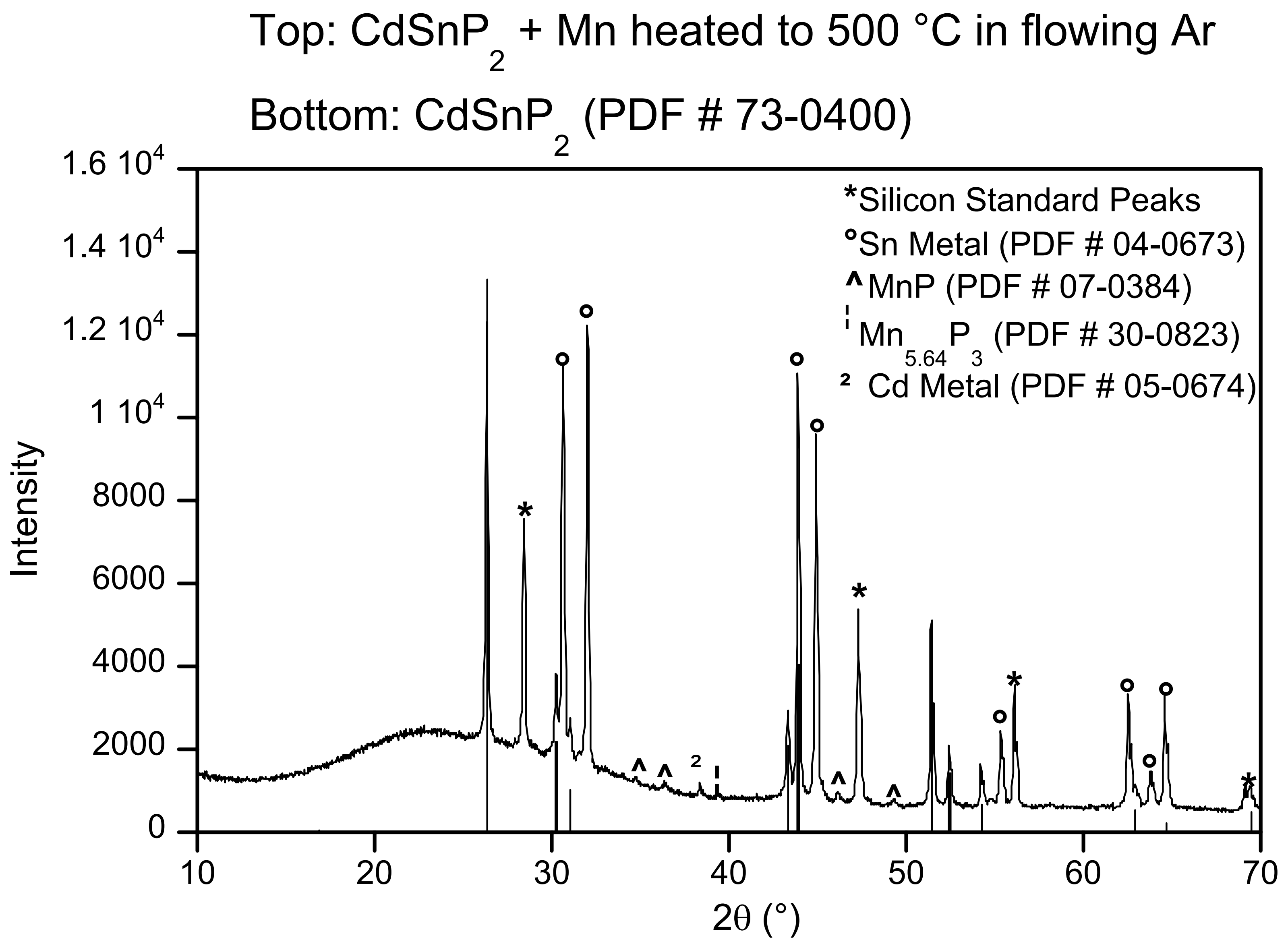
Bulk MnP prepared by solid-state reaction



Bulk MnP prepared by solid-state reaction

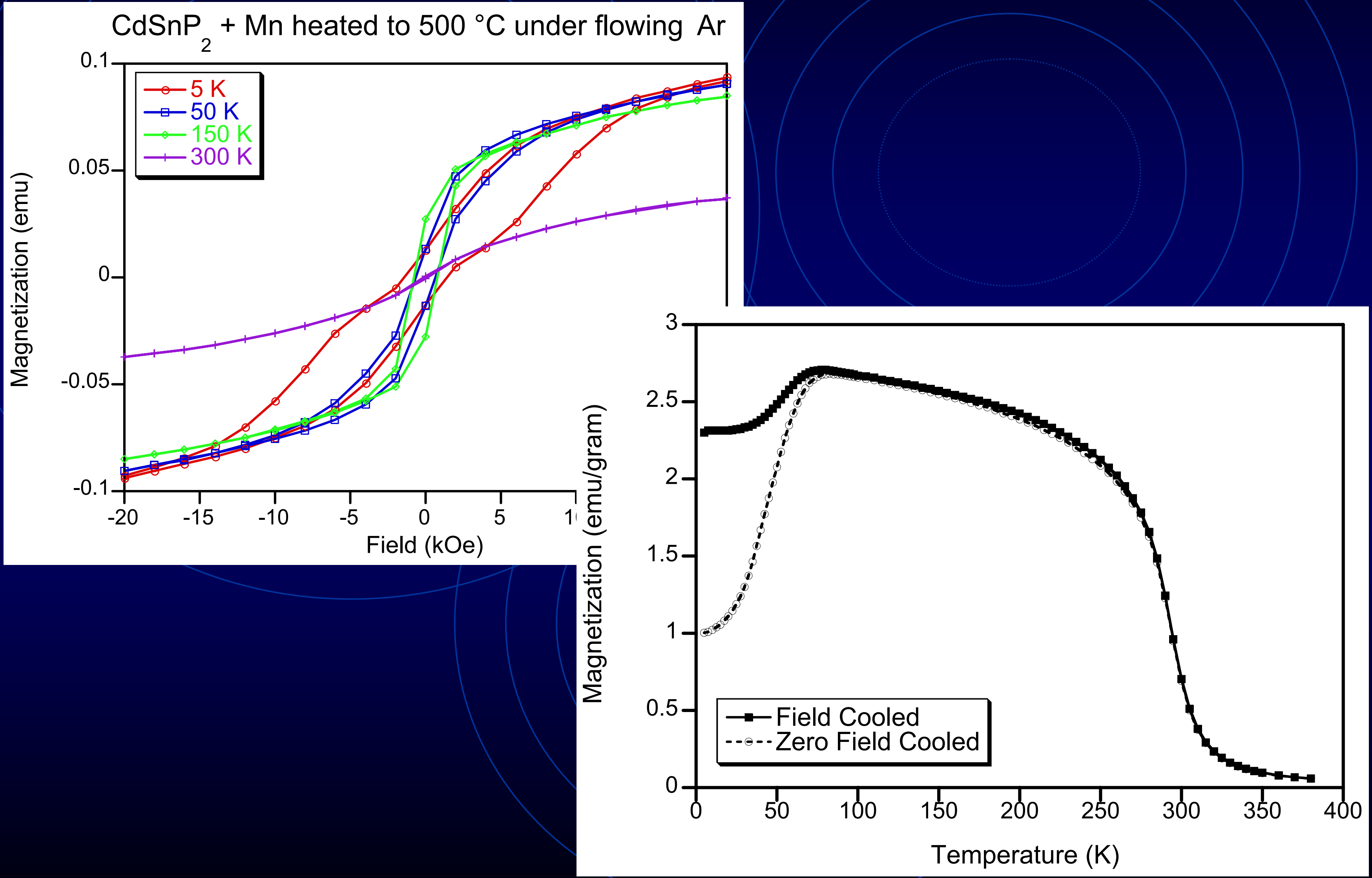


$CdSnP_2$ + Mn heated at 500 °C


Top: $CdSnP_2$ + Mn heated to 500 °C in flowing Ar

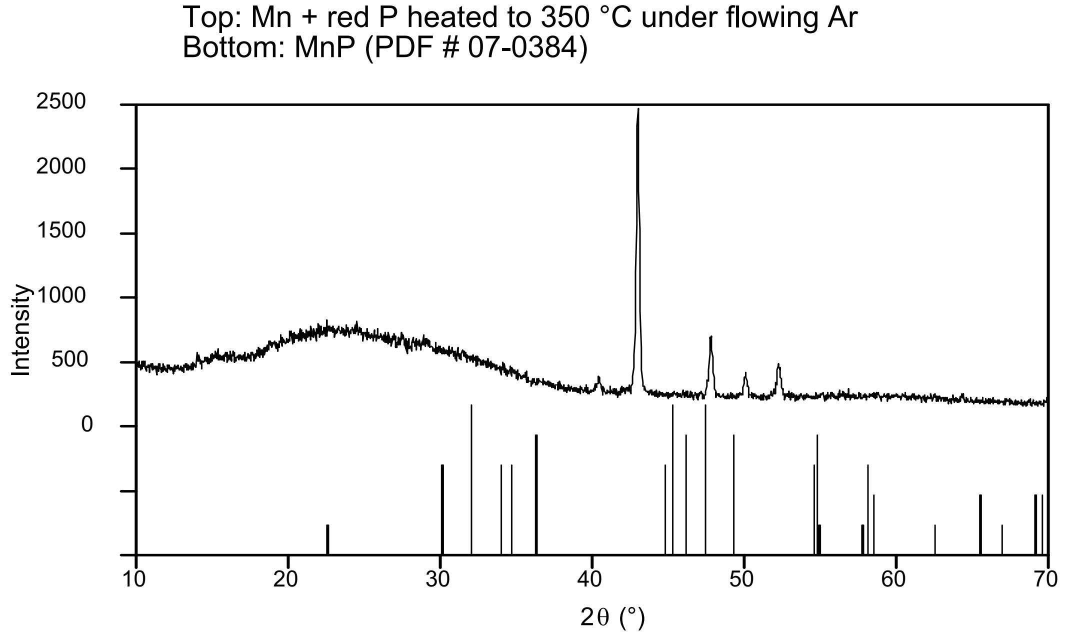
Bottom: $CdSnP_2$ (PDF # 73-0400)

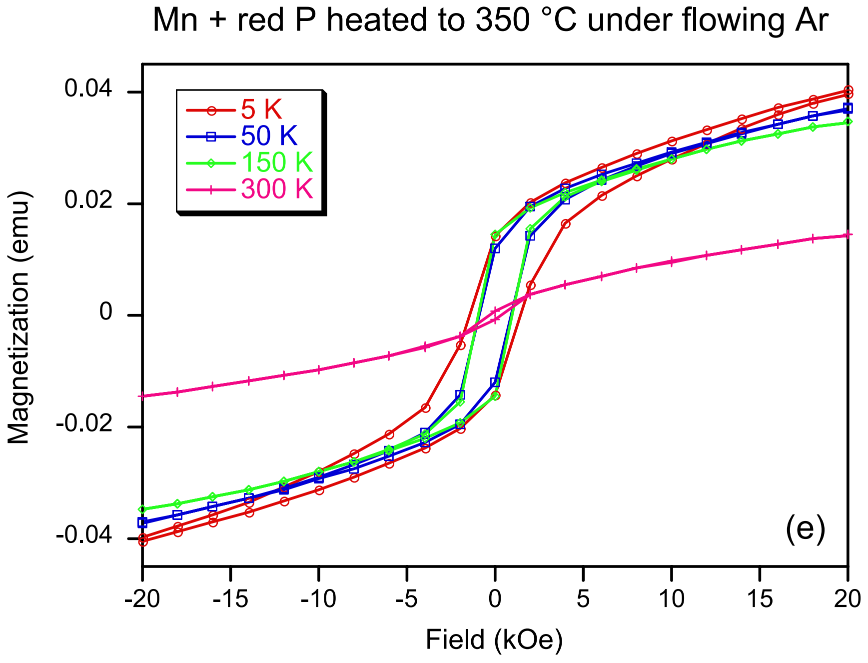
$CdSnP_2$ + Mn heated at 500 °C

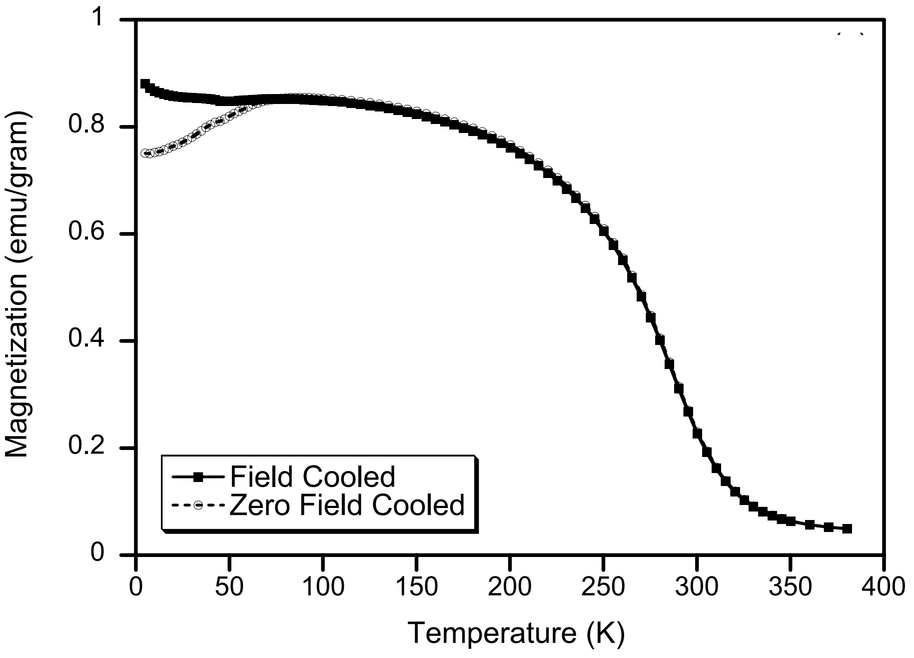


Control Reaction:

Mn + P under flowing argon @ 350 °C


Top: Mn + red P heated to 350 °C under flowing Ar
Bottom: MnP (PDF # 07-0384)


Mn + red P heated to 350 °C under flowing Ar



Reactivity of Metal Carbonyls Towards Solvents

$Fe(CO)_5$ + TOPO $\longrightarrow$ Fe nanoparticles

$Mn_2(CO)_{10}$ + TOPO $\longrightarrow$ Mn_2O_3 nanoparticles

$Mn_2(CO)_{10}$ + TOP $\longrightarrow$ MnP nanoparticles

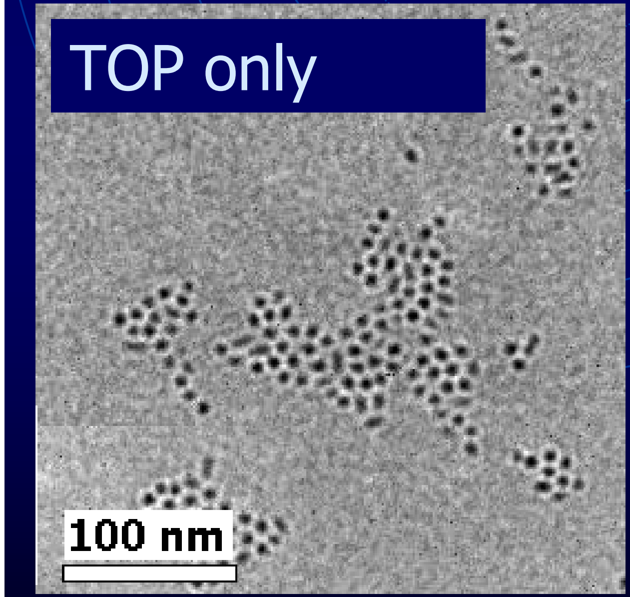
$Fe(CO)_5$ + TOP $\longrightarrow$ FeP nanoparticles

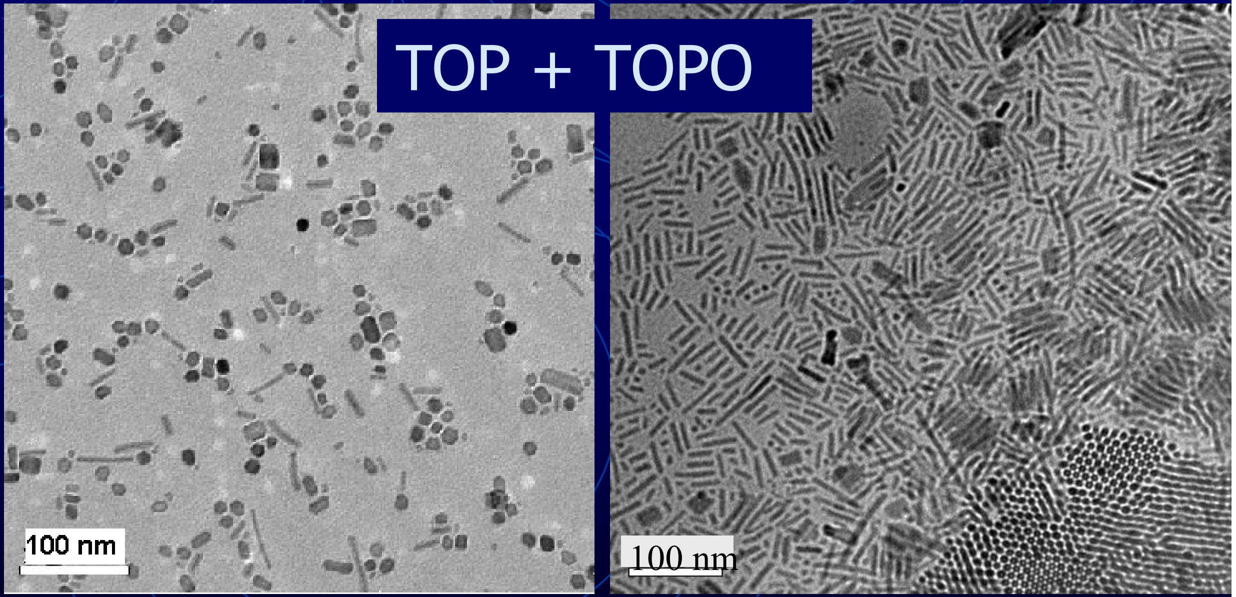
Lower reactivity phosphines can be used to form transition metal phosphide nanoparticles

Effect of Phosphorous Source on the Reaction

$Mn_2(CO)_{10} + P(octyl)_3 \longrightarrow$ MnP nanoparticles

Less reactive phosphines are employed as solvent and reactant.

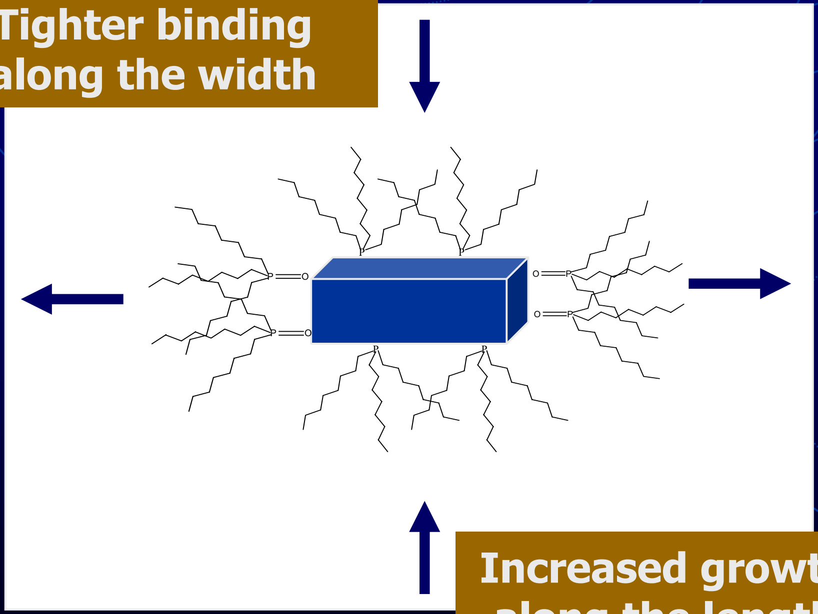

TOP only


TOP + TOPO

Depending on conditions, different shapes can result

Inducing Anisotropy into Nanoscale Magnets: How and Why?

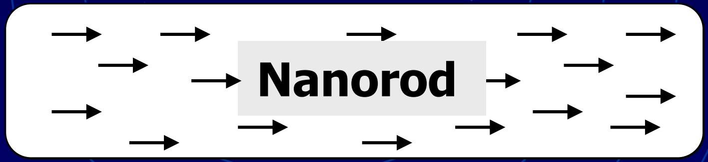
How: Anisotropic Growth is driven by preferential growth along a specific crystal face. This can be achieved using co-solvents with different binding preferences



Tighter binding along the width

Increased growth along the length

Why: Influence of Shape Anisotropy on Coercivity



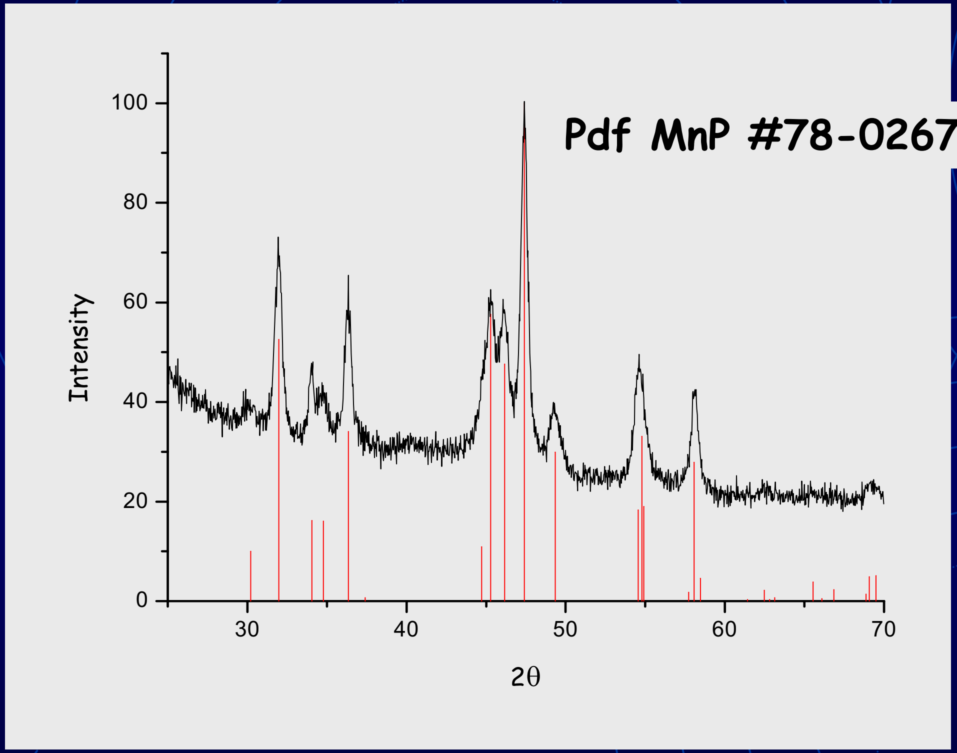
Lower energy process for spins to align along the length of the rod. As spin flip occurs, it takes more energy to rotate the spins through the short axis, therefore:

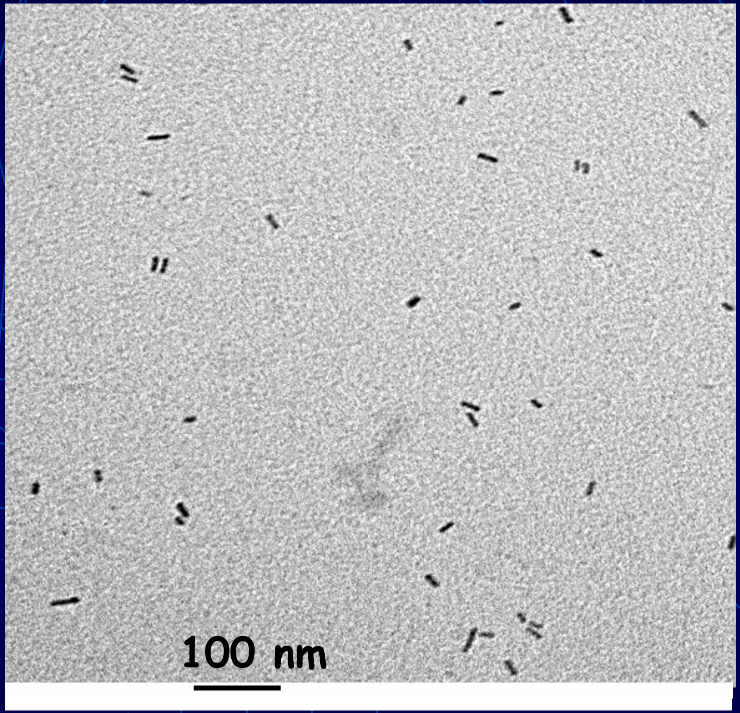
-The coercivity (H_c) increases

-The particles are more stable to thermal fluctuation so the blocking temperature (T_B) increases

Synthesis of MnP Nanorods

$$Mn_2(CO)_{10} + \text{TOP/octadecene} \xrightarrow[\text{one hour}]{\text{Inject into TOP/TOPO @ 340-350 °C}}$$





Ave. width = 5.2 nm ± 0.89

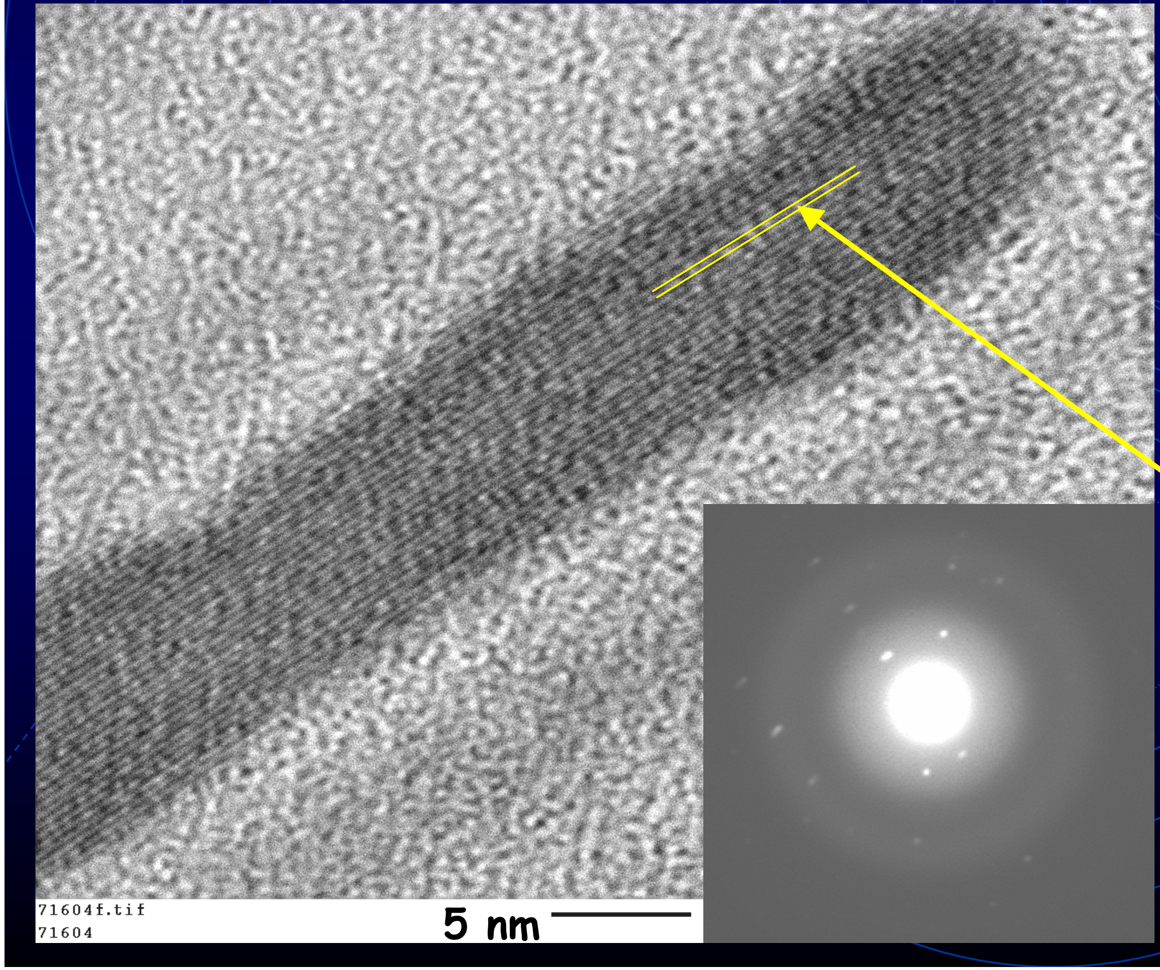
Ave. length = 20.3nm ± 3.6

Ave. aspect ratio = 3.9

Rods are Single Crystals

Electron Diffraction

d-spacing (meas)	d-spacing MnP	hkl
3.04	2.95464	002
2.718	2.7966	011
1.039	1.0939	403
1.361	1.3621	312

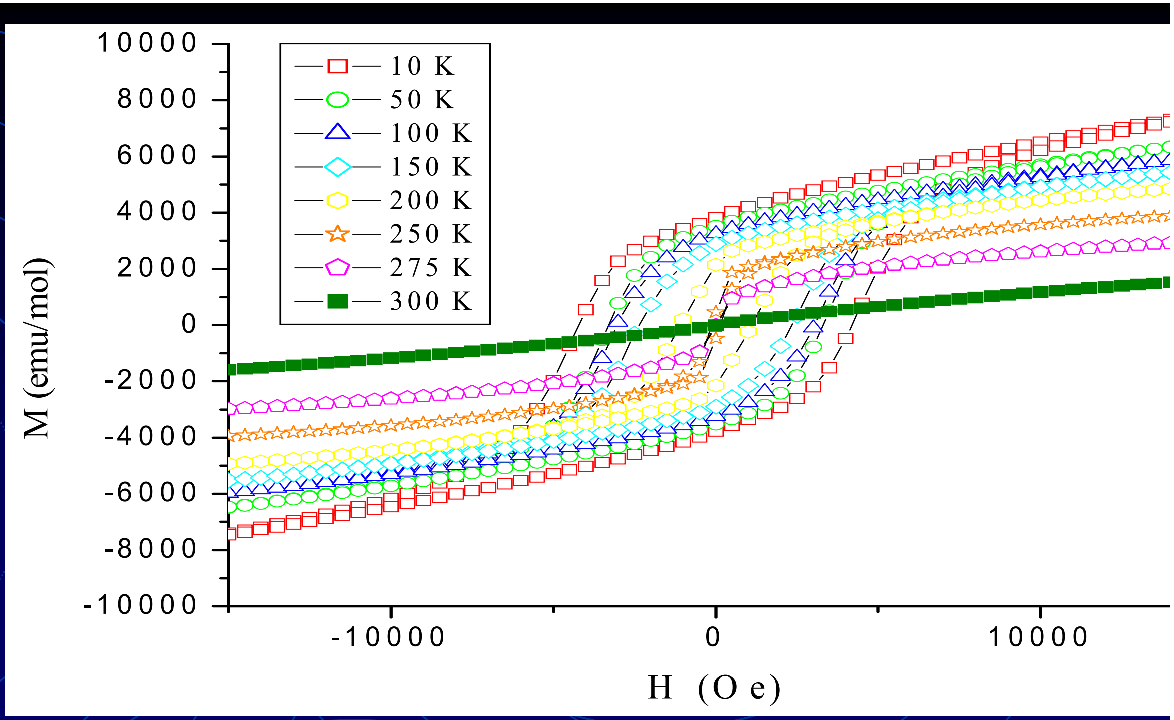


Lattice fringes correspond to a d-spacing of 2.97 Å = (002)

MnP Nanorod Magnetic Data

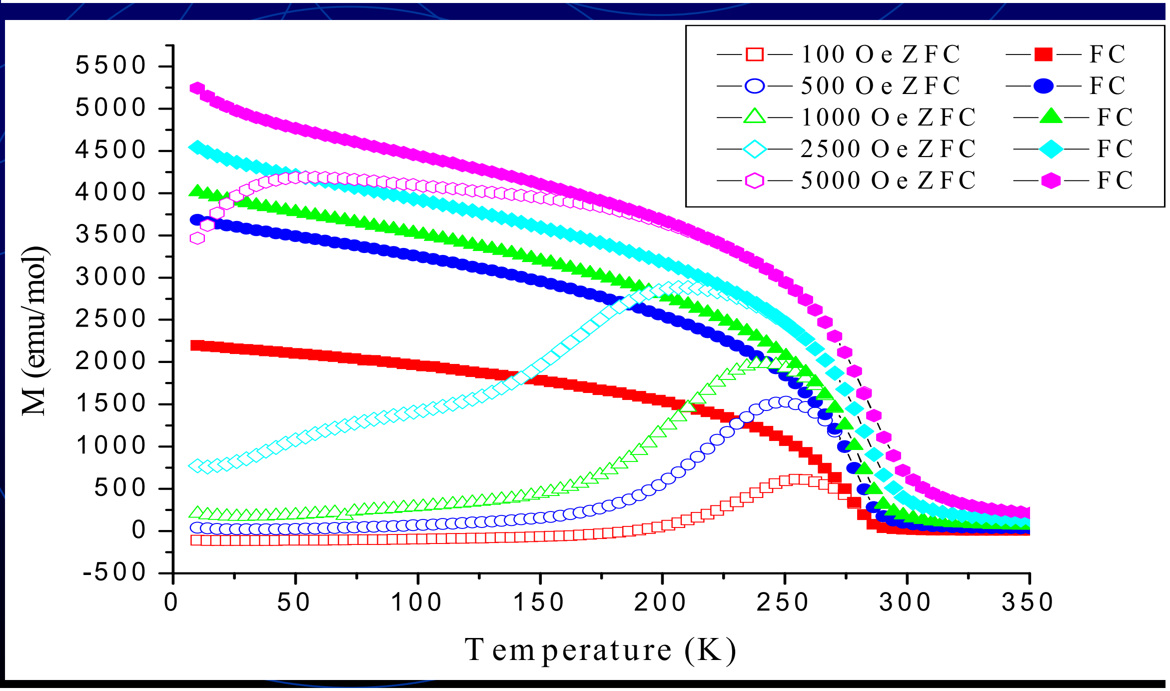
Vs. Field

- Coercivity shown up to 250 K. H_c = 4200 Oe at 10 K
- Comparison: spherical MnP (6.7 nm) showed H_c = 5000 Oe



Vs. Temp

- Blocking temp, T_B = 250.4 K at 500 Oe
- Comparison: spherical MnP (6.7 nm) blocking temp, T_B=70.3 K at 500 Oe



Magnetism of Rods Versus Spheres

	Rods	**Spheres**
Size	**20.3 ± 3.6 x 5.2 ± 0.89 nm**	**6.7 ± 0.33 nm**
Volume, V	**430.9 ±166 nm^3**	**155.3 ± 23 nm^3**
Coercivity, H_c @ 10K	**4200 Oe**	**5000 Oe**
Blocking Temp., T_b @ 500 Oe	**250.4 K**	**74.3 K**
Saturation Magnetization, M_s	**9,950 emu/mol**	**8,950 emu/mol**
Anisotropy Constant, K_1	**$2.0 \times 10^6 \pm 7.7 * 10^5$ erg/cm^3**	**$1.65 \times 10^6 \pm 2.4 * 10^5$ erg/cm^3**
Anisotropy Constant, K_{2eff}	**3.48×10^6 erg/cm^3**	**4.70×10^6 erg/cm^3**

The anisotropy constant (K) can be computed from either the blocking temperature (T_B) and/or the coercivity (H_C) and saturation magnetization (M_S)

$$E = K_1 V \sin^2\theta = k_b T_b \ln(t/\tau_0)$$

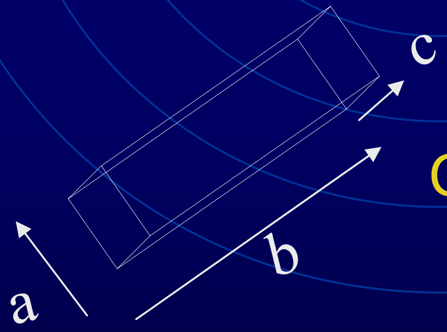
$$H_c = \alpha(2K_{2eff}/M_s)\ [1-(T/T_b)^{1/2}]$$

Gregg, K. A.; Perera, S. C.; Lawes, G.; Shinozaki, S.; Brock, S. L. *Chem. Mater.* **2006**, *18*, 879-886

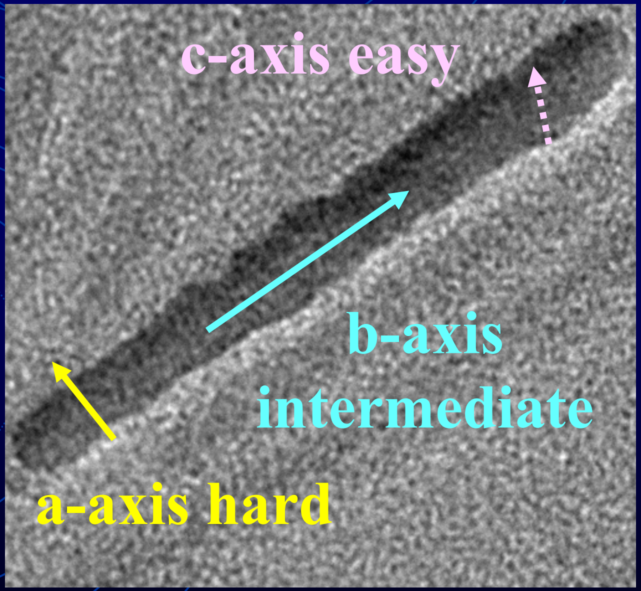
Magnetism of Rods Versus Spheres

Due to shape anisotropy we expect the coercivity of the rods to be higher than that of the spheres.

However, if the magnetocrystalline easy axis does not fall along the preferred moment direction arising from the shape anisotropy, the competition between magnetocrystalline and shape anisotropy actually may reduce the effective anisotropy in the rods.



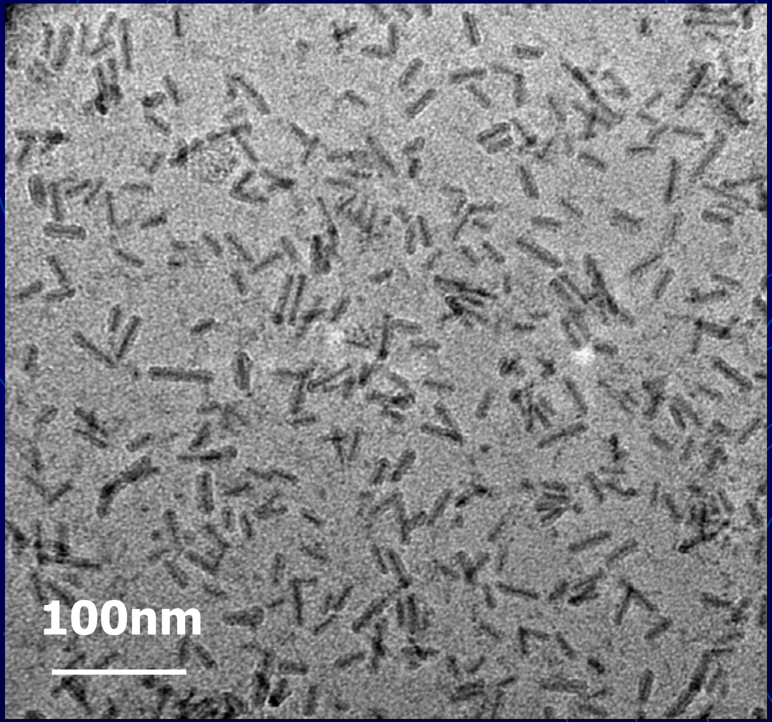
Growth direction is along the intermediate axis



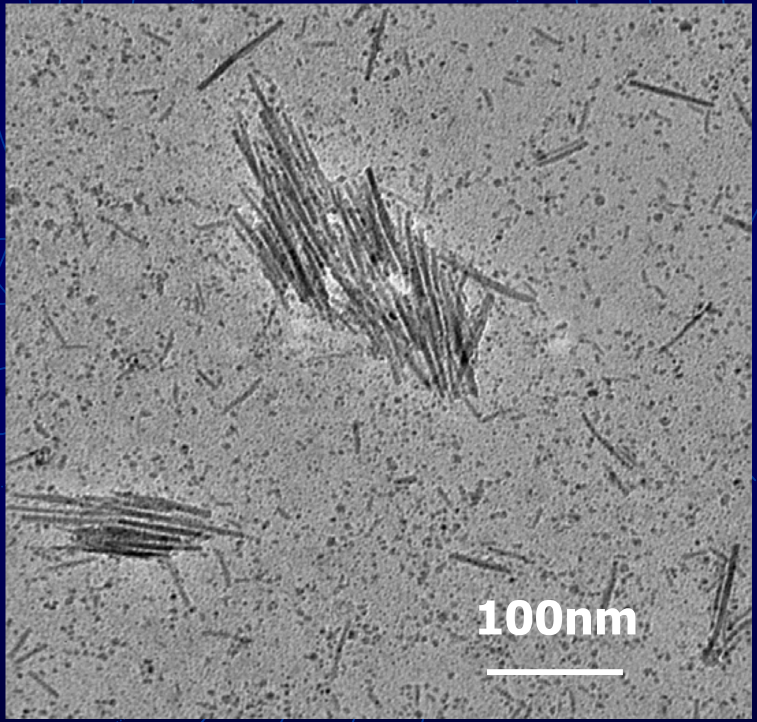
Would an alternate method yield crystals grown along another axis?

Influence of Time on the Growth of the Rods

2 days (80 °C)



3 days (80 °C)



~ 10 x 35 nm rods

~ 10 x 180 nm needles,
~ 5-10 nm particles

Self Assembly of Nanoparticles by Oriented Attachment at Low Temperatures (< 100 ºC)

ZnO

Pacholski, C.; Kornowski, A. *Angew. Chem. Int. Ed.* **2002**, *41* 1188-1191.

CdTe

Tang, Z.; Kotov, N. A.; Giersig, M. *Science*. **2002**, *297*, 237-240.

Iron

Park, S. J.; Kim, S.; Lee, S.; Khim, Z. G.; Char, K.; Hyeon, T. *J. Am. Chem. Soc.* **2000**, *122*, 8581-8582.

Attachment driven by dipole forces (magnetic, electric) between particles…these "anneal" to give 1-D single crystals

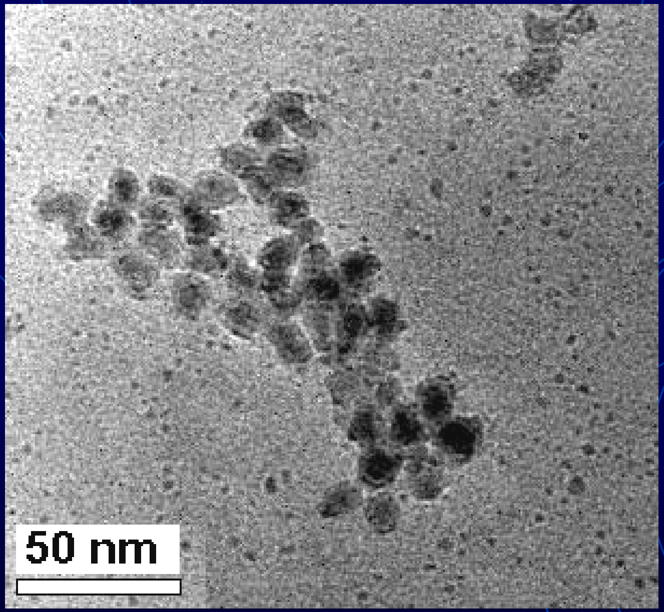
No reports for phosphides!?

What's going on in our system? Oriented attachment? Unreacted precursors nucleating to form rods at low temperature? Ostwald ripening? More experiments needed!

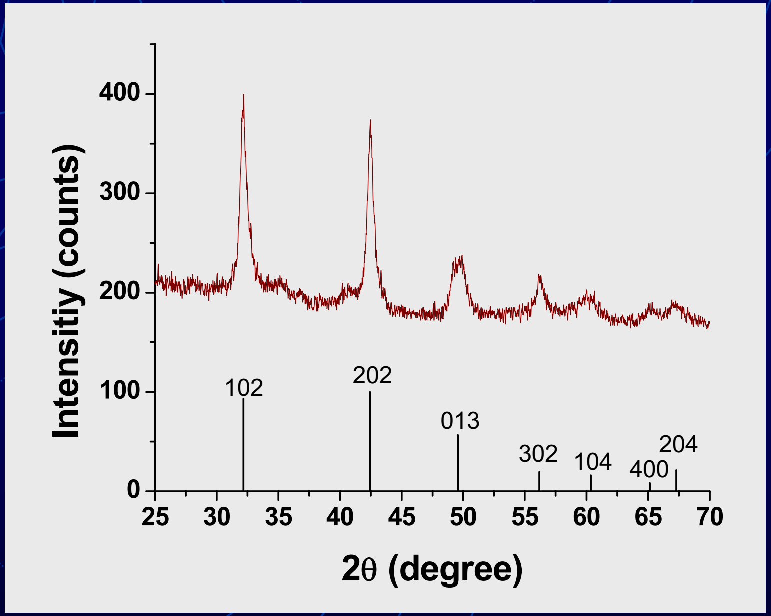
Application to Transition Metal Arsenide Phases

In lieu of $As(SiMe_3)_3$, inexpensive, easily handled arsines can be used to make nanoparticulate arsenides

$Mn_2(CO)_{10}$ + TOPO + Octadecene + $As(Ph)_3 \longrightarrow$ **MnAs !**



MnAs nanoparticles at medium magnification (x80K)



MnAs nanoparticles and line diagram for orthorhombic (MnP-type) MnAs (PDF # 71-0923)

Reduction of Pnict*ates* to Pnict*ides*

Product	Precursor	Conditions
FeP	$NH_4FePO_4 \bullet H_2O$	800 °C, H_2 + Ar, 7 h
Fe_2P	$FePO_4$	1000 °C, H_2 + Ar, 9 h
Co_2P	$NH_2CoPO_4 \bullet H_2O$	980 °C, H_2 + Ar, 2 h
Ni_2P	$NH_4NiPO_4 \bullet H_2O$	820 °C, H_2 + Ar, 2 h
MoP	$MoOPO_4$	800 °C, H_2, 1 h
MoP	$MoO_2HPO_4 \bullet H_2O$	870 °C, H_2 + Ar, 1 h
WP	$W_2O_3(PO_4)_2$	800 °C, H_2, 2 h
RuP	$RuP_2O_7 \bullet 2H_2O$	600 °C, H_2, 6 h

NiAs, CoAs, $CoSb_2$, $NiSb_2$, and $CoSb_3$ were also produced by this method

…but more elecropositive metals (e.g. Mn) do not yield pnictides

J. Gopalkrishnan, S. Pandey, K. K. Rangan, *Chem. Mater*. **1997**, *9*, 2113.

J. Gopalkrishnan, S. Pandey, K. K. Rangan, *Chem. Mater*. 1997, *9*, 2113.

Synthesis of Iron Phosphate Nanoparticulate Precursor*

$FeCl_3$
+
H_3PO_4

TEHP, tri-n-octylamine

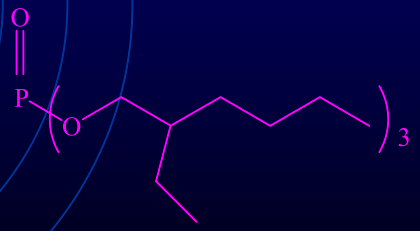
160 ºC, 12 h

clear brown solution

ppt/wash with MeOH

Yellow, non-crystalline solid

TEHP

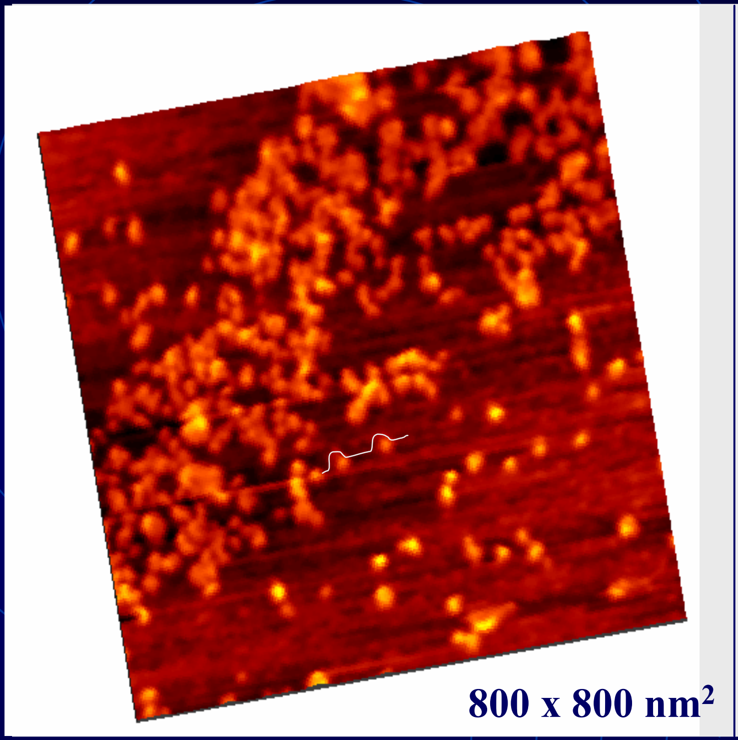


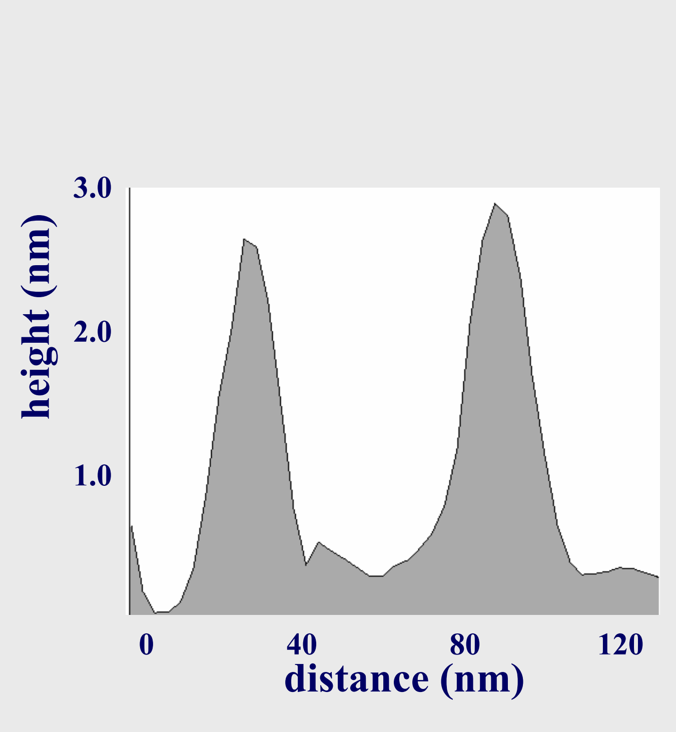
Fe/P = 0.92

Soluble in hexane, toluene, & pyridine

*$LaPO_4$ nanoparticle syn. Riwotzki et. al., *J. Phys. Chem. B*, **2000**, *104*, 2824-2828

Precursor Analysis by Atomic Force Microscopy



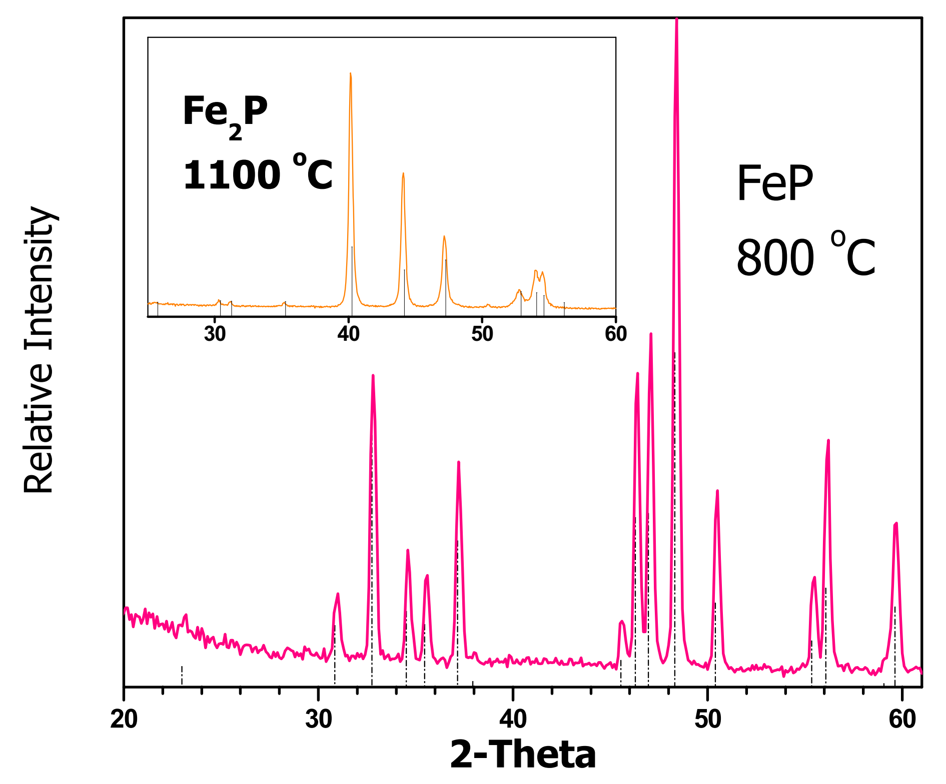


800 x 800 nm² atomic force microscopy image of iron phosphate nanoparticles on mica

Cursor profile of two nanoparticles measuring 2.7 and 3.9 nm
Range in size: 1.4 to 4.6 nm, average value of 2.8 ± 0.6 nm

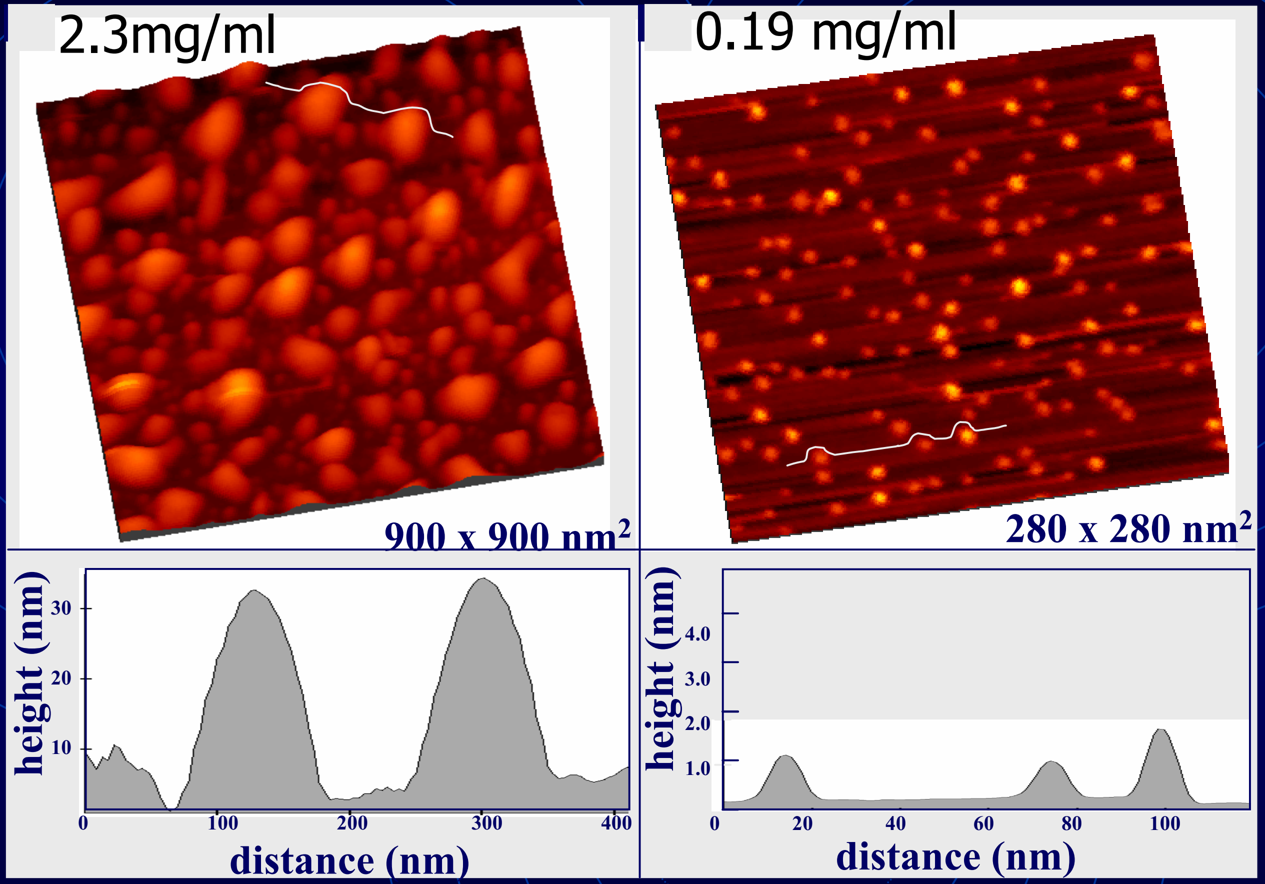
Stamm, K. L.; Garno, J. C.; Liu, G.-Y.; Brock, S. L. *J. Am. Chem. Soc.* 2003, *125*, 4038-4039

H_2 Reduced Nanoparticle Precipitate



Phase can be controlled by H_2 reduction temperature…but sintering is a problem!

Effect of Dilution: Casting Phosphate Nanoparticles onto Mica *Before* Reduction



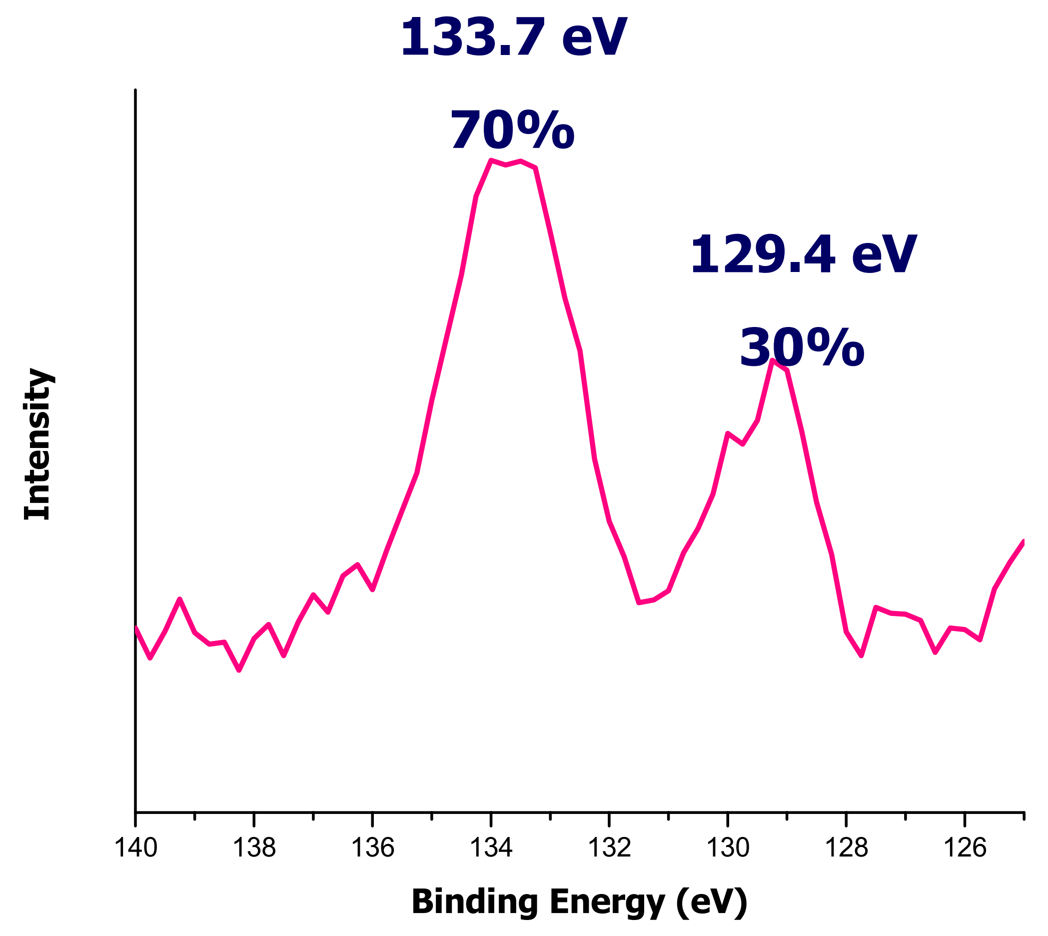
Average size 13.4 ± 8.7 nm

Average size 1.41 ± 0.5 nm

~75% volume reduction, consistent with phosphate to phosphide reduction.

K. L. Stamm, J. C. Garno, G.-Y. Liu, S. L. Brock, *J. Am. Chem. Soc.* **2003**, *125*, 4038

X-ray Photoelectron Spectroscopy of Particles on Mica



P *2p3*

Representative BE's*:
$FePO_4$= 133.75 eV
FeP= 129.5 eV

*http://srdata.nist.gov/xps/

K. L. Stamm, J. C. Garno, G.-Y. Liu, S. L. Brock, *J. Am. Chem. Soc.* **2003**, *125*, 4038

Dispersed Phosphide Nanoparticles

We can't make large quantities of phosphide nanoparticles because they need to be dispersed

Is there a value to having highly dispersed phosphide nanoparticles?

Transition metal phosphides as hydrotreatment catalysts:

Supported phosphides of Fe, Mo, W, Co, and Ni show excellent activity with respect to catalytic hydrogenation and removal of S, N, O from fuels

Typically produced by incipient wetness impregnation from phosphate solutions followed by reduction—poor control of particle size

See Keerthi Senevirathne's poster for more on Ni_2P

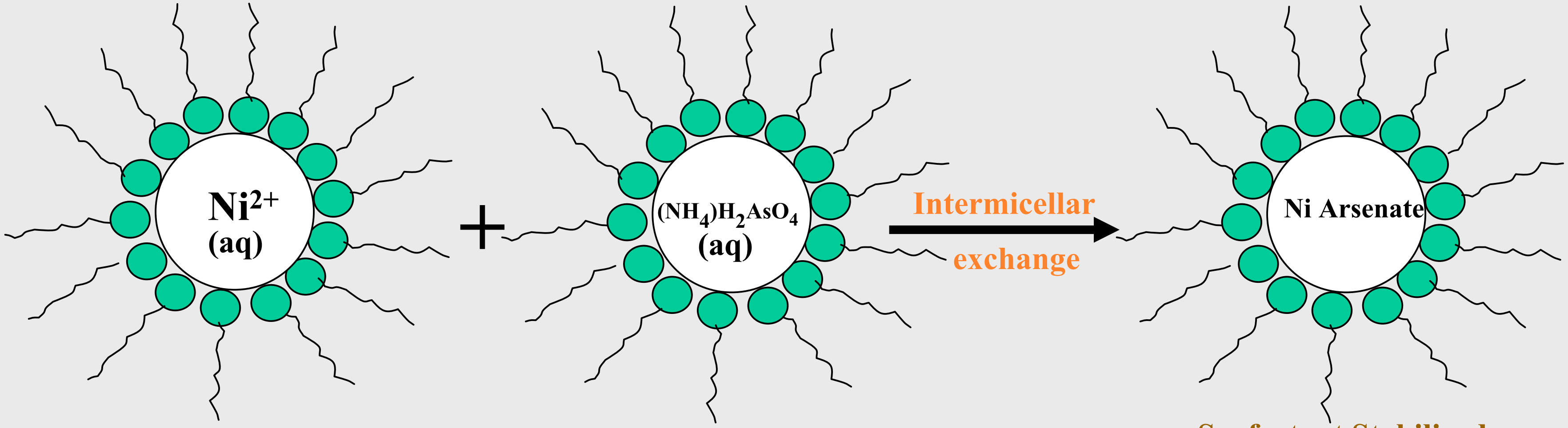
How general is this approach? Can it be used to pattern nanoparticles on surfaces?

Application to arsenates and 1-D nanoparticle arrays

Arsen*ate* Nanoparticle Reduction to Arsen*ide*

Initial focus: Nickel arsenate nanoparticles: chemistry & structure of bulk nickel arsenate phases well known

Microemulsion Based Solvothermal Method (MBSM)



Reverse Micelle

Reverse Micelle

Intermicellar exchange

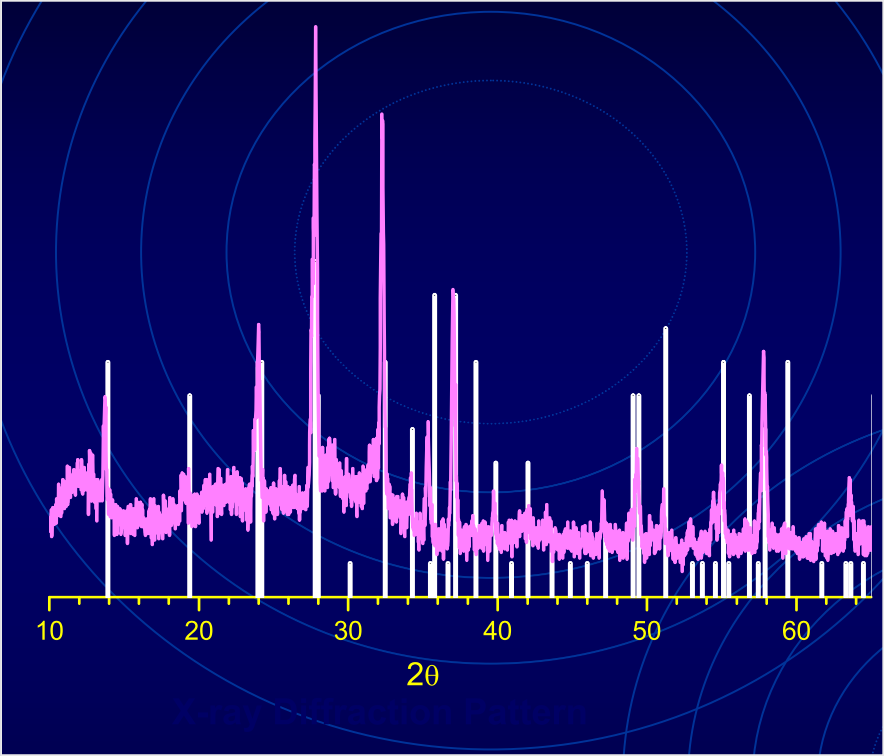
Surfactant Stabilized Precursor Nanoparticles

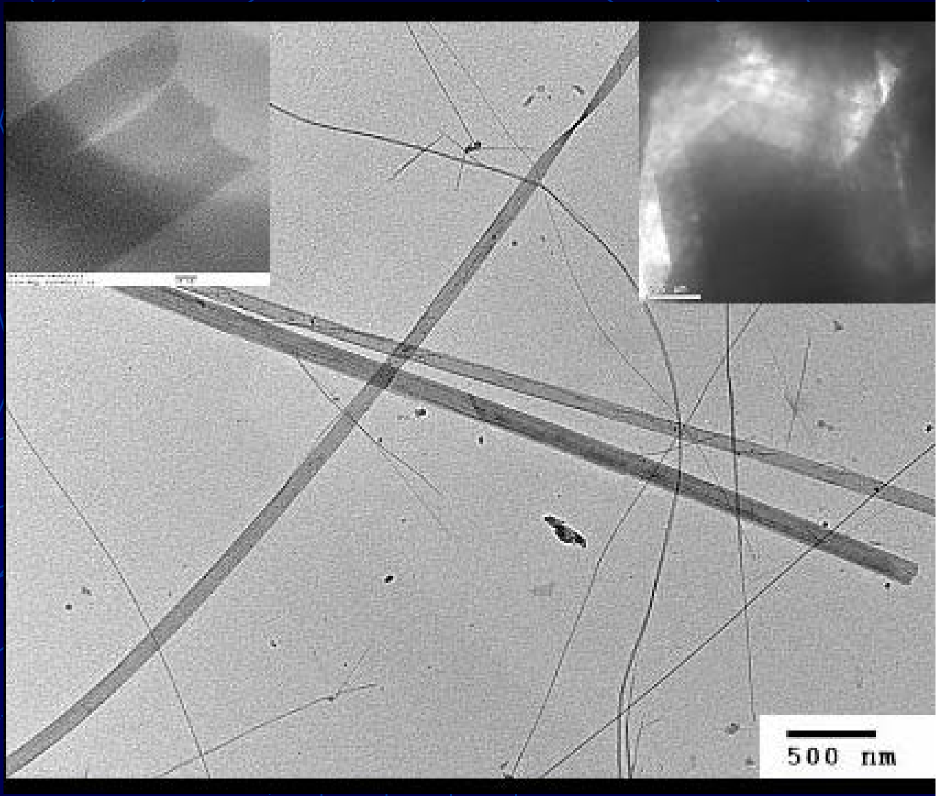
1. Solvothermal 165°C, 48hrs
2. Purification w/EtOH

Gello-like green product, soluble in ethanol

Surfactant – Cetyltrimethyl ammonium bromide (CTAB)
Ni source – $NiBr_2$
As source – $(NH_4)H_2AsO_4$
Solvents – Hexane, Butanol and Water mixture

Powder Pattern and TEM Micrograph of Nickel Arsenate



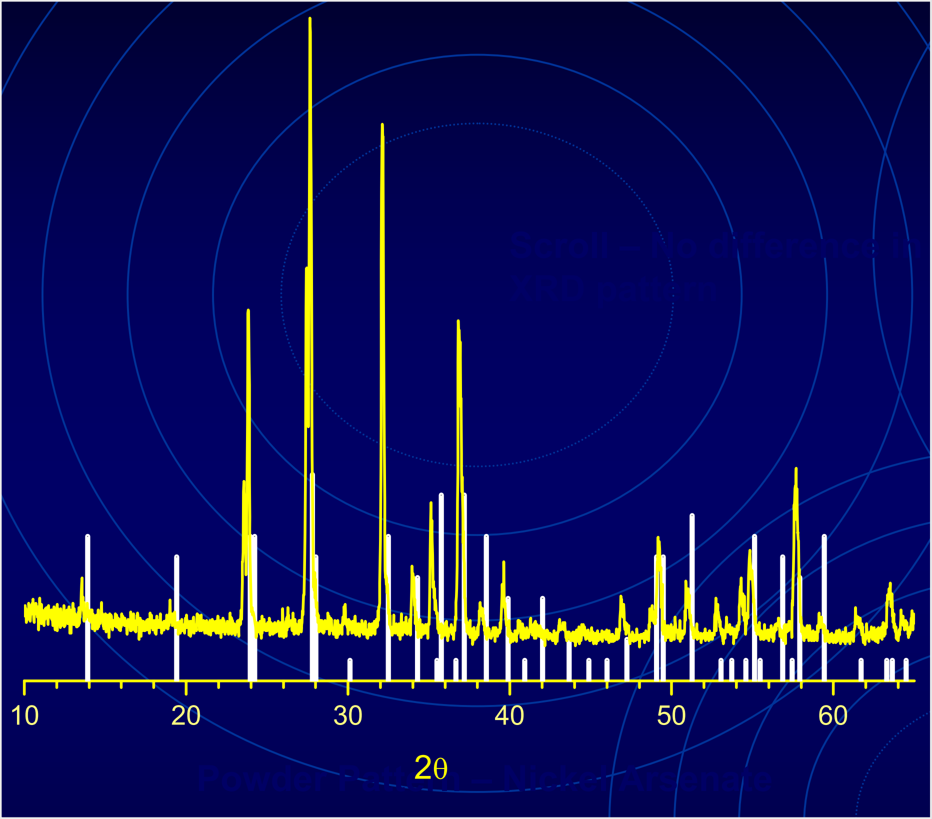


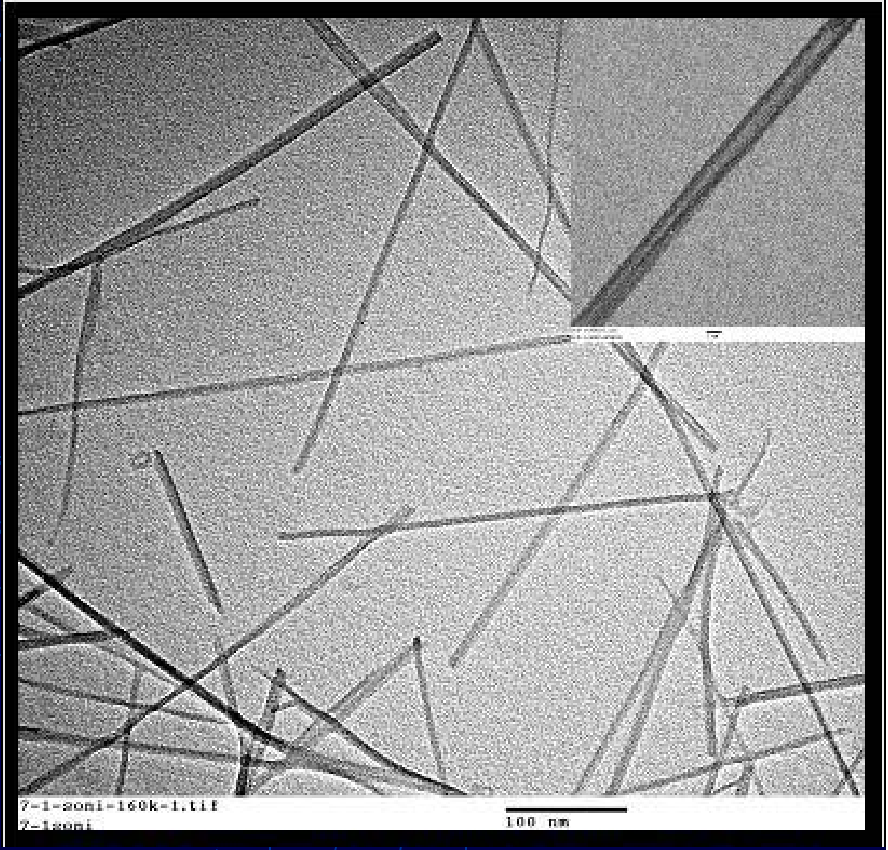
- Powder pattern matches layered structured $Ni_3(AsO_4)_2{\cdot}H_2O$ [pdf #37-0228]
- **Layered structure of nickel arsenate is manifested in the TEM as -**

  Sheets: if precursor ratio Ni:As = 1:1 (TEM insets)
  Ribbons: if precursor ratio Ni:As = 1:0.67 (i.e. stoichiometric)

P. Arumugam, S. S. Shinozaki, R. Wang, G. Mao, S. L. Brock Chem. Comm. **2006**, 1121-1123

Effect of Sonication on Ni-arsenate Morphology





Nanoscroll/Nanotube Ni arsenates

- The diameter of the nanoscroll can be varied depending on the sonication time
- No control on the length of the nanoscroll

P. Arumugam, S. S. Shinozaki, R. Wang, G. Mao, S. L. Brock Chem. Comm. **2006**, 1121-1123

In situ TEM Reduction of Nickel Arsenate Nanoscrolls

Basis for in situ TEM study

Previous studies (FeP) used mica, hydrogen annealing, and AFM to evaluate

Can we use a TEM grid similarly?

Will carbon act as an *in situ* reductant?

Nickel arsenate nanoscroll →

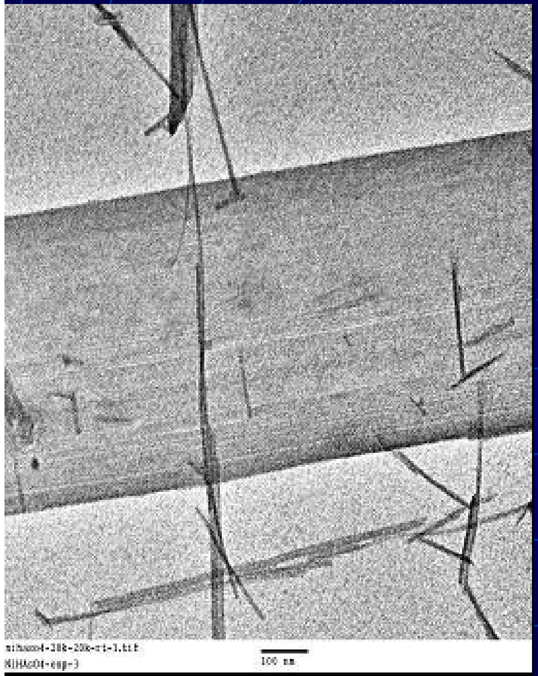
1. Deposit on carbon coated Cu-grid
2. Mount on heating stage and insert in TEM

→

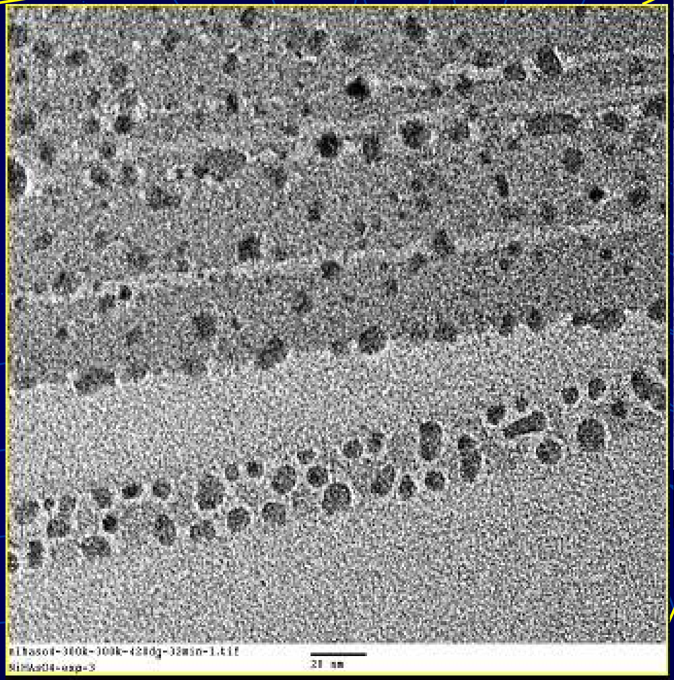
3. Heat up to 420^{0}C hold for ~2hrs
4. Cool down to 30°C

→ Ni_XAs_Y nanoparticles

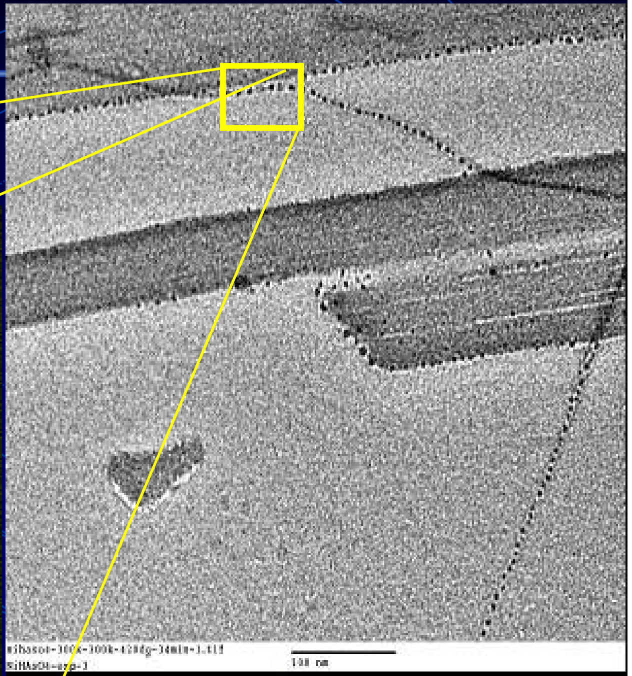
Temperature Influence



Before heating



420°C, 36 min



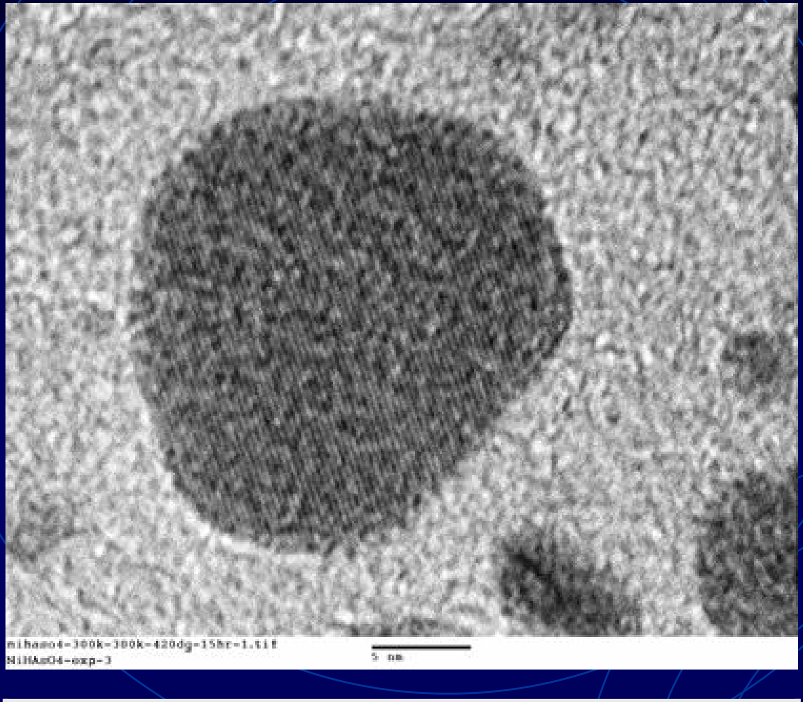
420°C 34 min

Ribbons break into particles!

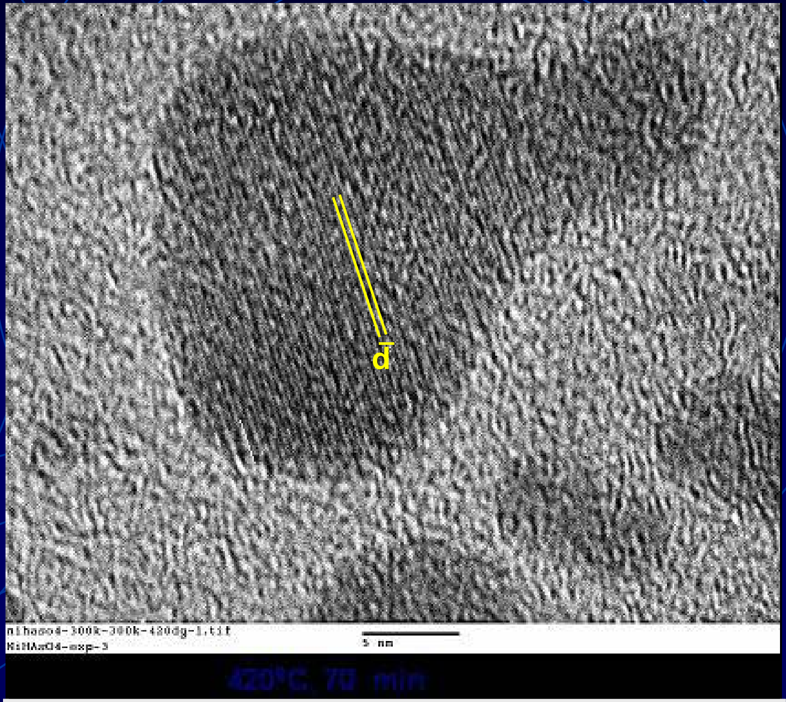
Nucleation/particle growth starts at ribbon edge

P. Arumugam, S. S. Shinozaki, R. Wang, G. Mao, S. L. Brock Chem. Comm. **2006**, 1121-1123

Identifying the Product from Lattice Planes



Phase/d-spacing value	d-spacing (nm)	Calculated from TEM image
$Ni_{11}As_8$	0.322 (106)	0.317
NiAs	0.314 (100)	0.317

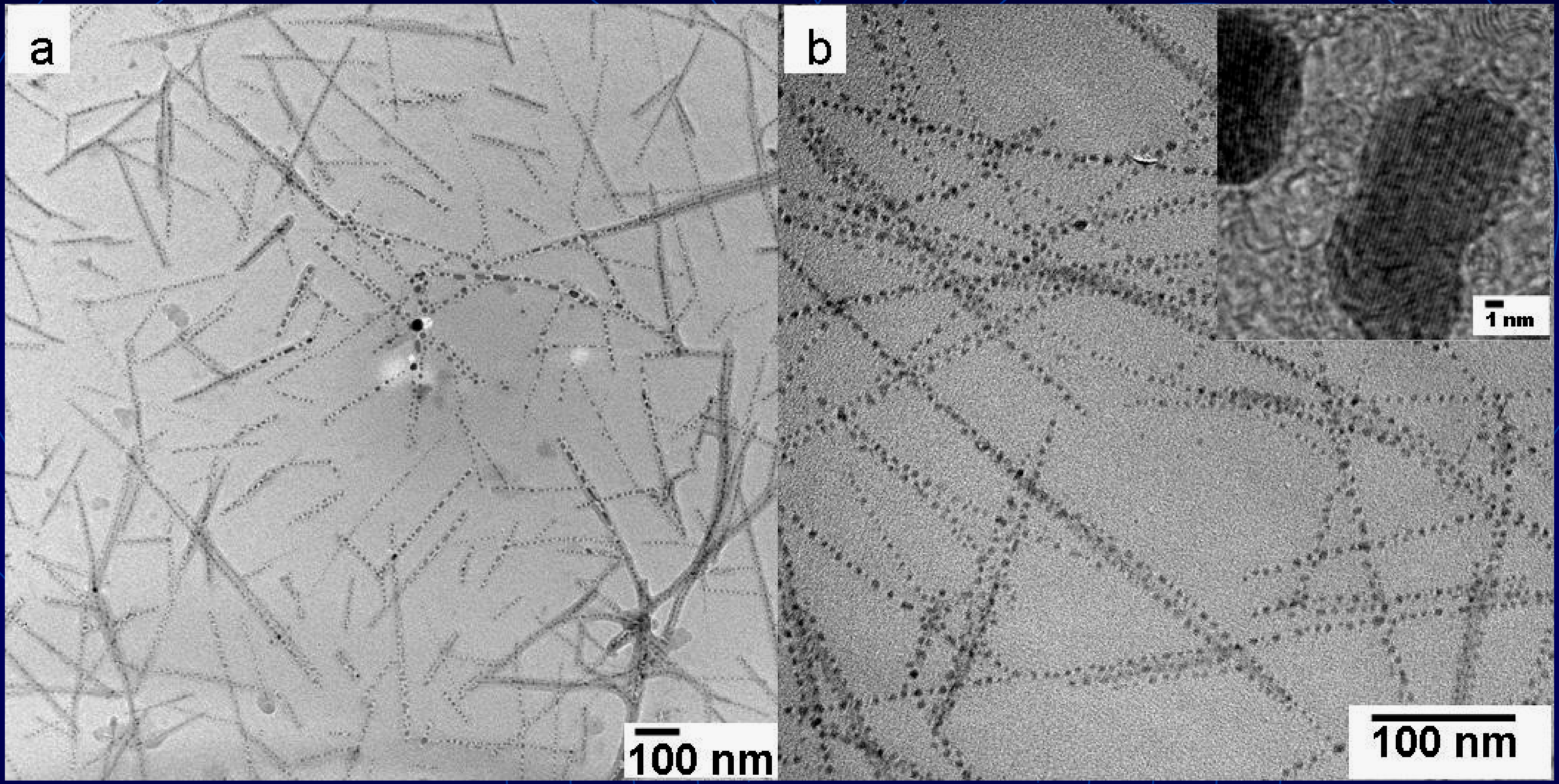


Phase/d-spacing value	d-spacing (nm)	Calculated from TEM image
$Ni_{11}As_8$	0.307 (210)	0.308
NiAs	0.314 (100)	0.308

Reduction has occurred !

P. Arumugam, S. S. Shinozaki, R. Wang, G. Mao, S. L. Brock Chem. Comm. **2006**, 1121-1123

1-D Nanoarray Formation



"thin" nanoribbons lead to uniform arrays

The electron beam contributes to particle formation

P. Arumugam, S. S. Shinozaki, R. Wang, G. Mao, S. L. Brock Chem. Comm. **2006**, 1121-1123

Conclusions

Nanoparticle pnictates are suitable precursors for nanoparticulate pnictide formation by reduction using hydrogen or carbon when dispersed on high surface area substrates

Spherical precursors lead to spherical products; whereas 1-D precursors (ribbons or nanotubes) lead to spherical nanoparticle arrays.

The ability to pattern reduced particles based on controlling the geometry of the precursor may be quite general…we have also observed this for nanoscrolls of Co arsenates, but oxide to metal transformations, or sulfate to sulfide transformations, should also be feasible.

In the past 5 years, a wide range of methods suitable for producing nanoscale transition metal pnictides, particularly phosphides, with control of size and shape have been developed.

The parameters that dictate stoichiometry in transition metal pnictide nanoparticles remain unclear, and much work needs to be done to understand how size and shape impact physical properties.

Acknowledgements

The Brock Research Group

left to right: Kennedy Kalebaila, Kristy Gregg, Valentina Ganzha-Hazen, Qinghong Yao, Indika Arachchige, Keerthi Senevirathne, Elayaraja Muthuswamy, Hongtao Yu; *Not pictured:* Albert Gjeluci, Mehul Barat

Alumni: Jaya Mohanan, Susanthri Perera, Kimber Stamm, Buddhi Jayasekera, Kanchana Somaskandan, Palaniappan "Pops" Arumugam, Dhammika Herath, Jen Aitken

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$$ WSU, PRF-G, NSF-IGERT, NSF-CAREER $$