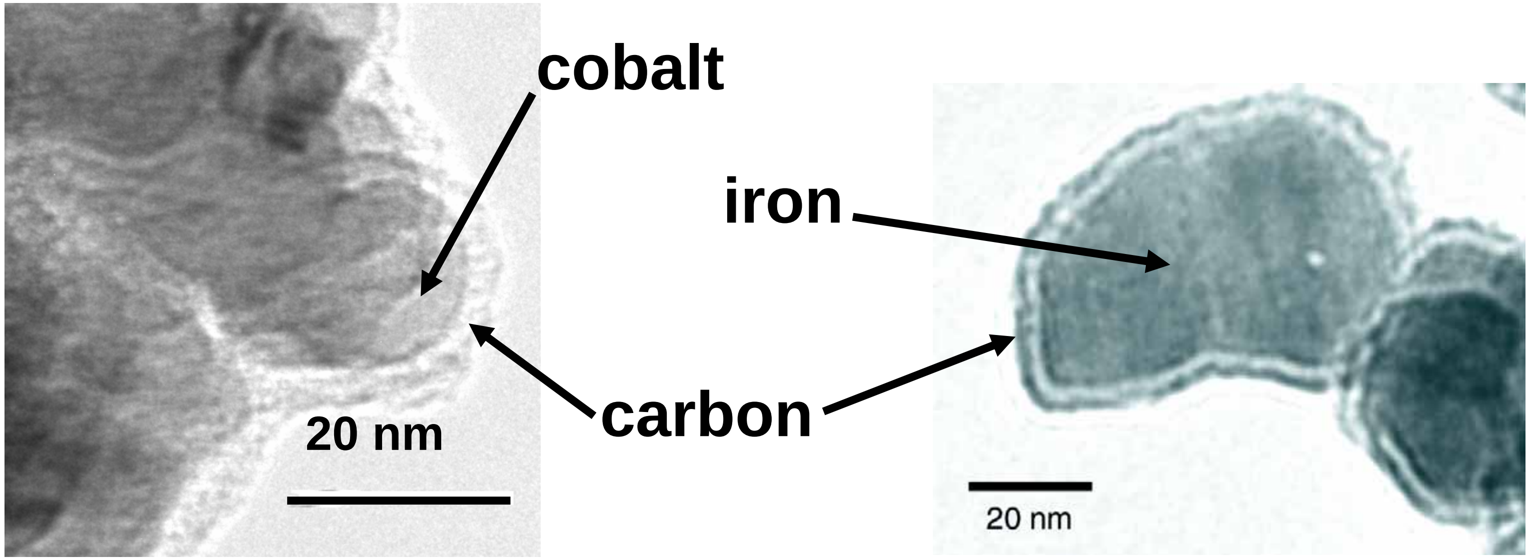
Introduction –*Carbon covered metal nanoparticles* –

Easy to synthesize (ion-exchange and neutralization in Ar)

$$CaC_2 + MCl_2 \xrightarrow[\text{acetonitrile}]{\sim 80\ ^{o}C} MC_2 + CaCl_2 \xrightarrow[\text{acetonitrile}]{> 200\ ^{o}C} M@C$$

nano-size carbon-covered metals (~ 20 nm)



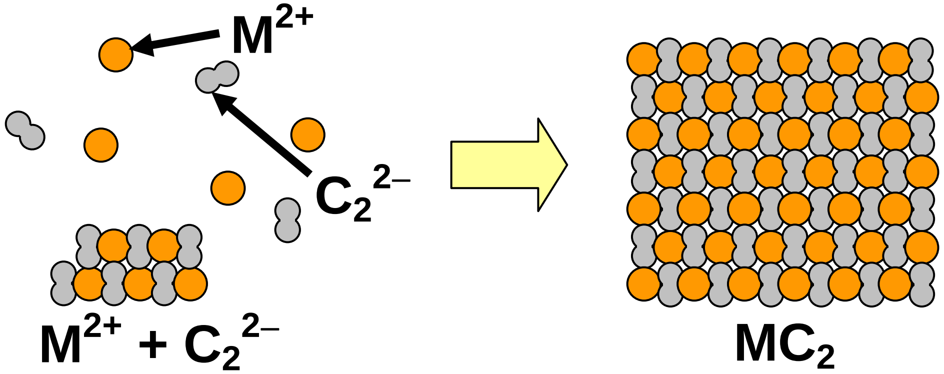
carbon covered cobalt

carbon covered iron

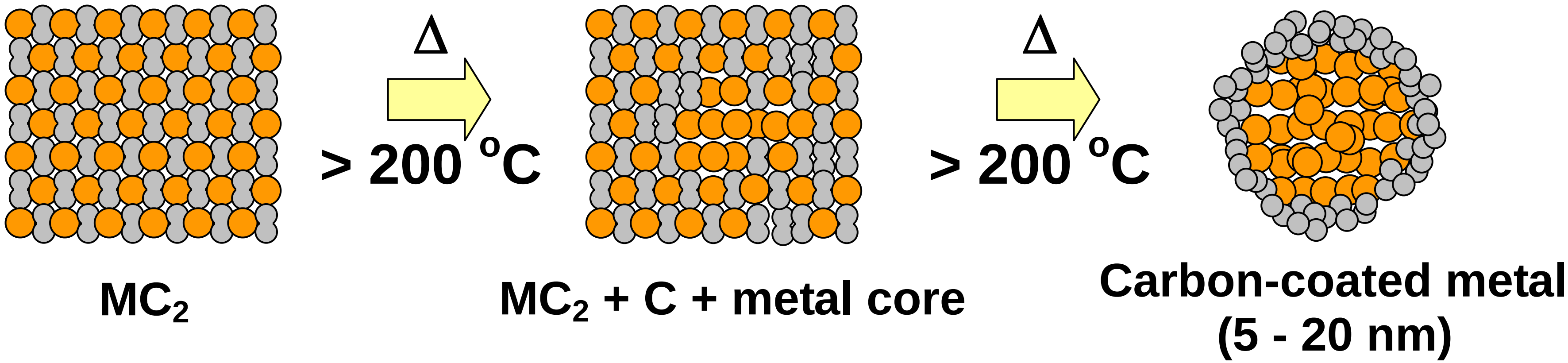
cf. *Appl. Phys. Lett.* 84 (2004), 1753-1755

Mechanism of the carbon-covered nanoparticle formation

1st step: formation of metal acetylide MC_2



2nd step: reduction of M^{2+} by C_2^{2-} and segregation



Advantage of carbon covered metal nanoparticles

Carbon shell protect the inner metal particle from environmental chemical species.

- **Oxidation resistant**

  This feature enable to treat the particle under air

- **Acid resistant**

  The particles can survive even at pH = 1 condition over few hours

Suggestion: Can we obtain the carbon-covered nano-alloy by using the mixture of MCl_2 and $M'Cl_2$?

Sample preparation

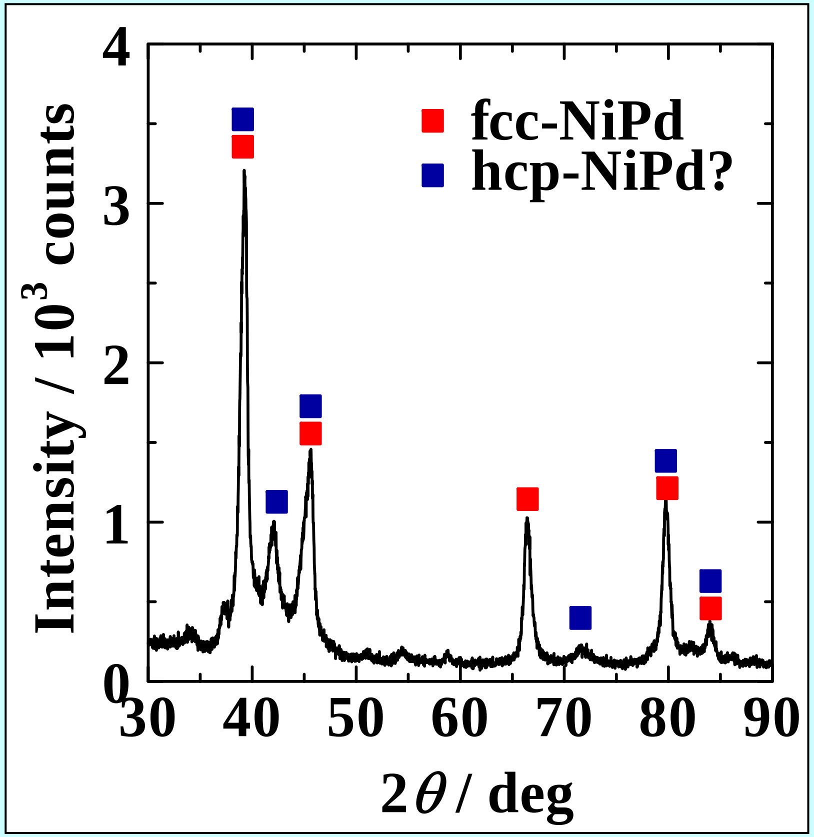
Metal nano-alloys

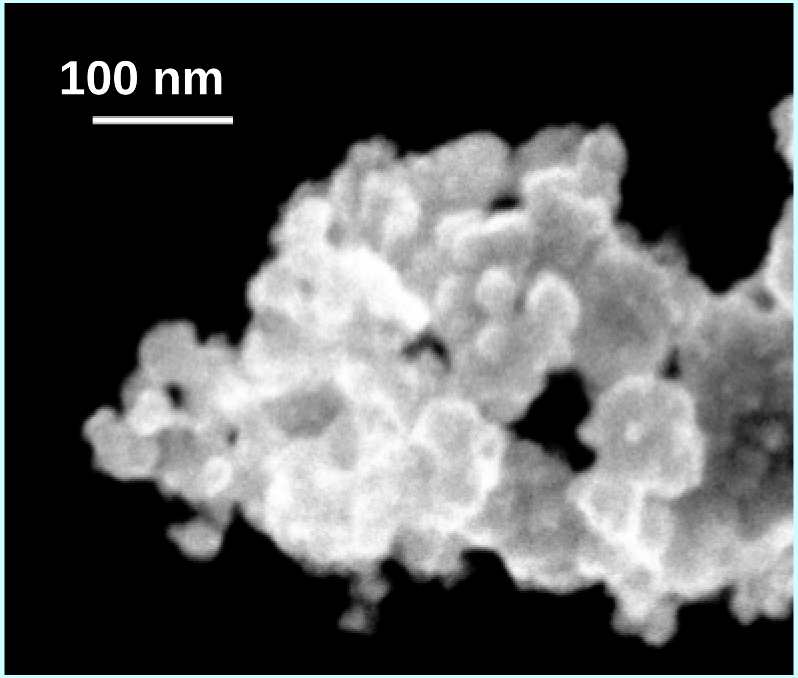
1. $NiCl_2$ (2.5 mmol) + $PdCl_2$ (2.5 mmol) + CaC_2 (5mmol)
2. $FeCl_2$ (3 mmol) + $CoCl_2$ (2 mmol) + CaC_2 (5mmol)
3. $EuCl_2$ (1 mmol) + $CoCl_2$ (4 mmol) + CaC_2 (5mmol)
4. $NdCl_3$ (2 mmol) + $FeCl_2$ (3 mmol) + CaC_2 (6mmol)
5. $SmCl_3$ (2 mmol) + $CoCl_2$ (3 mmol) + CaC_2 (6mmol)

Blue metals can form MC_2 compound
Red metals cannot form MC_2 compound

Reaction temperature: 240 ^{o}C, 6 hours / acetonitrile

1. Ni-Pd system (XRD & SEM image)

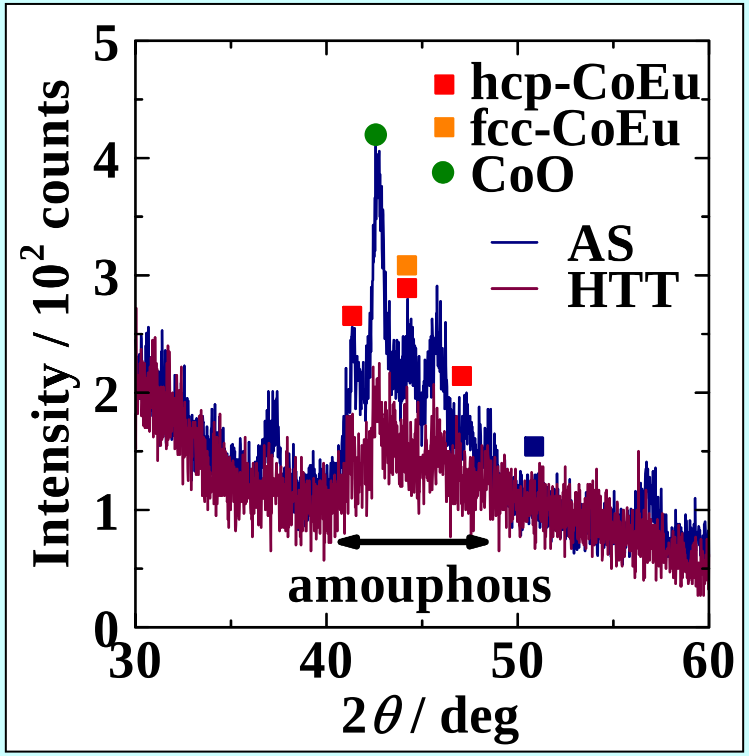


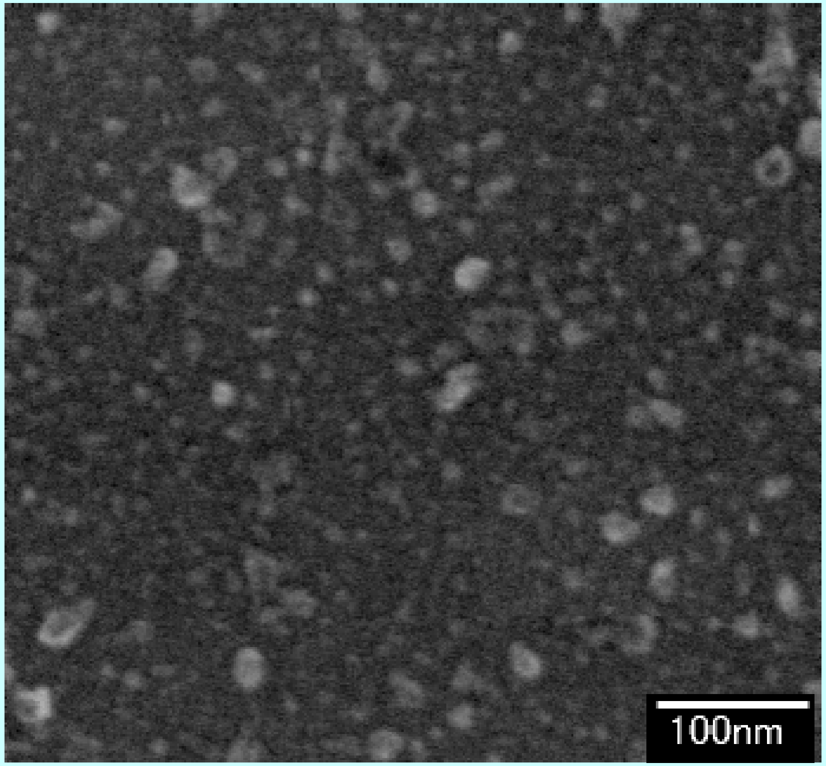


fcc-lattice (lattice constant > Pd)
and
hcp-lattice (lattice constant < Pd)

Particle size: ~ 30 nm
(particles easily disperse by sonication)
EDS analysis: Pd:Ni ~ 1:1

3. Eu-Co system (XRD & SEM image)

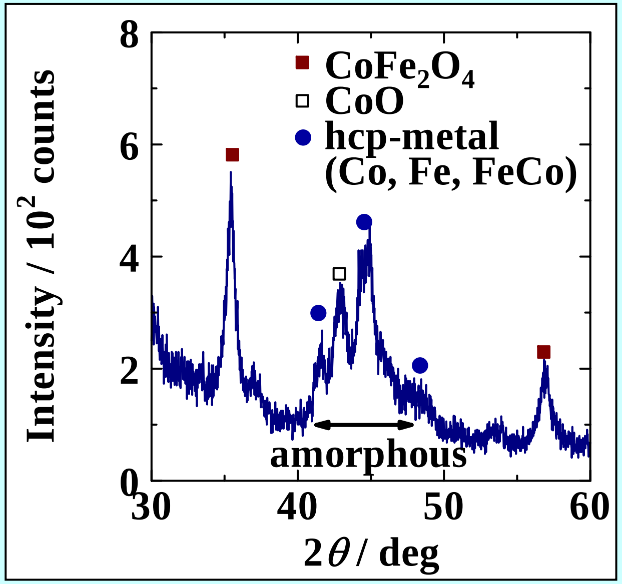




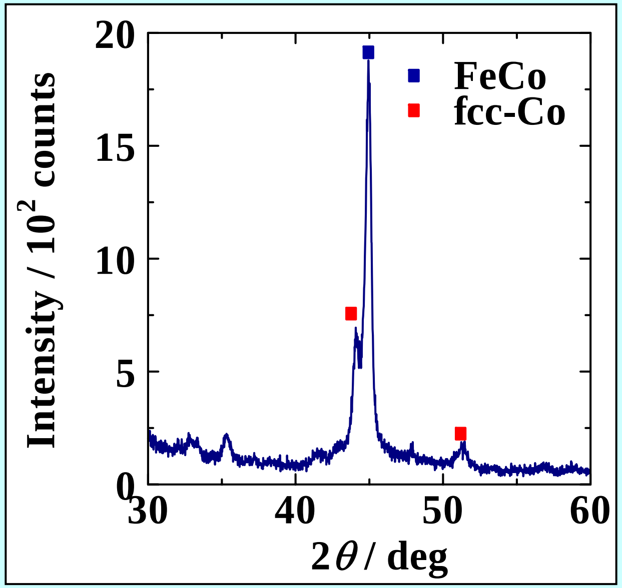
AS: hcp-CoEu + amorphous
HTT400 ^{o}C 1h: amorphous

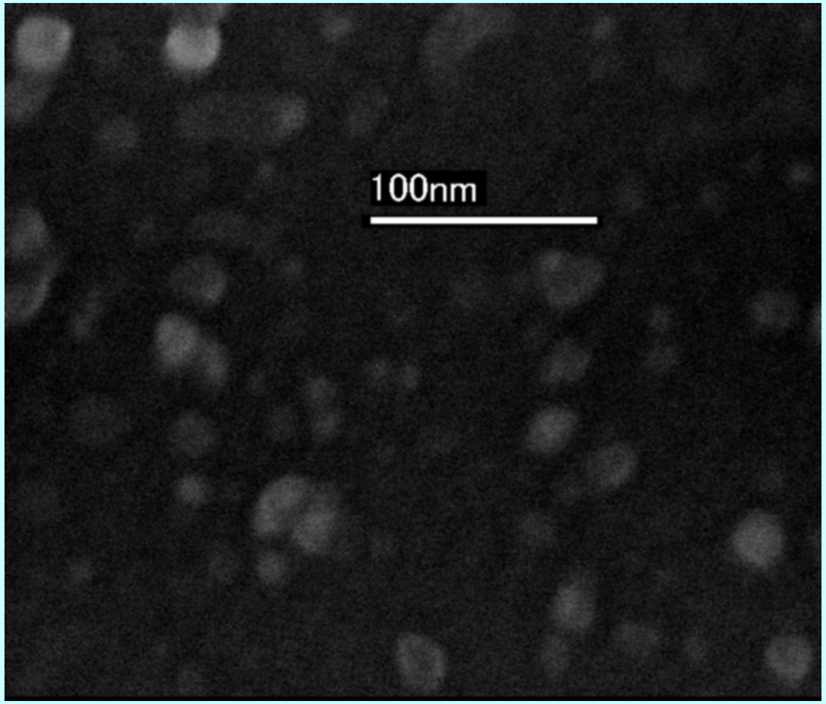
Particle size: ~ 10 nm
EDS analysis: Co:Eu ~ 8:1

2. Fe-Co system (XRD & SEM image)



HTT600 °C 1h

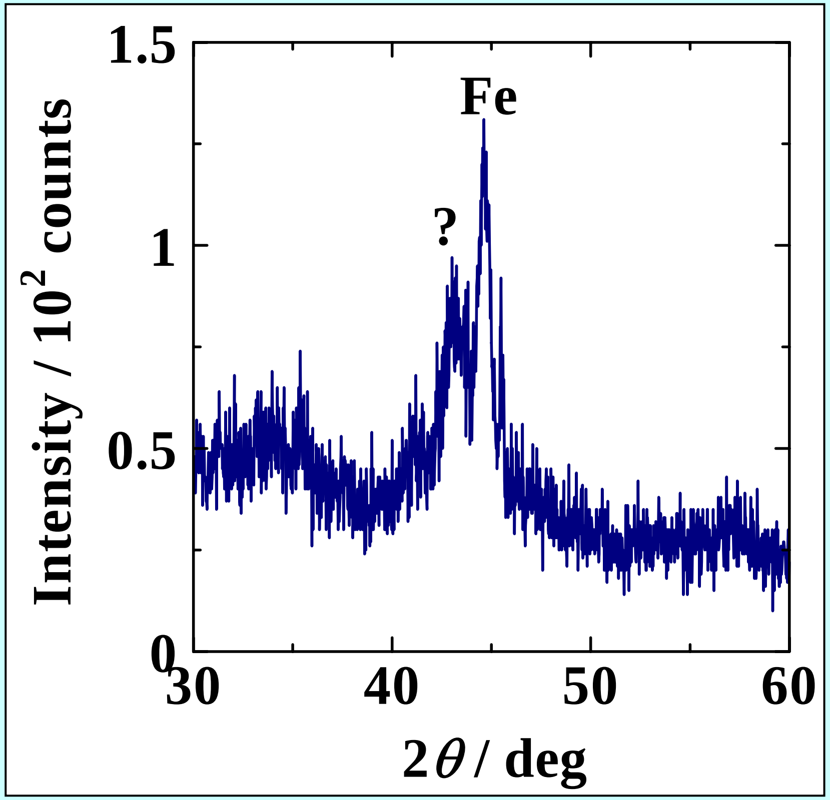




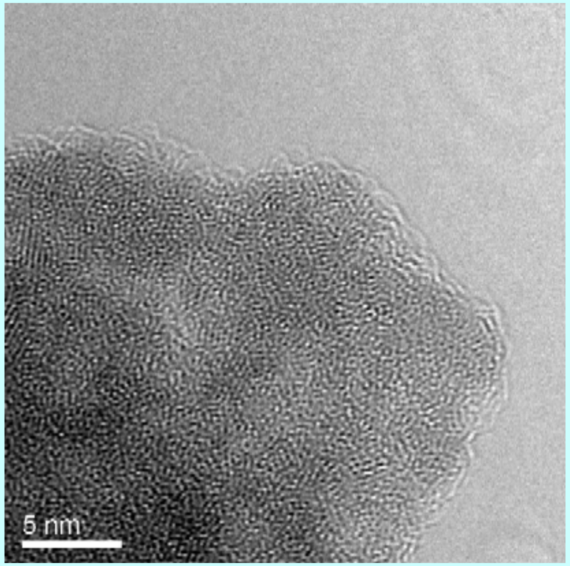
AS prepared: amorphous phase
HTT400 °C 1h: FeCo crystalline alloy

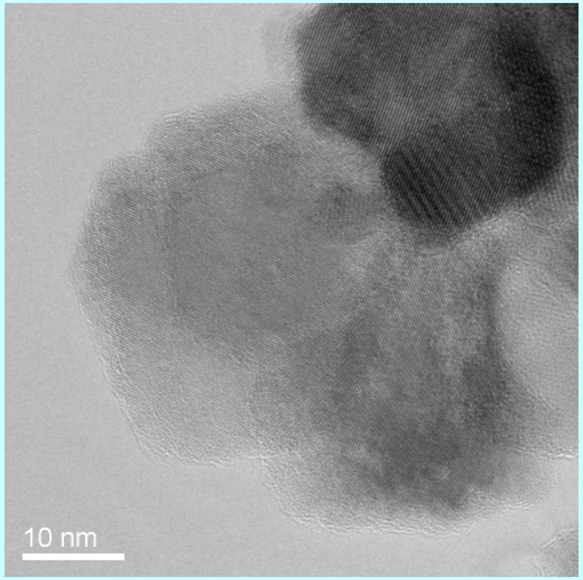
Particle size: ~ 10 nm
EDS analysis: Fe:Co ~ 1:1

4. Fe-Nd system (XRD & TEM image)



an iron peak
and
an unknown peak (alloy?)

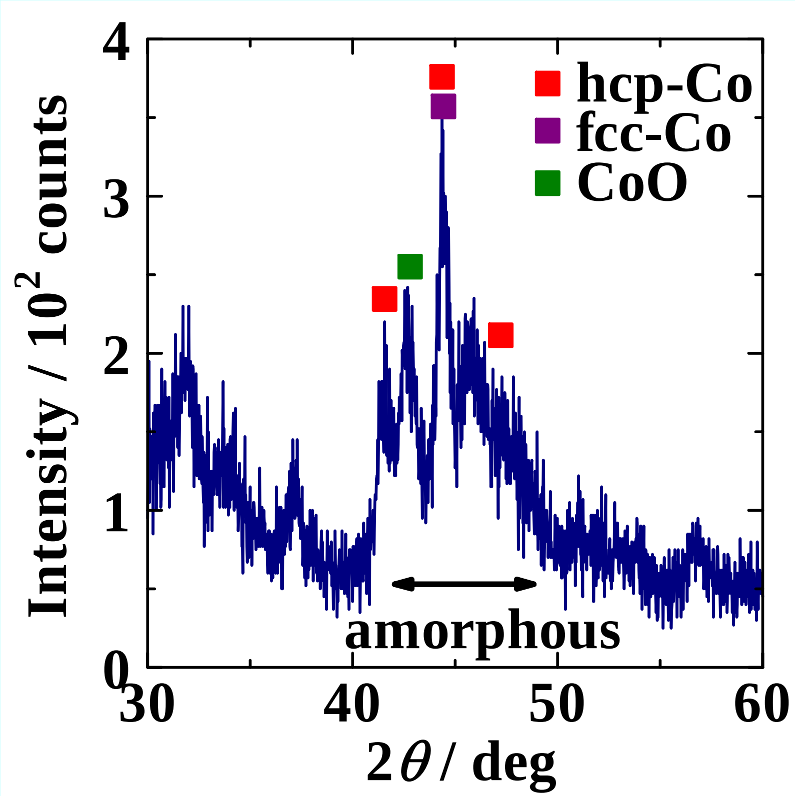


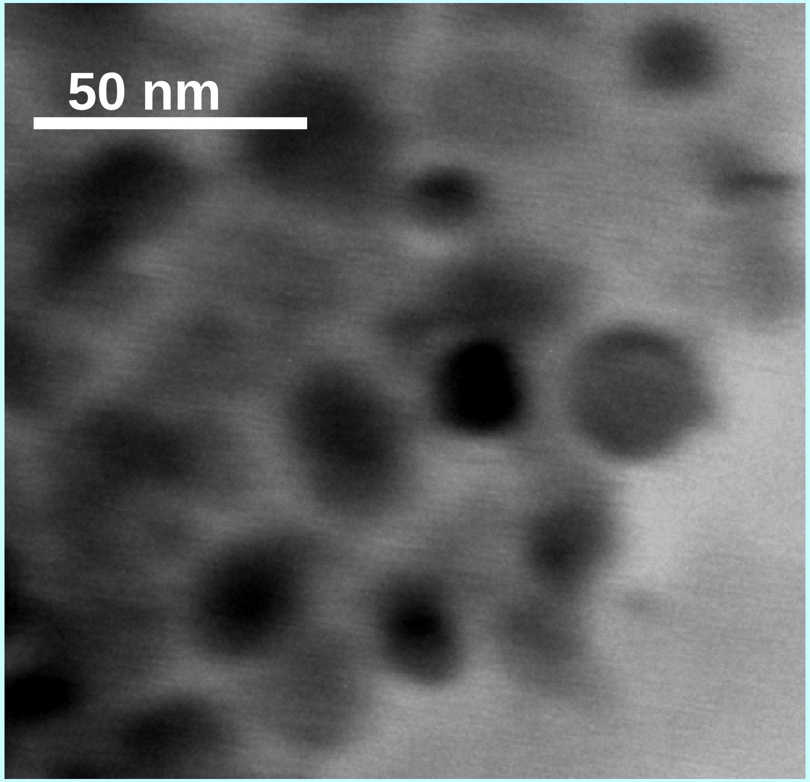


Amorphous particle (left) and crystalline particle (right) coexist.

EDS result: Fe:Nd ~ 14:1
small amount of Nd

5. Co-Sm system (XRD & TEM image)

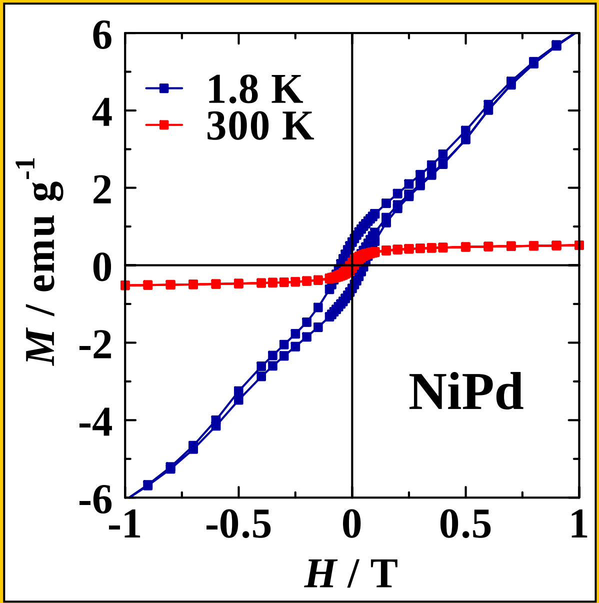


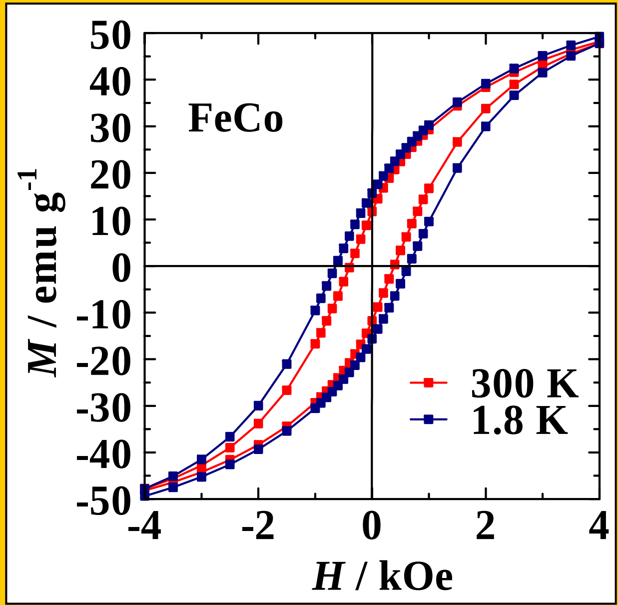


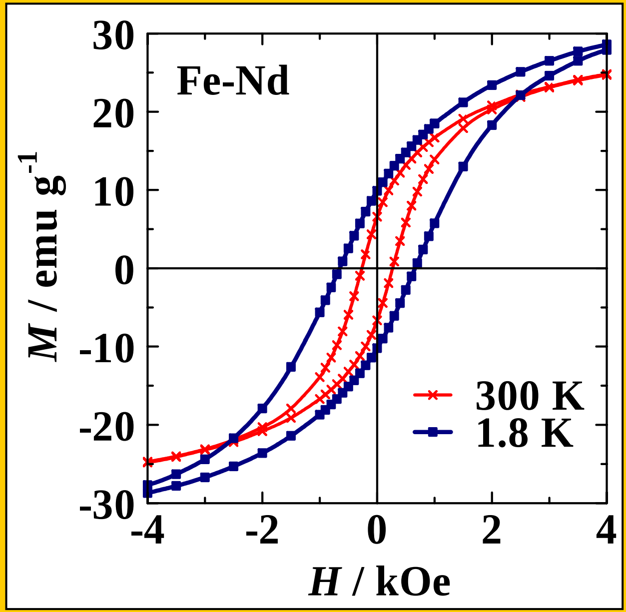
hcp-Co and fcc-Co
The effect of the Sm is quite small

EDS: Co:Sm ~ 20:1
Quite little Sm embedded in particle

Magnetism (NiPd, FePt)







NiPd: paramagnet
(cf. Ni: ferromagnet)

Ni atoms well disperse in Pd atoms (alloy)

H_c: 400 Oe (300 K)
650 Oe (1.8 K)

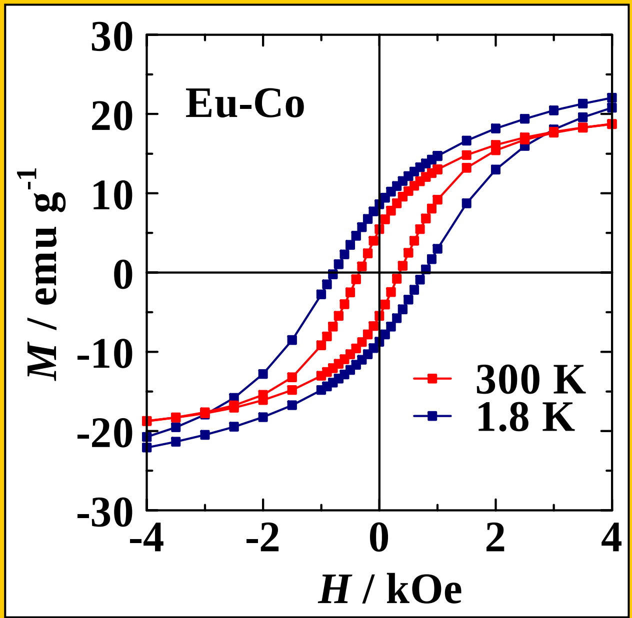
roughly same as Co@C and Fe@C

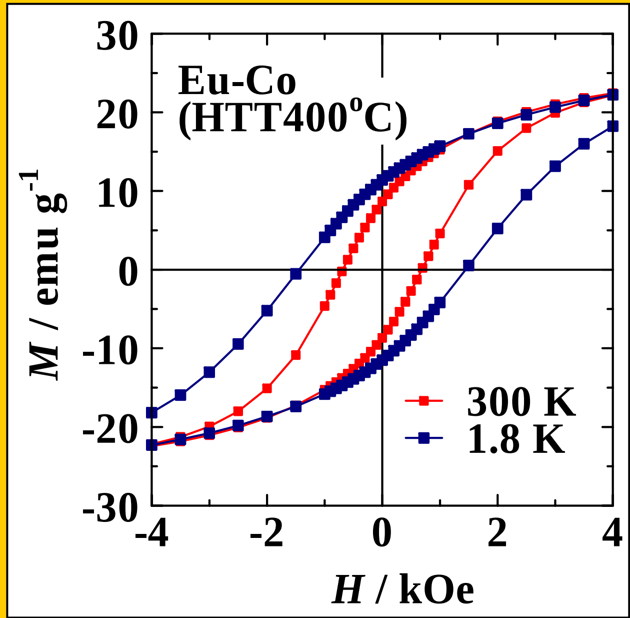
H_c: 300 Oe (300 K)
650 Oe (1.8 K)

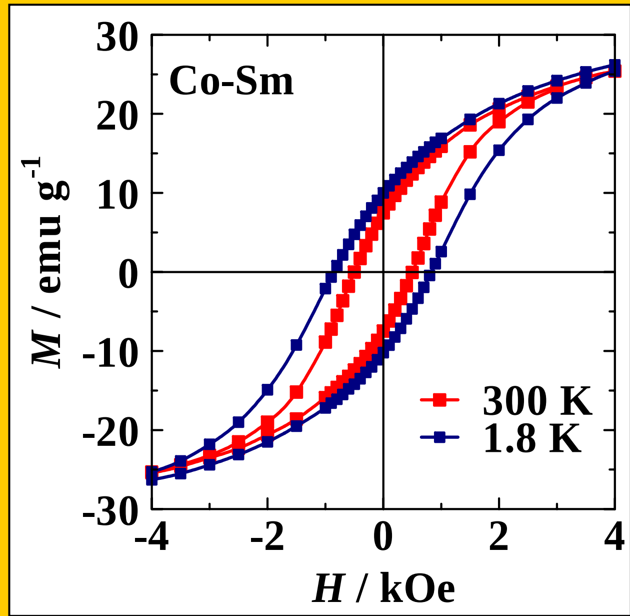
cf. Fe@C
H_c: 250 Oe (300 K)
400 Oe (1.8 K)

enhanced by Nd

Magnetism (EuCo, FeNd, CoSm)







H_c: 350 Oe (300 K)
800 Oe (1.8 K)

cf. Co@C
H_c: 300 Oe (300 K)
600 Oe (1.8 K)

H_c: 700 Oe (300 K)
1500 Oe (1.8 K)

H_c: 500 Oe (300 K)
800 Oe (1.8 K)

cf. Co@C
H_c: 300 Oe (300 K)
600 Oe (1.8 K)

enhanced by Sm

Summary (nano-alloy)

Group A: Fe, Co, Ni, Pd, Eu (the metals can form MC_2)

Group B: Nd, Sm (the metals cannot form MC_2)

Group A + Group A ⇨ nano-alloy (well mixed)

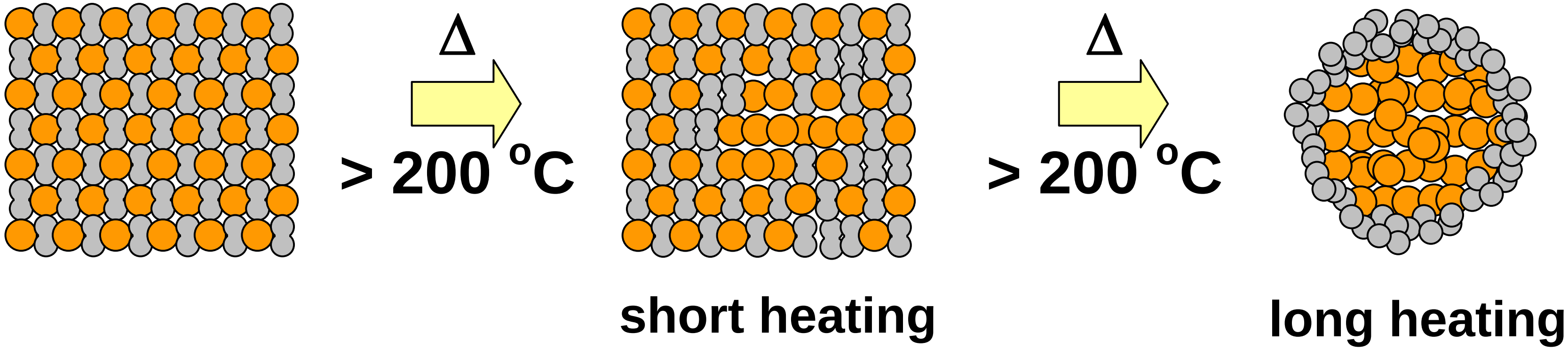
Group A + Group B ⇨ nanoparticle of A with small amount of B

Despite the small amount, B enhance the coercive force of A

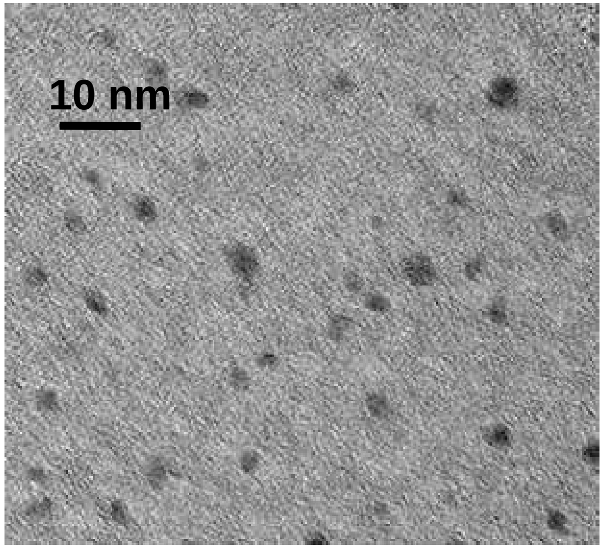
Size control of nanoparticle

When the application of the metal nanoparticle/nano-alloy is considered, the size control is important

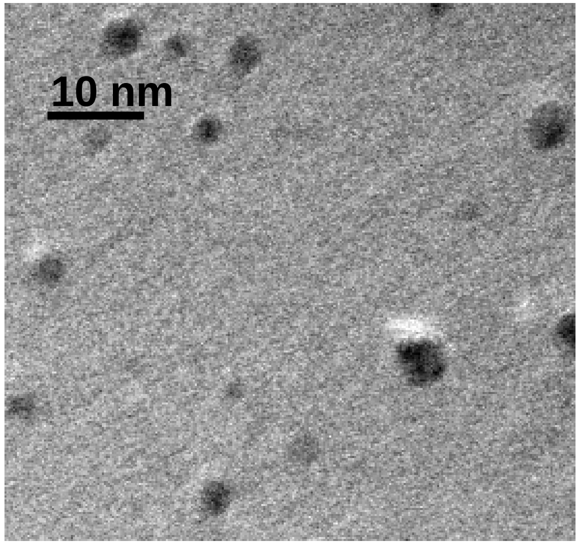
On the basis of the model shown below, short heating time gives small nanoparticle covered with carbon and MC_2



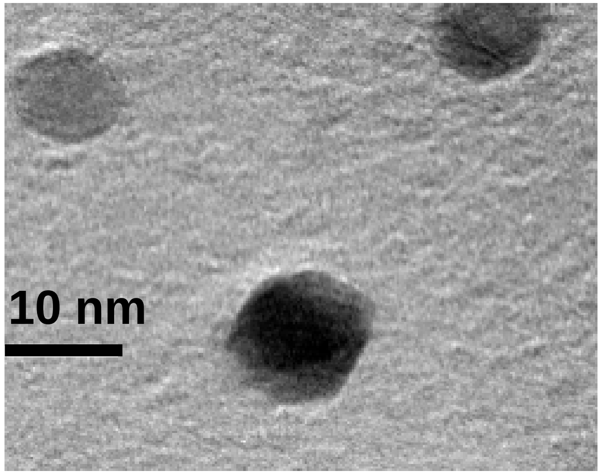
Size control of Ni@C



240 ^{o}C, 1h
(Amorphous)



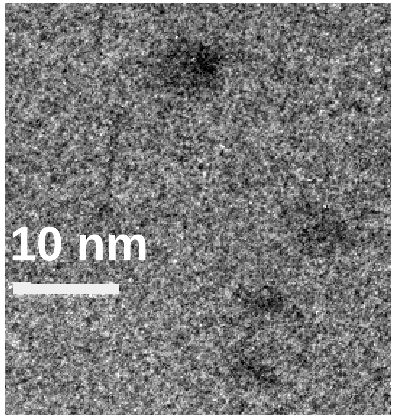
240 ^{o}C, 2h
(crystal)



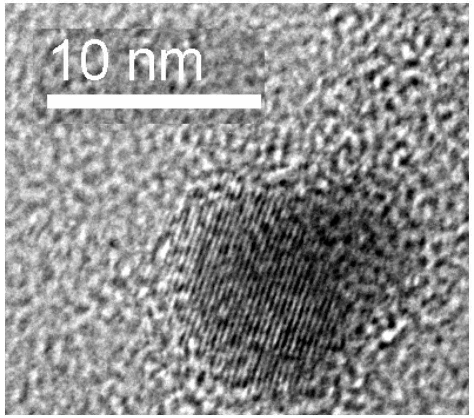
240 ^{o}C,8h
(Crystal)

- Particle size is controlled
- 30 min: Amorphous, > 2h: Crystal

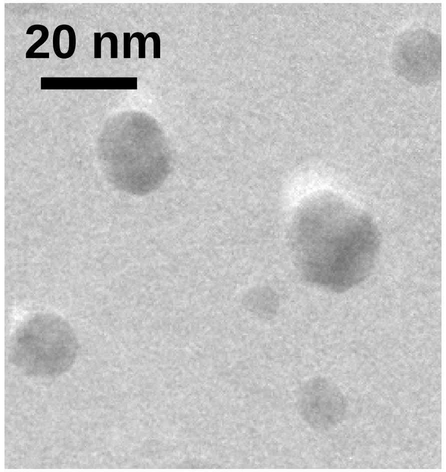
Size control of CoEu@C



240 ^{o}C, 1h
(amorphous)



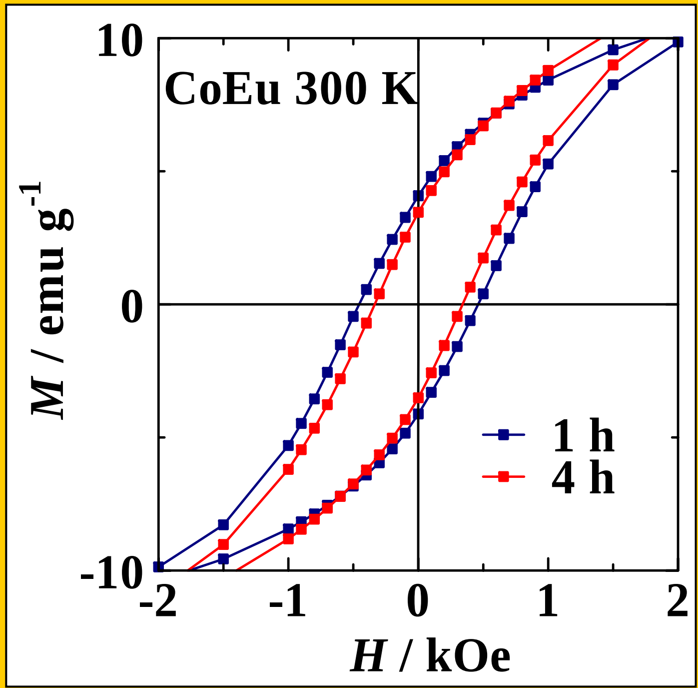
240 ^{o}C, 2h
(crystal + amorphous)

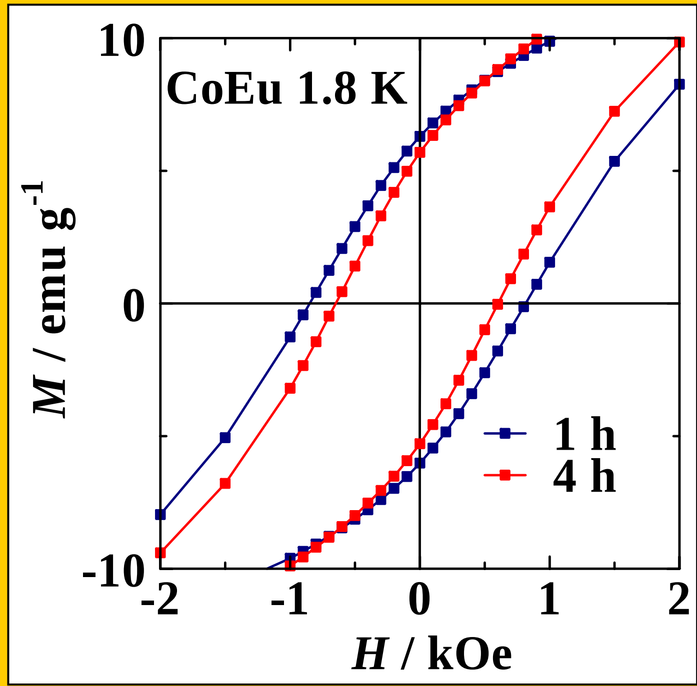


240 ^{o}C, 4h
(crystal + amorphous)

- The particle size increases from ~ 5 nm to 20 nm.
- 30 min: Amorphous, > 2h: Crystal + amorphous

Magnetism of size controlled CoEu@C





H_c: 450 for 1 h
350 for 4 h

H_c: 650 for 1 h
850 for 4 h

Despite smaller particle size, H_c of 1 h heating particle is higher.

Does outer layer of MC_2 enhance the magnetic anisotropy?

cf. H_c of Co enhanced by CoO layer, *J. Appl. Phys.*, 92 (2002) 491

Summary (size control)

- The particle size can be controlled by heating time

  Short heating time: small particles (few nm)

  Long heating time: large particles (few decades nm)

- Structural change from amorphous to crystal

  Short heating time: amorphous particles

  Long heating time: crystalline particles

- Small particles covered with MC_2 shows superior magnetism

  Promising for magnetic devices