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# Magnetic Nanoparticle Formation From Ferric Acetylacetonate Decomposition on Cold Substrates using Supercritical Fluids

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## Introduction and Overview

*New synthetic routes for the preparation of magnetic nanoparticles and thin films are under constant investigation. In particular iron oxide magnetic particles have attracted interest due to their application as recording media, ferrofluids, catalysts and targeted drug delivery.* ***Ferric acetylacetonate Fe(acac)$_3$ is known to undergo thermal decomposition to form either $Fe_3O_4$ or $\alpha$-$Fe_2O_3$ magnetically ordered materials when heated above 180 °C. We decompressed a mixture of ferric acetylacetonate (Fe(acac)$_3$) in supercritical $CO_2$ to deposit magnetic nanoparticle films at room temperature.*** *Two different processes were developed: one based on the Rapid Expansion of a Supercritical Solution (RESS) and another based on the depressurization of the saturated supercritical mixture in a fixed volume (BATCH process). The rate of decompression varies dramatically between the two processes, RESS (μsec scale) and BATCH (sec scale).*

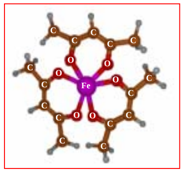
## Supercritical Fluid

**A fluid above its critical point**

**$CO_2$: $T_c$ = 31.1 °C, $P_c$ = 73.8 bar**

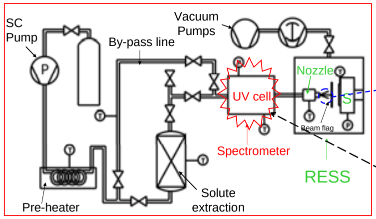
❖ Single phase with properties of both a liquid and a gas
❖ Ability to dissolve low vapor pressure solids at high pressures but modest temperatures
❖ Applications include decaffeination of coffee, toxic waste combustion, dry cleaning, particle and thin film formation

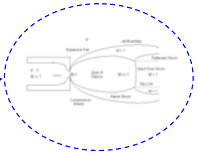
## Ferric Acetylacetonate (Fe(acac)$_3$)



## RESS Experimental Apparatus

***The magnetic thin films are produced by expanding the supercritical solution and directing the resulting supersonic jet onto cold silicon wafers***

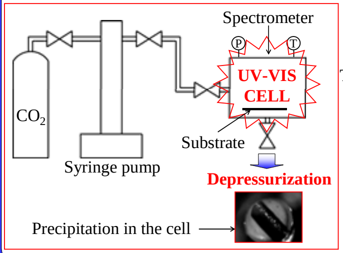


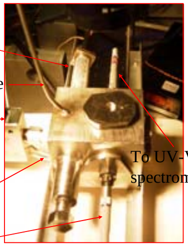



UV-VIS high pressure cell to monitor concentration

## BATCH Experimental Apparatus

***Depressurization of the supercritical mixture within the fixed volume UV-VIS cell causes the solute to precipitate and deposit on a silicon wafer, placed within the cell.***

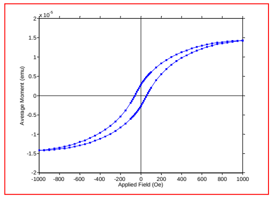


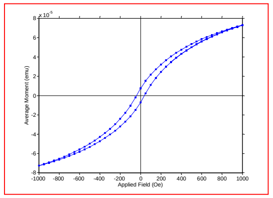

UV-VIS Cell

## Results: Magnetic Measurements

Quantum Design **SQUID magnetometer**



M(H) at 300K for RESS particle film (vacuum, $N_2$)



M(H) at 300K for BATCH particle film (slow depressurization)

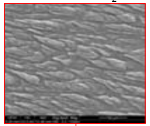
❖ **Ferromagnetic** signal with similar properties at 2K and 300K for both RESS and BATCH processes
❖ Comparable **paramagnetic** signal strengths only for RESS samples
❖ At 300K: $M_s$=7.3x10$^{-5}$ emu, $H_c$=35 Oe, $M_r$=2.1x10$^{-6}$ emu (BATCH)
❖ At 300K: $M_s$=1.4x10-5 emu, $H_c$=55 Oe, $M_r$=8.3x10-6 emu (RESS)
❖ Fe(acac)3 starting material is paramagnetic

Fe(acac)$_3$ **decomposition** shown to occur at $T < T_{decomp}$!

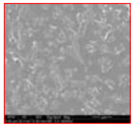
## Results: SEM imaging

### RESS process

Pb = 1 atm/$N_2$

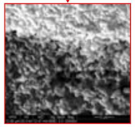


Pb = 10 Torr

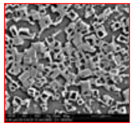


Size: 30-100 nm

Pb = 1 atm/air



Size: 100-700 nm

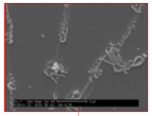


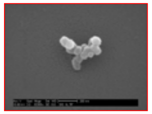
Size: 80-600 nm

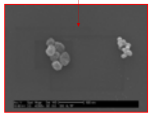
$T_o$=77°C, $P_o$=140bar, $D_n$=100 μm, $X_p/D_n$=100, growth time=10 min, $X_s$~10$^{-6}$ mole fraction

Smaller nanoparticles are formed when the expansion is into vacuum

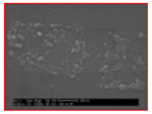
### BATCH process







Slow Depressurization



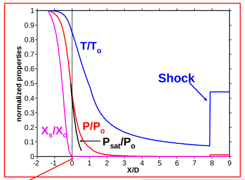
Fast Depressurization

Size: 10-100 nm

$P_o$ = 140 bar, $T_o$ = 313K
$X_s$ = 1.4x10$^{-4}$ mole fraction

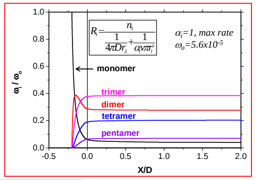
**Effect of shockwave structure?**

## Calculated Centerline Properties of $CO_2$ /Fe(acac)$_3$ RESS Expansion




Nozzle exit

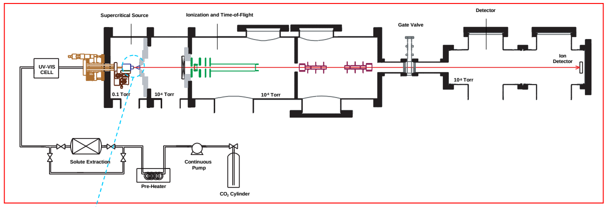
## Diffusion-kinetic model of Fe(acac)$_3$ cluster formation

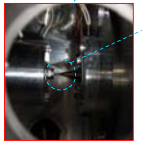



$P_o$ = 140 bar, $T_o$ = 343K, D = 100 μm

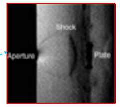
Since the RESS expansion is predicted to provide less than 10 nm scale clusters, **substantial growth must occur at the surface**

## Interface of RESS Source with a TOF Mass Spectrometer

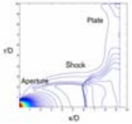




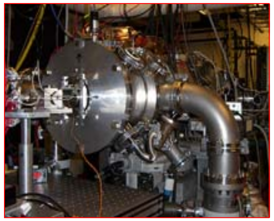
Nozzle-skimmer expansion region



$CO_2$ Free-Jet Shadowgraph



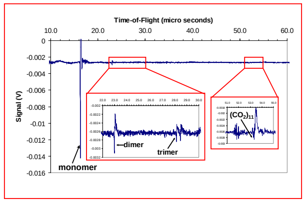
$CO_2$ Computed Density Contours (ASFJ using RK)



Time-of-Flight Mass Spectrometer

❖ Sample a molecular beam from the high pressure supersonic free-jet RESS expansion
❖ Identify size and composition of the clusters and nanoparticles formed in the jet
❖ Compare experimental data with kinetic models

## Preliminary Results




❖ Verified the detection of $CO_2$ monomer and $CO_2$ clusters in the RESS expansion

❖ Need to optimize the interface between the RESS expansion and the Time-of-Flight Mass Spectrometer

❖Improve detection of higher order clusters

## Conclusions

❖ Thin magnetic nanoparticle films were produced on cold substrates with RESS and BATCH processes
❖ All films were magnetically ordered with coercivities between 30-60 Oe
❖ Heating of Fe(acac)$_3$ above $T_{decomp}$ to produce the magnetic nanoparticles was not necessary
❖ The mechanism for Fe(acac)$_3$ decomposition in supercritical $CO_2$ at $T < T_{decomp}$ needs further investigation
❖ The RESS expansion was coupled with a Time-of-Flight Mass Spectrometer and preliminary measurements were performed

## Acknowledgements

❖ National Science Foundation
❖ Dr. James R. O' Brien of Quantum Design: SQUID