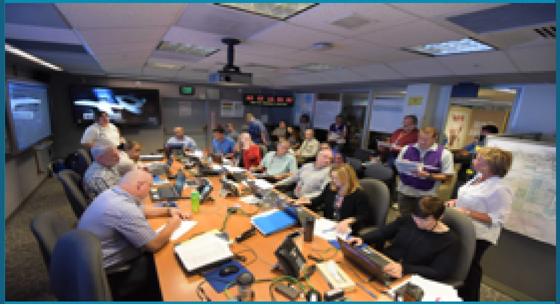
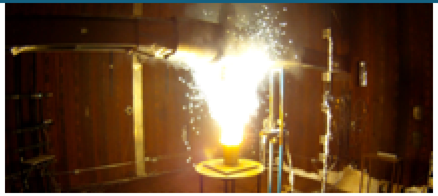
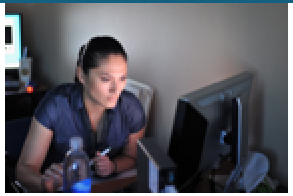
SAND2022-1391C

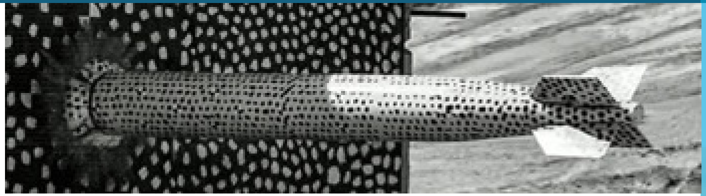
Sandia National Laboratories

Repeatability in Ferrite Nanomaterials Synthesis









Timothy A. Dreier, Ph. D.

ACS National Meeting Spring 2022

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. SAND: SAND2021-12180 PE

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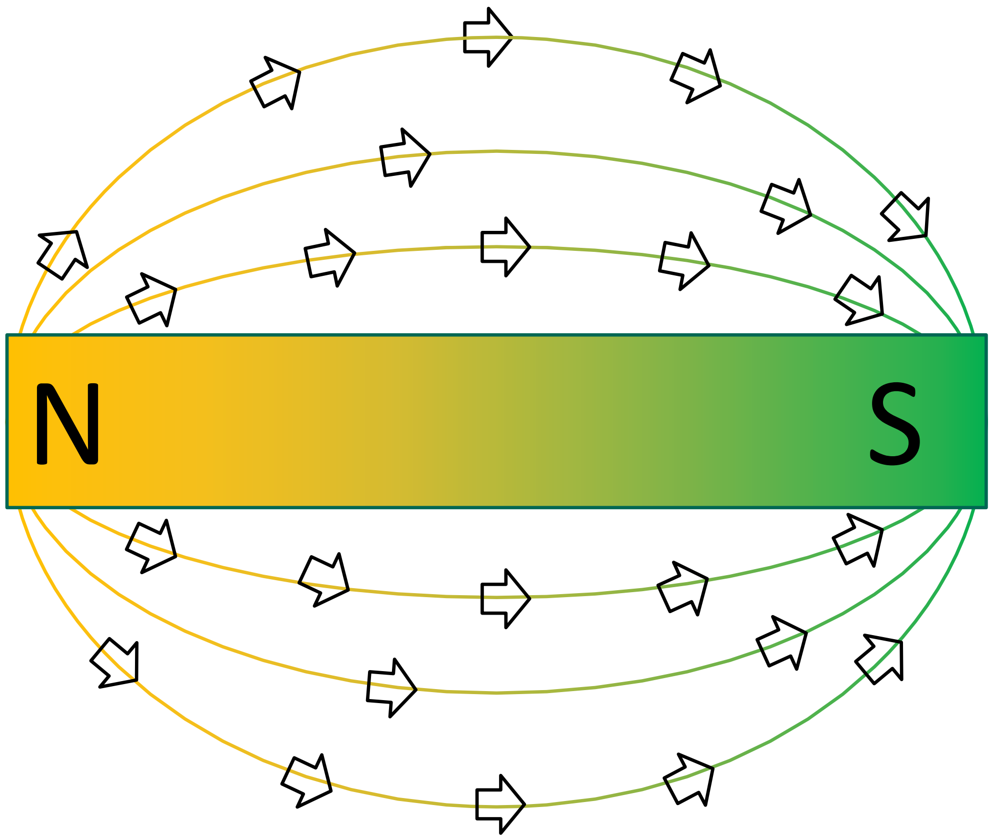
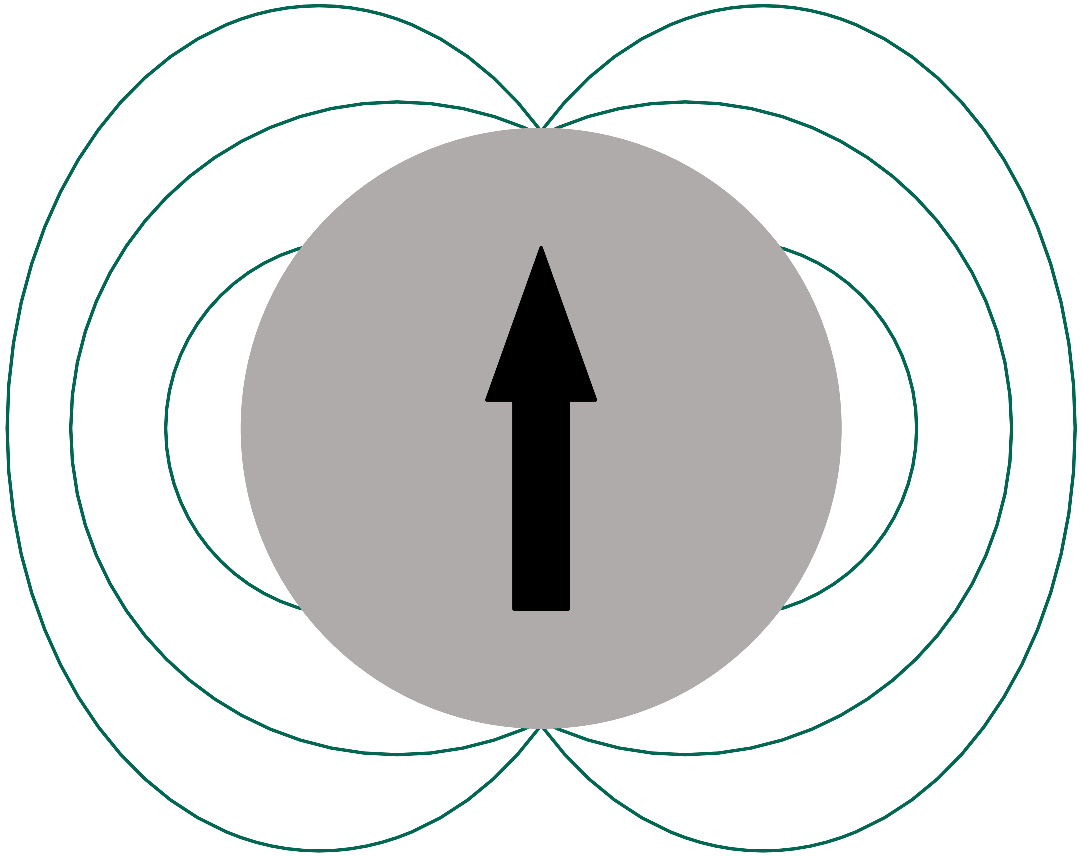
A Brief Introduction to Magnetism



- Diamagnetism – weakly repulsive, present in all materials, repulsion between applied field & moving electrons. No T dependence or saturation. (bulk gold, superconductors)
- Paramagnetism – weakly attractive, attraction between unpaired electrons & external field. T dependence & saturation.
- Ferromagnetism – magnetic moments of individual paramagnetic atoms aligned in the same direction, reinforcing each other. (Fe, Ni, Co, etc)
- Nanoscale more interesting than

Magnetic Nanoparticles – the Other Paramagnetism

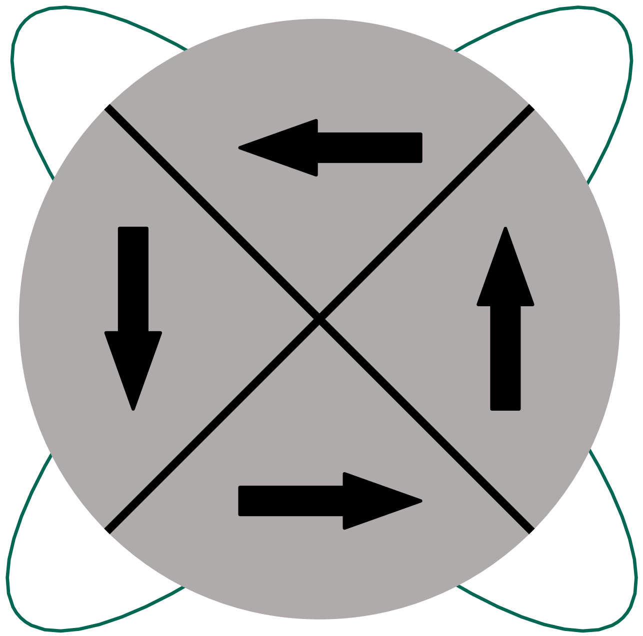
SUPERparamagneitc particles – single domain nanoparticles whose individual electron spins are aligned into a single magnetic moment.



<u>Single Domain</u>

More Flux Leakage

No Energy Lost to Domain Walls

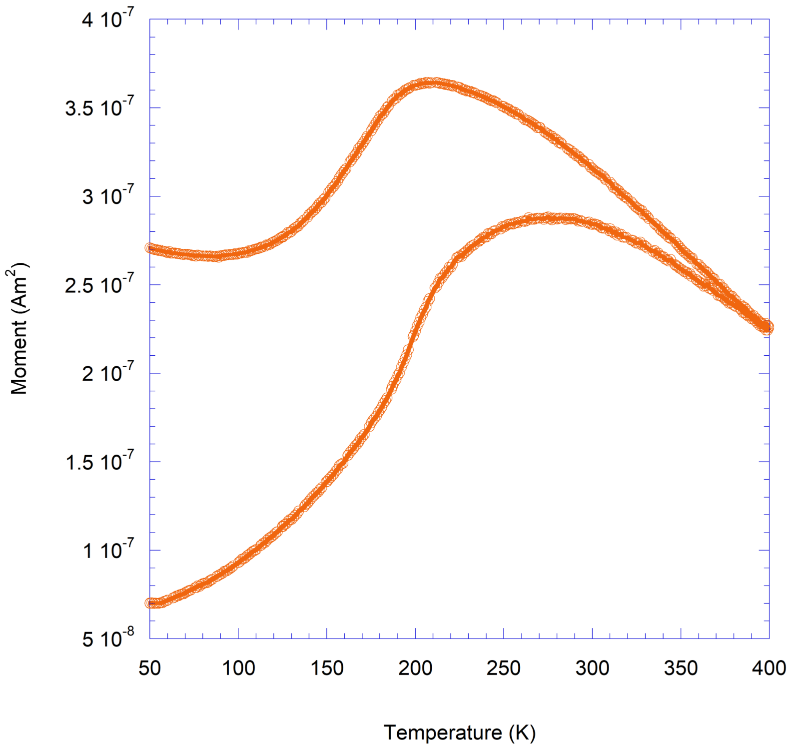


<u>Multi-Domain</u>

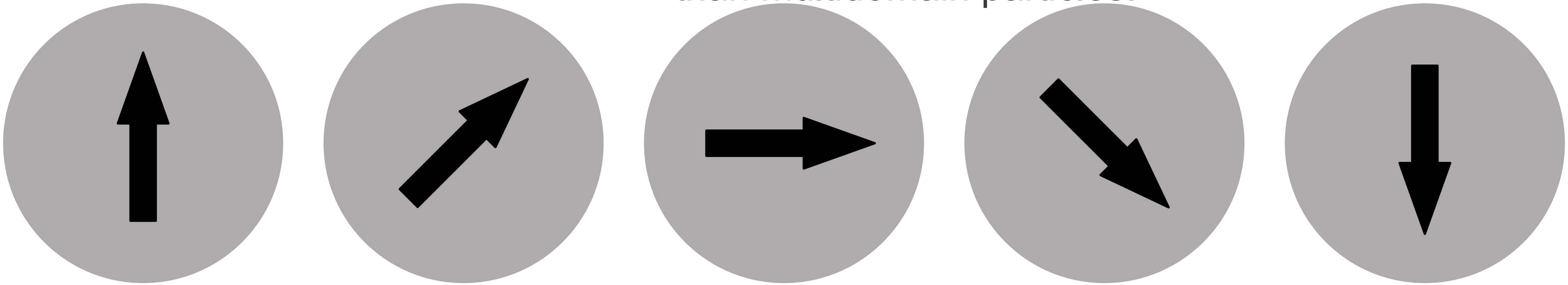
Less Flux Leakage

Energy Lost to Domain Walls

Size Dependent Magnetic Properties – Blocking Temperature



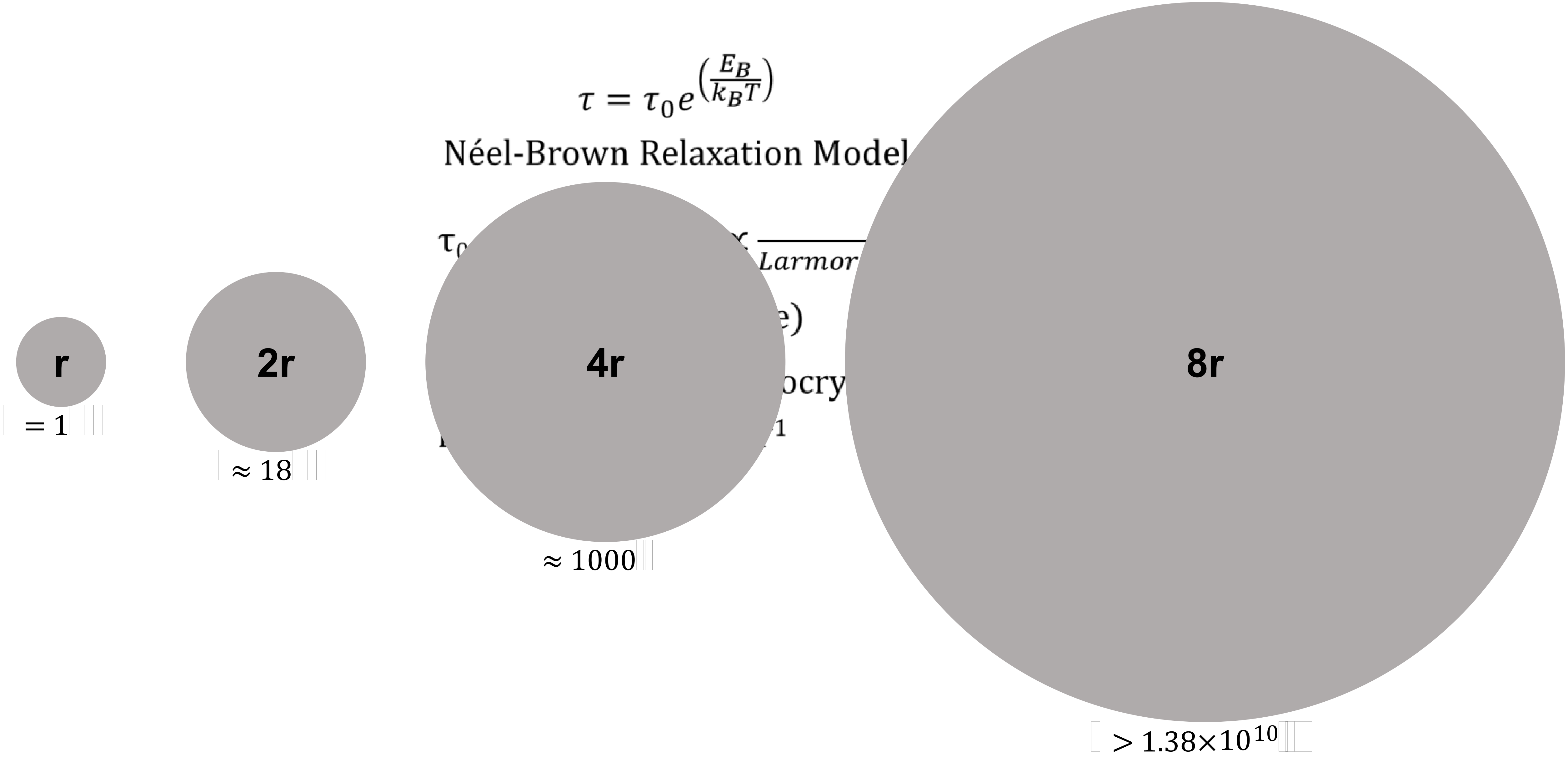
- T_B (blocking temperature): Temperature above which the dipole of the particle can freely reorient with an applied field on the timescale of the experiment.
- Above T_B – particles are superparamagnetic
- Below T_B – particles are (anti)ferromagnetic (hysteresis).
- Susceptibility (χ) is maximized at T_B
- χ is much larger for superparamagnetic particles than multidomain particles.



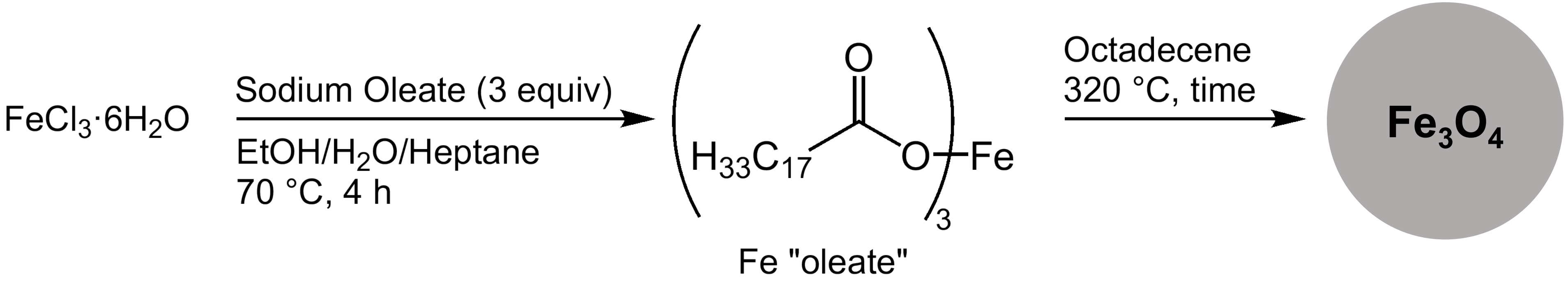
Magnetic Relaxation Time is Size Dependent

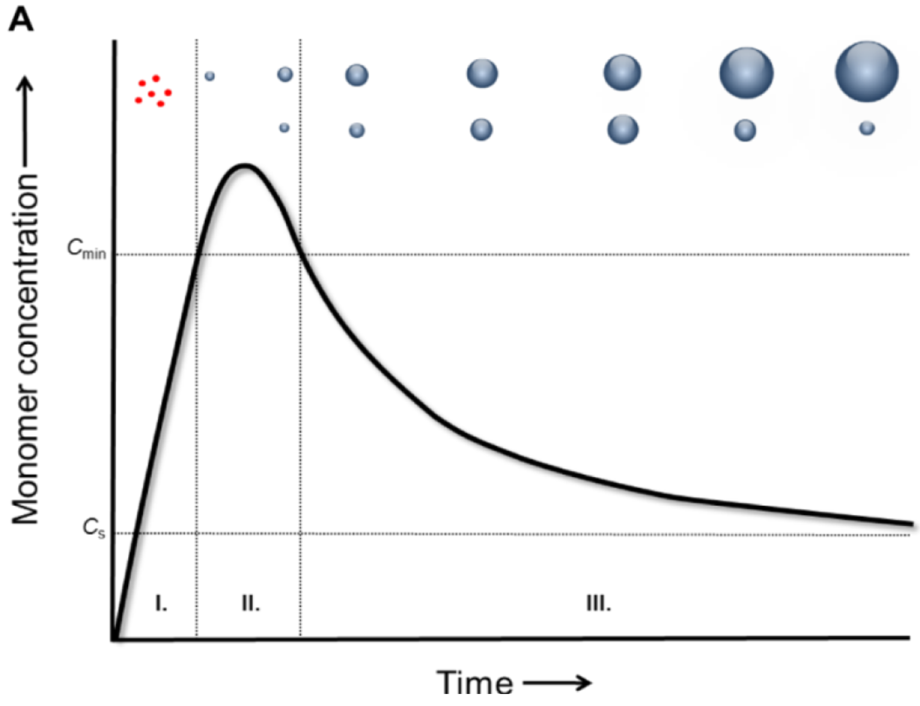
$$\tau = \tau_0 e^{\left(\frac{E_B}{k_B T}\right)}$$

Néel-Brown Relaxation Model



Typical Magnetite Nanoparticle Synthesis





Strengths

- Yields generally high
- Inexpensive starting materials

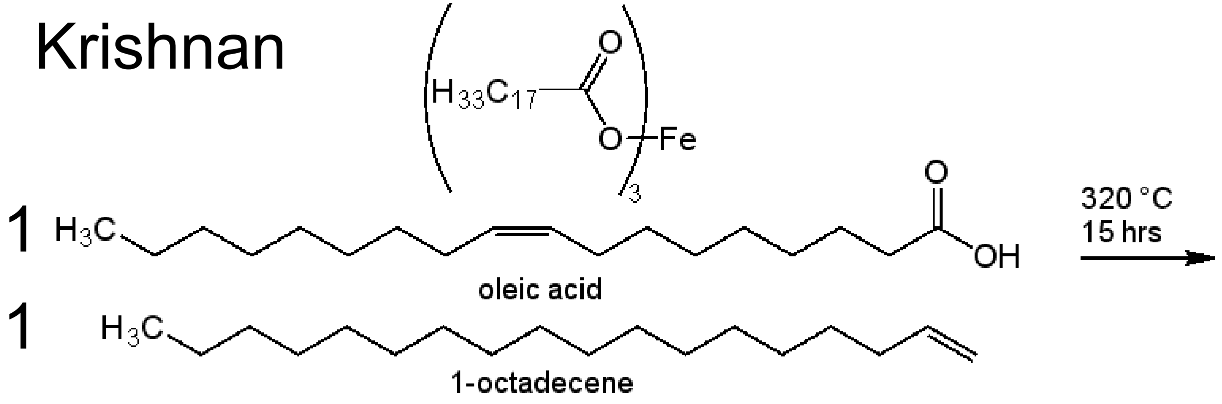
Weaknesses

- Size reproducibility hard to manage
- Requires purification of intermediate
- Iron oleate intermediate poorly characterized

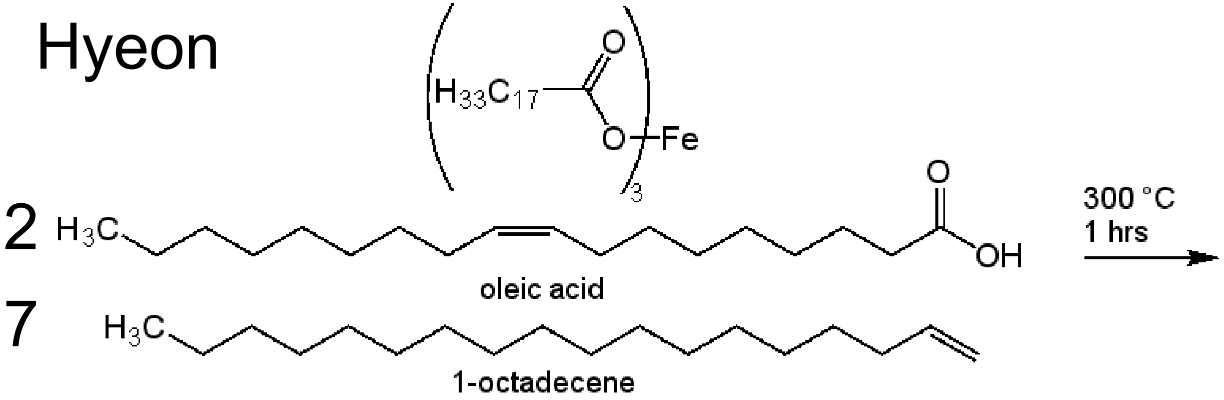
Hyeon, T. and coworkers, *Nat. Mater.* **2004**, *3,* 891-895.

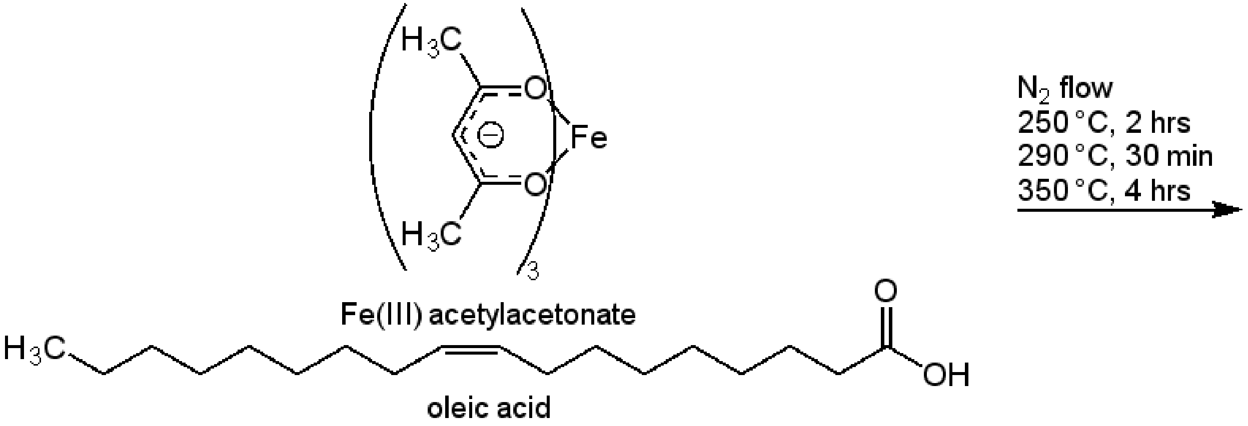
Literature Methods vs New One-Pot Approach

Krishnan



Hyeon

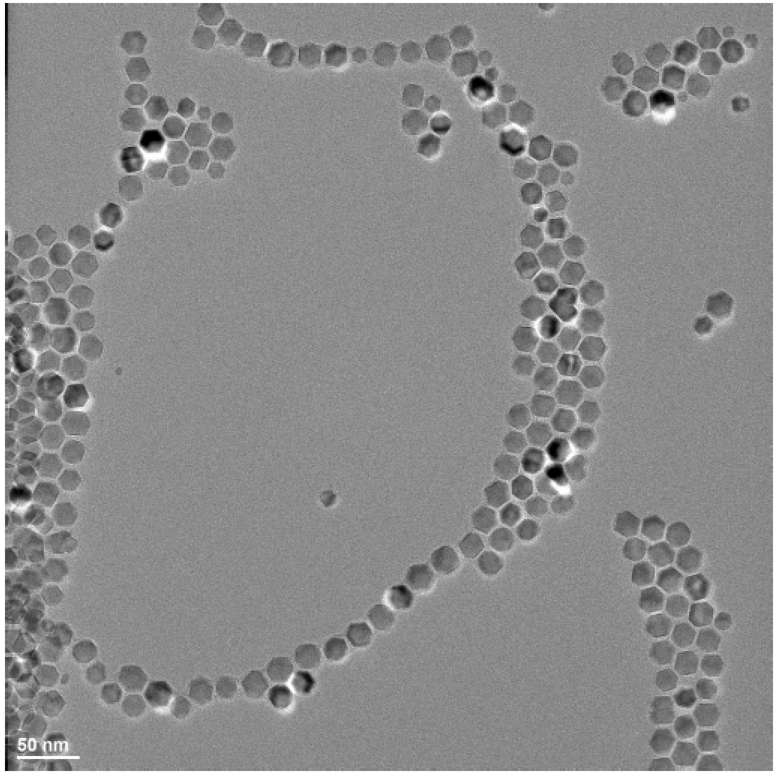


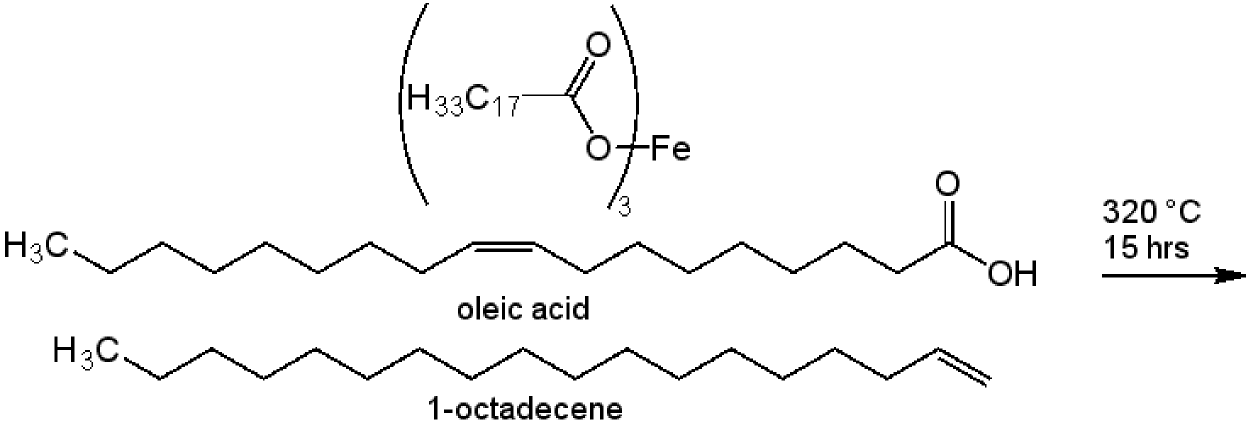


Park J., An K., Hwang Y., Park J. G., Noh H. J., Kim J. Y., Park J. H., Hwang N. M., Hyeon T. *Nat. Mater*. **2004**; *3,* 891-895.
Shokouhimehr M., Shin K.-Y., Lee J. S., Hackett M. J., Jun S. W., Oh M. H., Jang J., Hyeon T. *J. Mater Chem A.* **2014**, *2*, 7593-7599.
Hufschmid R., Arami H., Ferguson R. M., Gonzales M., Teeman E., Brush L. N., Browning N. D., Krishnan K. M. *Nanoscale* **2015**; *7*, 11142-11154.
Kim B. H., et al. *J. Am. Chem. Soc.* **2013**, *135*, 2407-2410.

Literature Method Reproducibility

Krishnan





	Size (nm) [σ, RSD]
1	20.01 [1.96, 9.8%]
2	22.58 [3.52, 15.6%]
3	31.75 [5.87, 18.5%]
4	33.07 [5.49, 16.6%]
5	29.13 [4.57, 15.7%]
Avg	27.31 [4.51, 16.5%]

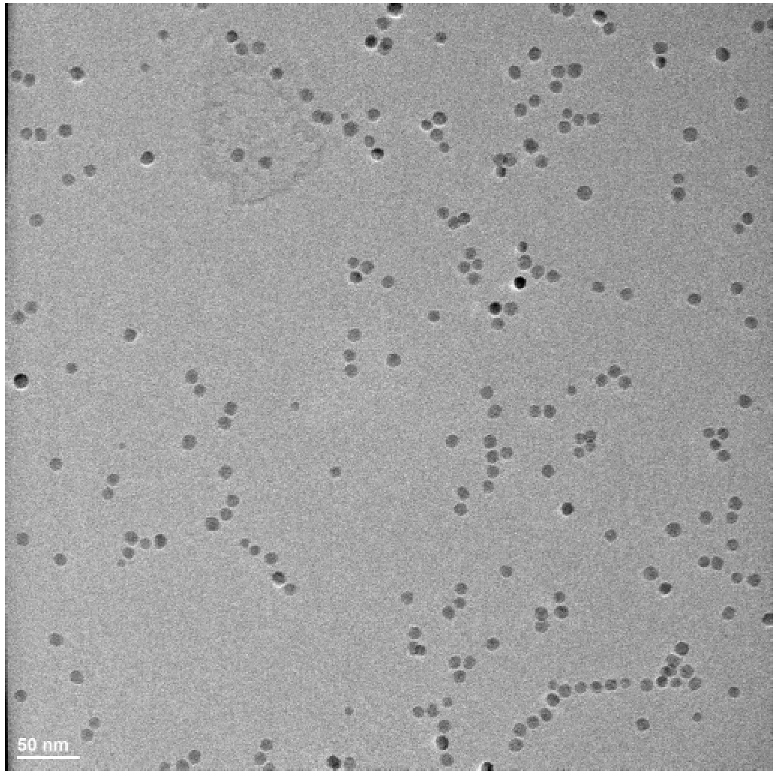
Coefficient Of Variation

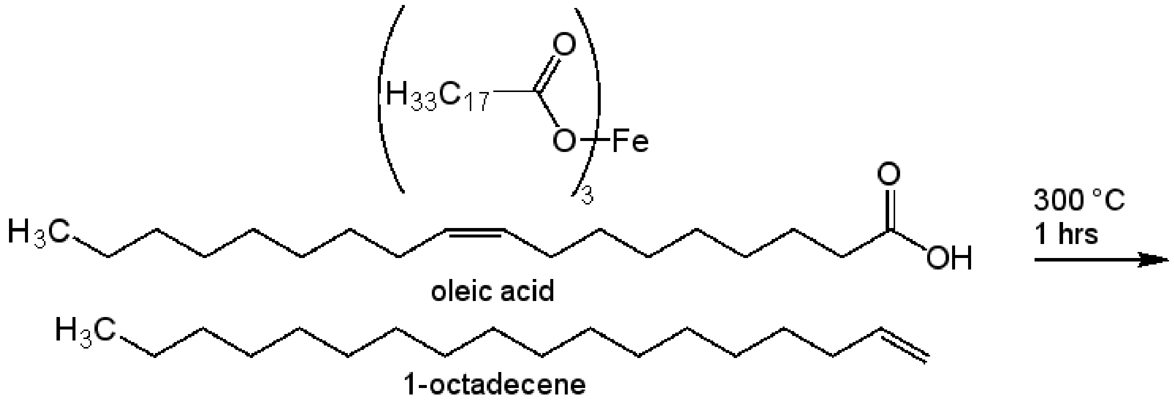
21.0% (5 samples)

Hufschmid R., Arami H., Ferguson R. M., Gonzales M., Teeman E., Brush L. N., Browning N. D., Krishnan K. M. *Nanoscale* **2015**; *7*, 11142-11154.

Literature Method Reproducibility

Hyeon





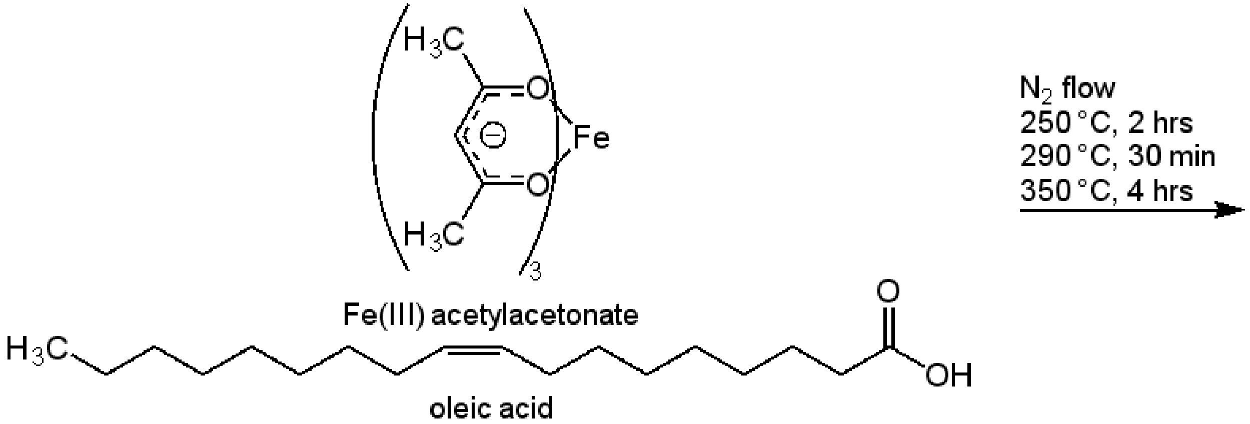
	Size (nm) [σ, RSD]
1	10.71 [1.16, 10.8%]
2	7.63 [0.66, 8.7%]
3	6.93 [0.85, 12.2%]
4	6.15 [0.67, 10.9%]
5	7.06 [1.06, 15.0%]
Avg	7.70 [0.90, 11.7%]

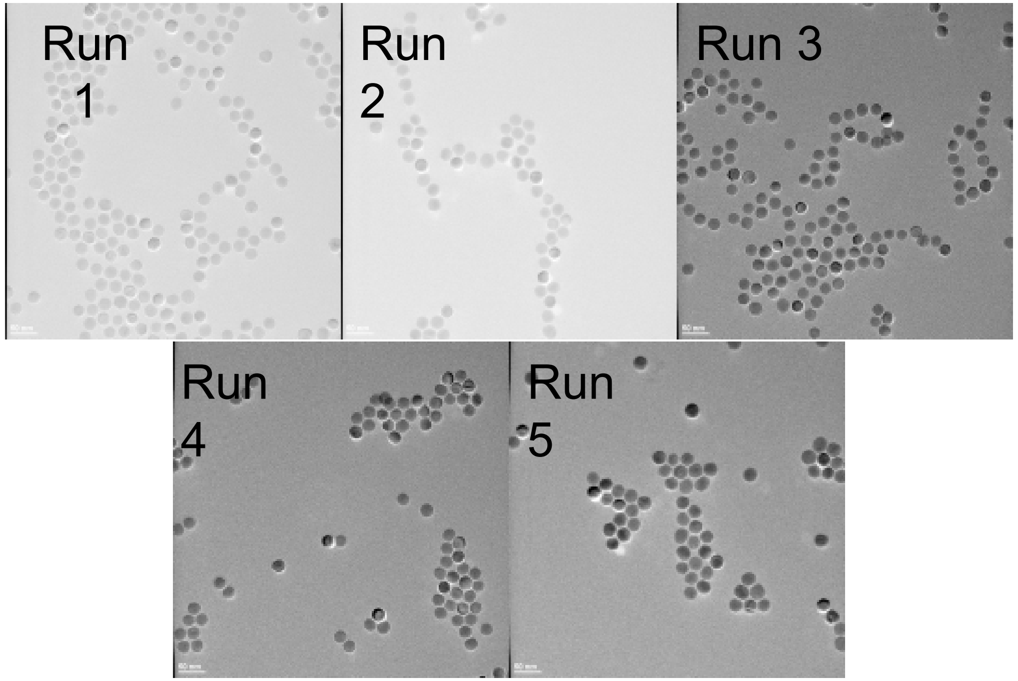
Coefficient Of Variation

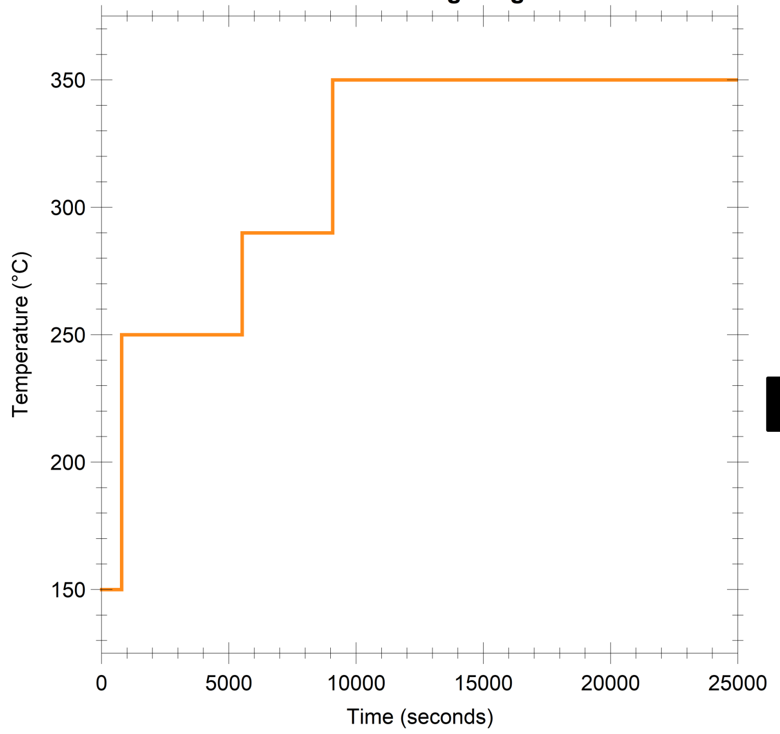
22.9% (5 samples)

Park J., An K., Hwang Y., Park J. G., Noh H. J., Kim J. Y., Park J. H., Hwang N. M., Hyeon T. *Nat. Mater*. **2004**; *3,* 891-895.
Shokouhimehr M., Shin K.-Y., Lee J. S., Hackett M. J., Jun S. W., Oh M. H., Jang J., Hyeon T. *J. Mater Chem A.* **2014**, *2*, 7593-7599.

Newly Developed One-Pot Procedure







	Size (nm) [σ, RSD]
1	23.52 [1.51, 6.4%]
2	24.15 [1.74, 7.2%]
3	22.34 [1.45, 6.5%]
4	22.89 [1.42, 6.2%]
5	24.43 [1.76, 7.2%]
Avg	23.47 [1.58, 6.7%]

Coefficient Of Variation

3.7% (5 samples)

Dreier, T.A.; Vreeland, E.C.; Watt, J.; Huber, D.L. *Nanotechnology,* Submitted (Invited Article)

Comparison and Summary

	Average Size	S_{pool}	CV
One Pot	23.47 nm	1.58 nm (6.7%)	3.7%
Krishnan	27.31 nm	4.51 nm (16.5%)	21.0%
Hyeon	7.70 nm	0.90 nm (11.7%)	22.9%

$$s_{pool} = \sqrt{\frac{s_1^2 + s_2^2 + \cdots + s_k^2}{k}}$$

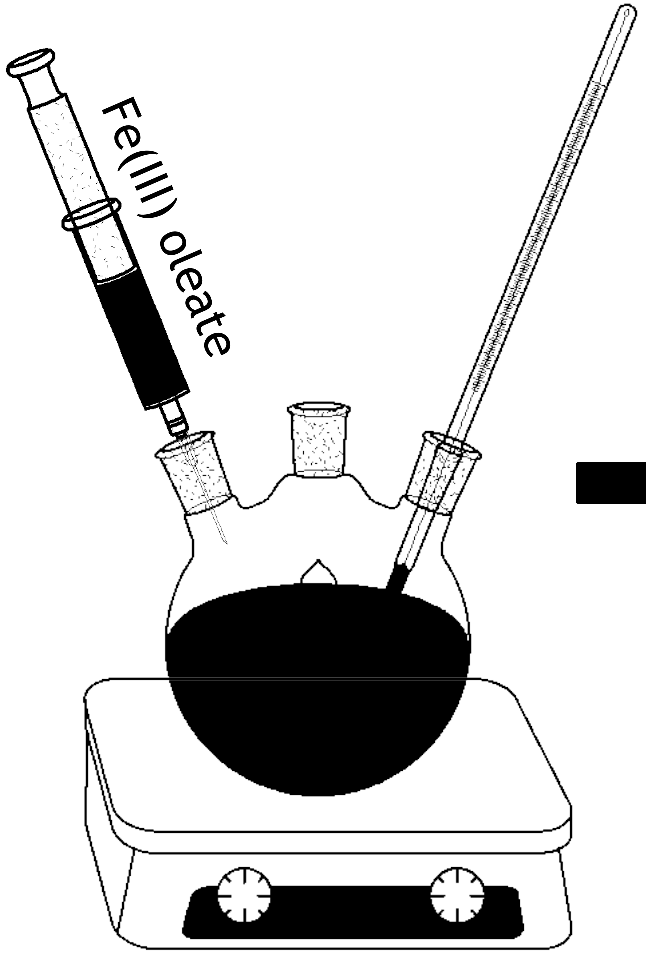
$$CV = \frac{\sqrt{\frac{1}{k}\Sigma(x_i - \mu)^2}}{\mu}$$

- One pot procedure is highly reproducible
- Low dispersity products
- Low variation between replications
- Compares favorably to existing methods

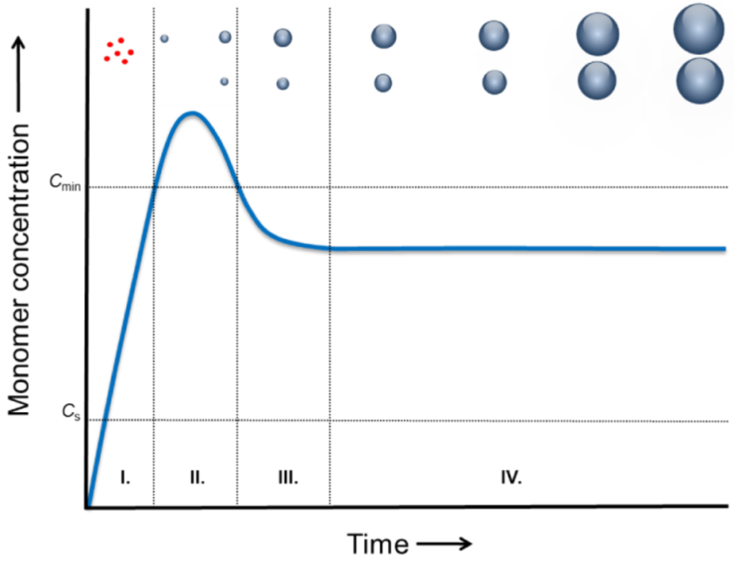
Remaining Questions:

- How scalable is the result?
- Other figures of merit?
- Best method of size control?
- Can other ferrites be made similarly?

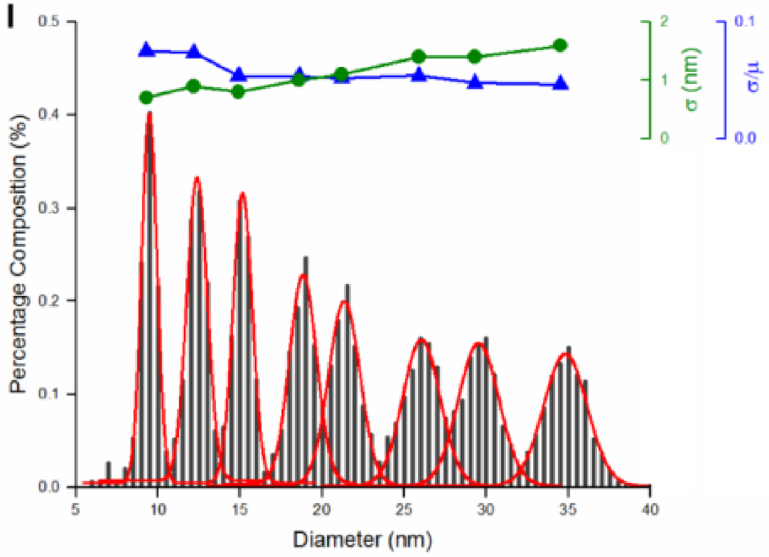
“Extended LaMer” Reaction For Magnetite



Continuous Precursor Addition



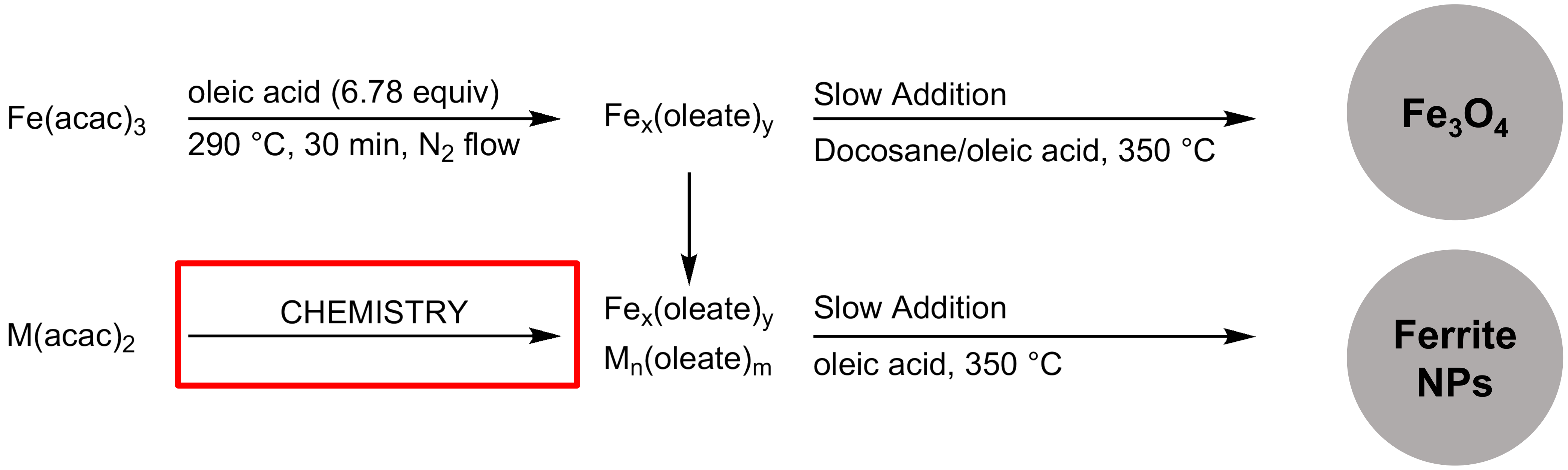
Extended LaMer Mechanism



Size Control

Vreeland, E.C.; et al. *Chem. Mater.* **2015**, *27*, 6059-6066.

Extended LaMer Approach to Mixed Ferrites

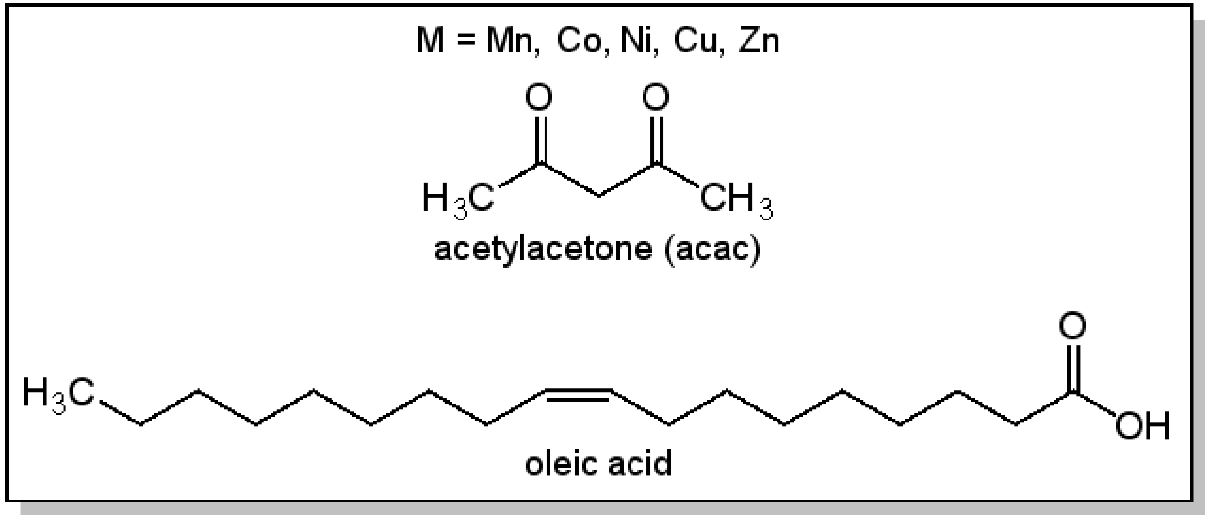


Vreeland, E.C.; et al. *Chem. Mater.* **2015**, *27*, 6059-6066.

Optimized Reaction Conditions

$$M(acac)_2 \xrightarrow[\text{3-12 hrs}]{\text{150 °C, oleic acid}} M(oleate)_2$$

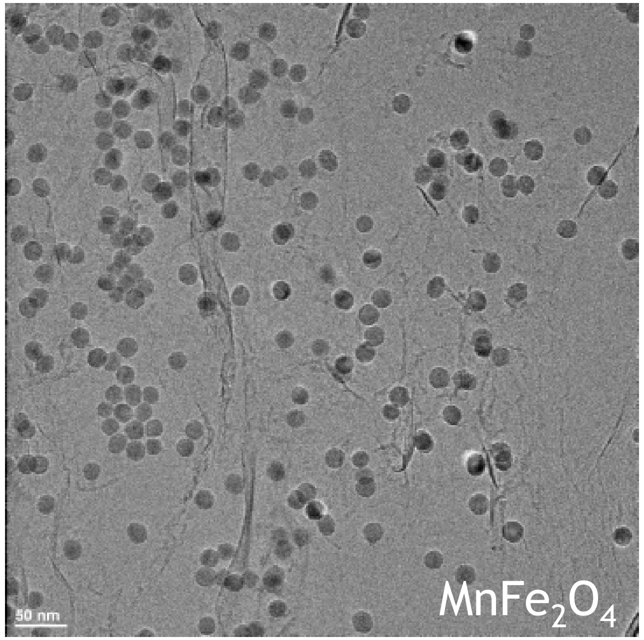
$$Fe(acac)_3 \xrightarrow[\text{30 min}]{\text{290 °C, oleic acid}} Fe(III)\,oleate$$

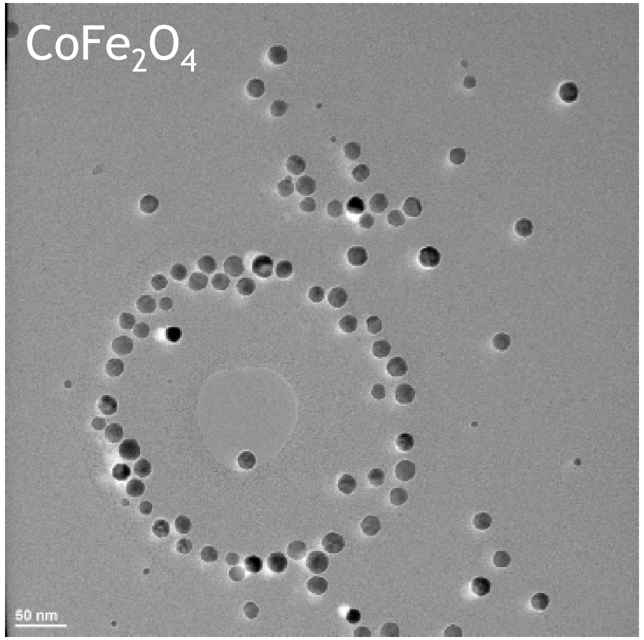


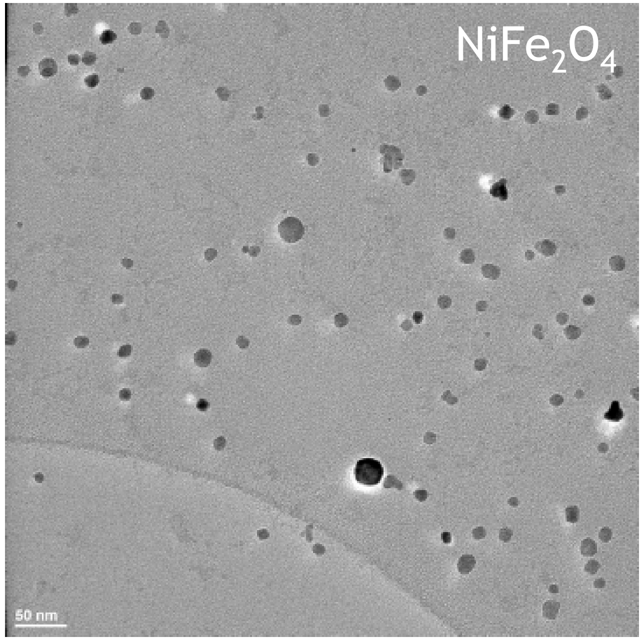
	Run 1	Run 2	Run 3	Average	CoV
Co Ferrite	18.13 (10.8%)	17.95 (11.6%)	18.54 (14.2%)	18.21 (12.3%)	1.66%
Mn Ferrite	19.10 (7.2%)	18.79 (8.7%)	18.34 (8.4%)	18.74 (8.1%)	2.04%
Cu Ferrite	28.56 (9.8%)	25.08 (10.8%)	24.65 (8.4%)	26.10 (9.8%)	8.22%
Zn Ferrite	29.56 (8.9%)	27.78 (10.0%)	31.57 (9.1%)	29.64 (9.3%)	6.40%

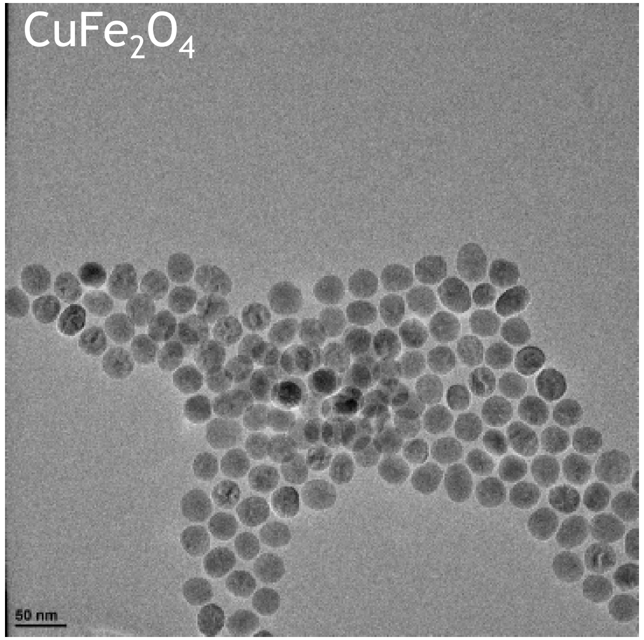
CoV for One Pot Magnetite: 3.7%
CoV for Hyeon Magnetite: 17.7%
CoV for Krishnan Magnetite: 21.0%

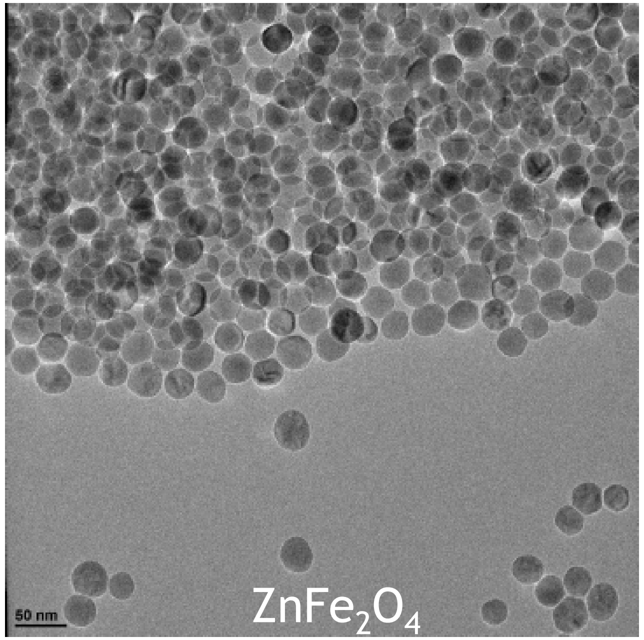
TEM Results


$MnFe_2O_4$
50 nm

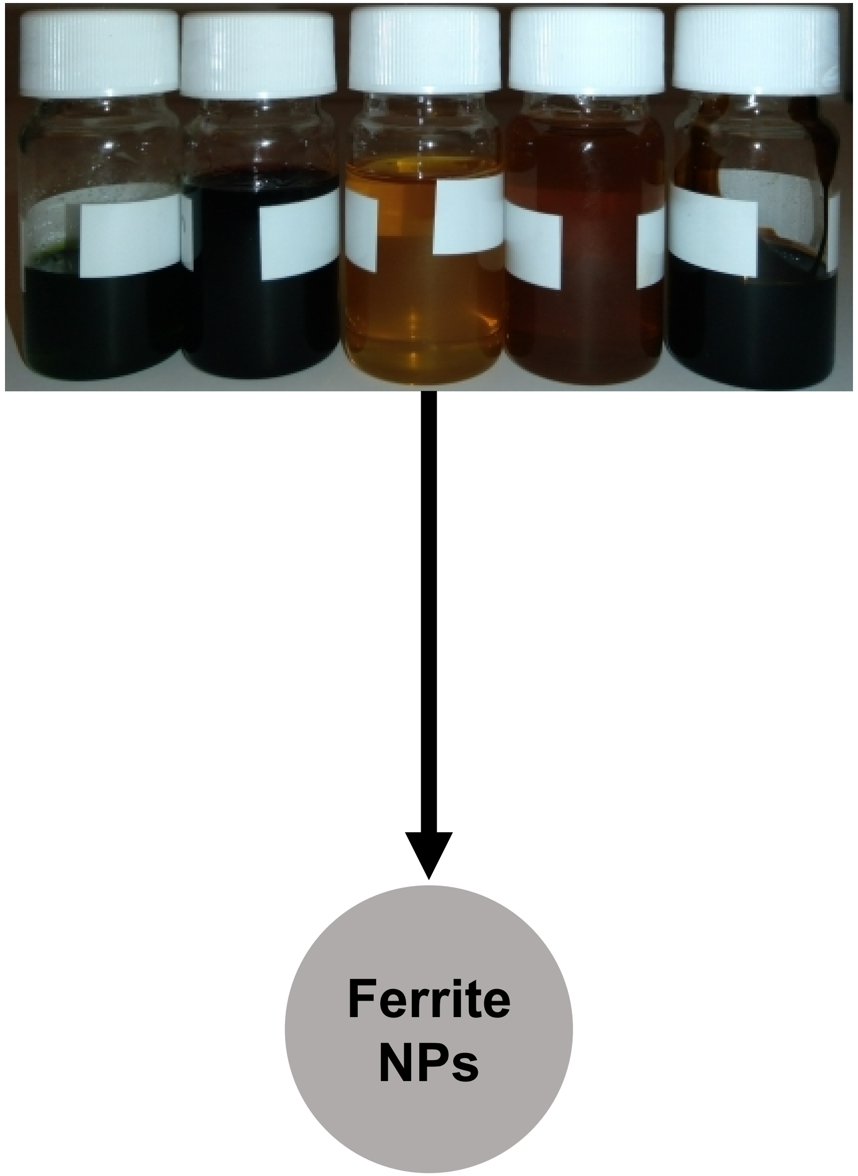

$CoFe_2O_4$
50 nm


$NiFe_2O_4$
50 nm


$CuFe_2O_4$
50 nm


$ZnFe_2O_4$
50 nm

Summary and Future Directions



- $M(acac)_2$ generally applicable precursors
- Structure of $M_x(oleate)_y$ → NP properties
- $M_x(oleate)_y$ structure controllable
- Modular approach to binary ferrites
- Same process for ternary ferrites?
- Pre-nucleation coordination dynamics?
- Universal size control strategy?

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Steve Jett

Erika Vreeland

Sandia LDRD

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