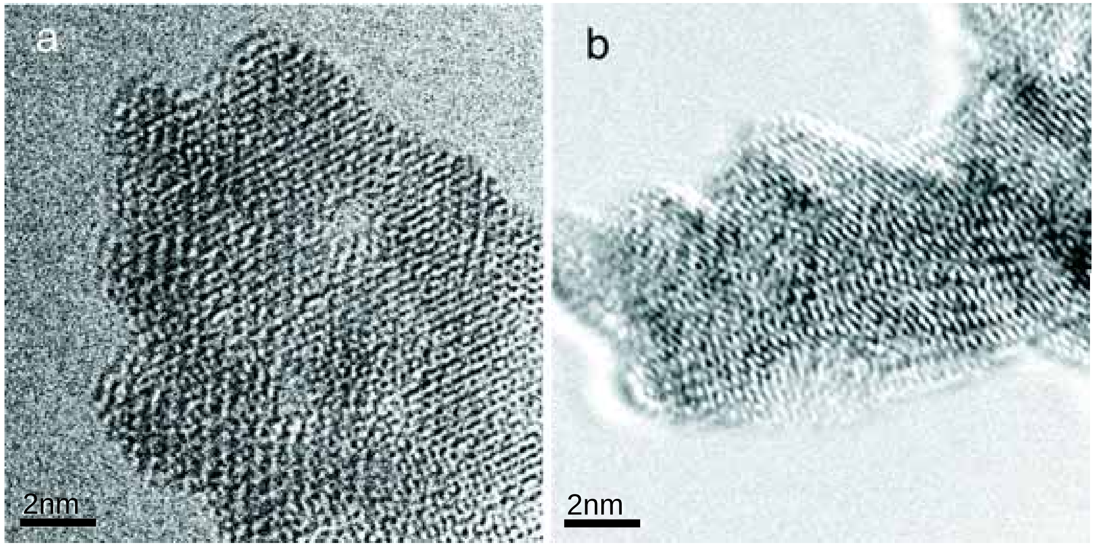
Introduction –*What is cobalt acetylide?* –

Easy to synthesize (ion-exchange reaction in Ar atmosphere)

$$CaC_2 + CoCl_2 \xrightarrow[\text{acetonitrile}]{78\,^{o}\text{C, 48 h}} CoC_2 + CaCl_2 \xrightarrow[H_2O]{\text{washing}} CoC_2$$

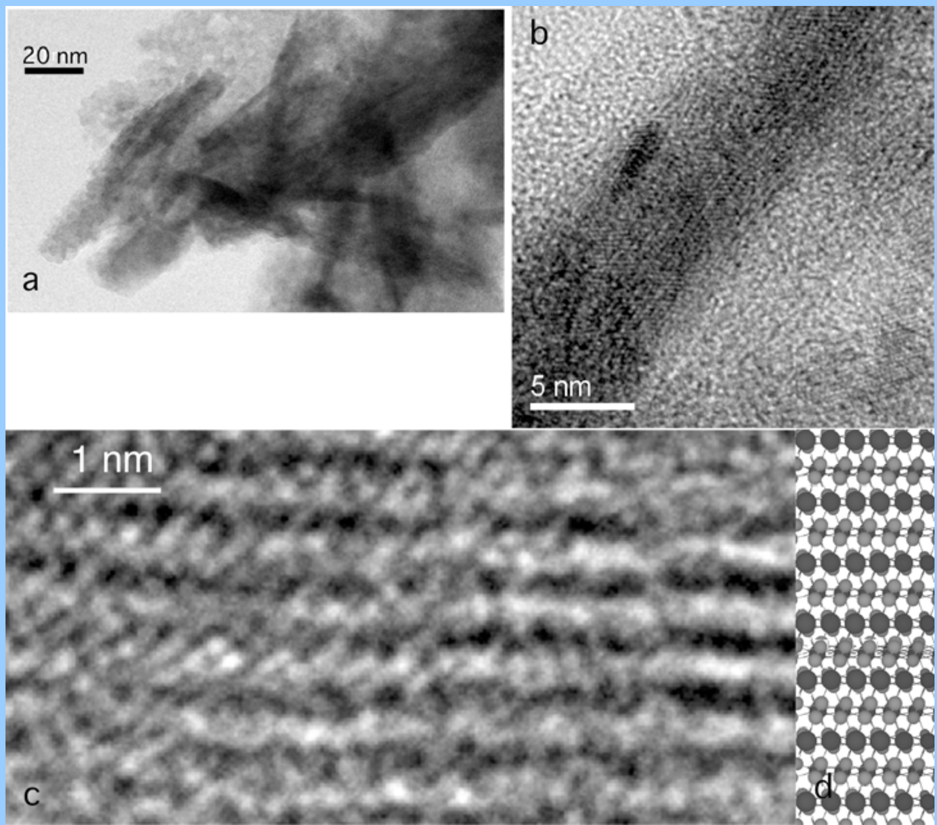
Small particle (~ 50 nm) and quite small crystallite size (~ 5 nm)



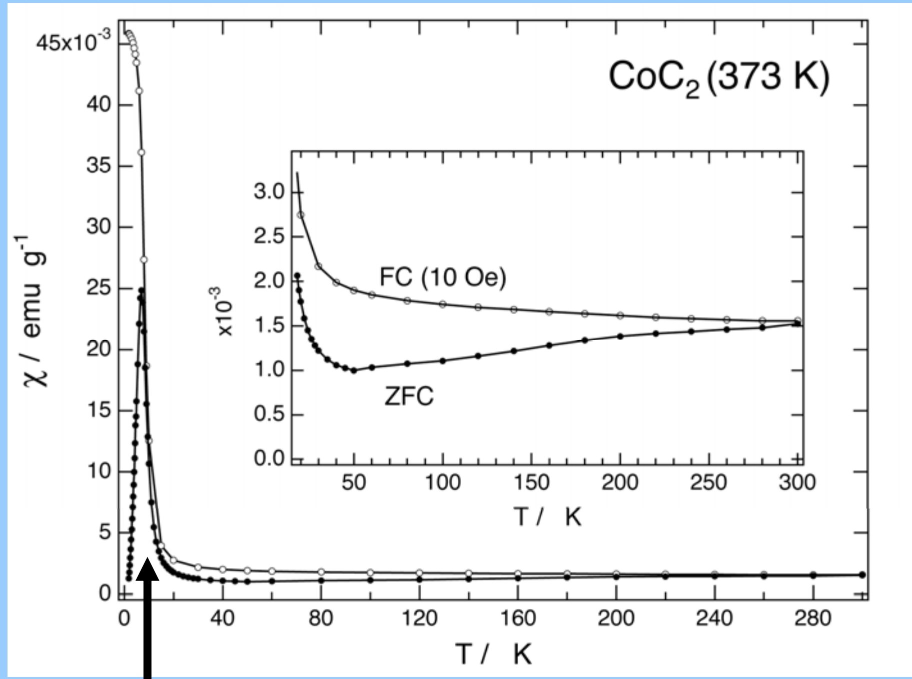
TEM images of CoC_2 (hydrous phase): The crystal lattice is highly distorted

cf. *Eur. Phys. J.* D24 (2003), 97-100 and *Chem. Phys. Lett.* 369 (2003), 198-203

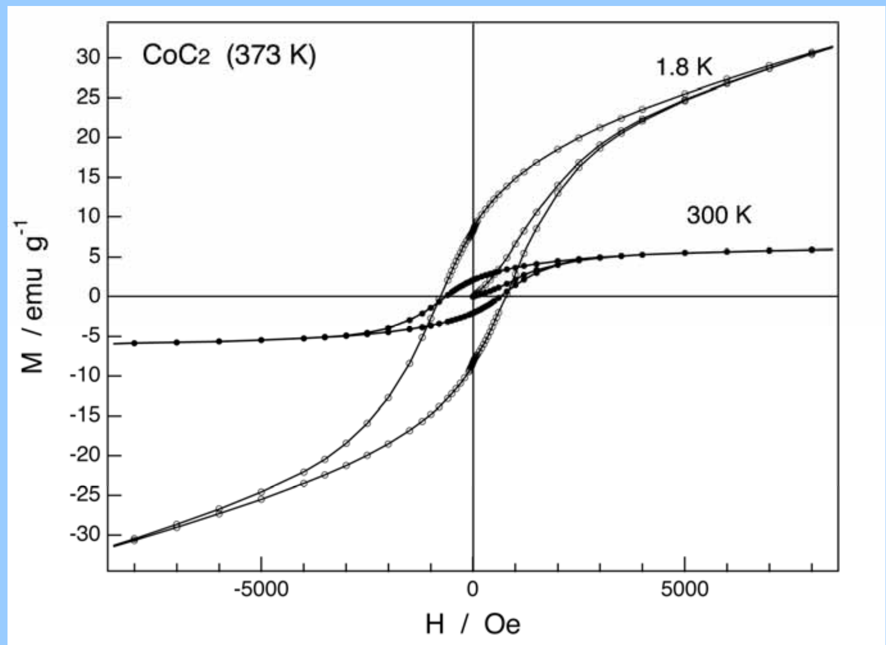
Rod-shape large crystallite particles can be synthesized at 100 °C



The particle shows ferromagnetism even in room temperature!



Ferromagnetism of smaller particles



Question: What's the role of the absorbed water?

CoC_2 ··· Highly absorbent of water (ca. 1-2 H_2O / Co^{2+})

CoC_2 is small, therefore such a large amount of the absorbed water must changes the crystal structure and the physical properties of CoC_2.

Here, we reveal the effect of the absorbed water

Sample preparation

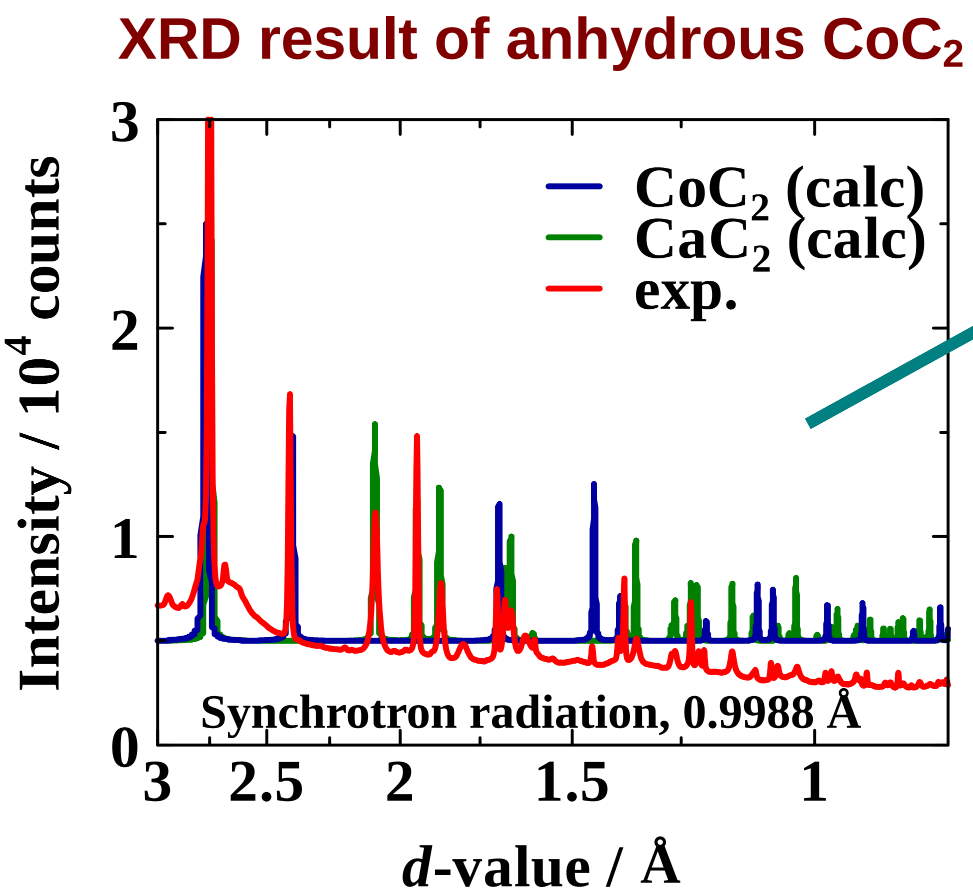
Anhydrous CoC_2:

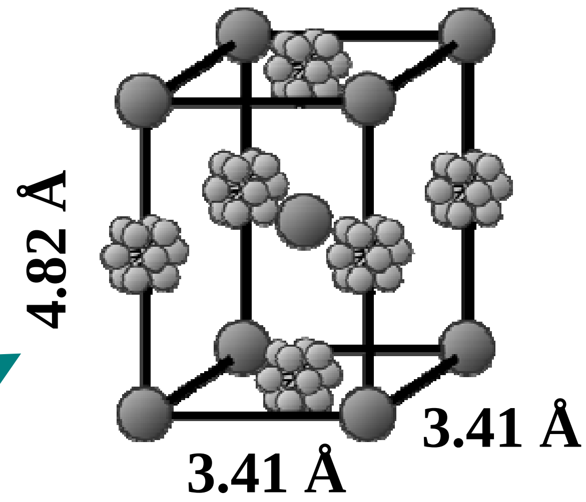
CaC_2 (5 mmol) and $CoCl_2$ (5.2mmol) in 300 ml of acetonitrile was heated at 78 ^{o}C, 130 h in grove-box.
*Anhydrous CoC_2 contains ca. 35 % of CaC_2

Hydrous CoC_2:

Anhydrous CoC_2 was exposed to air (25 ^{o}C, humidity 70 %) or washed with water (for XRD to remove CaC_2 peaks).

Crystal structure of the anhydrous CoC_2





Anhydrous CoC_2: Cubic

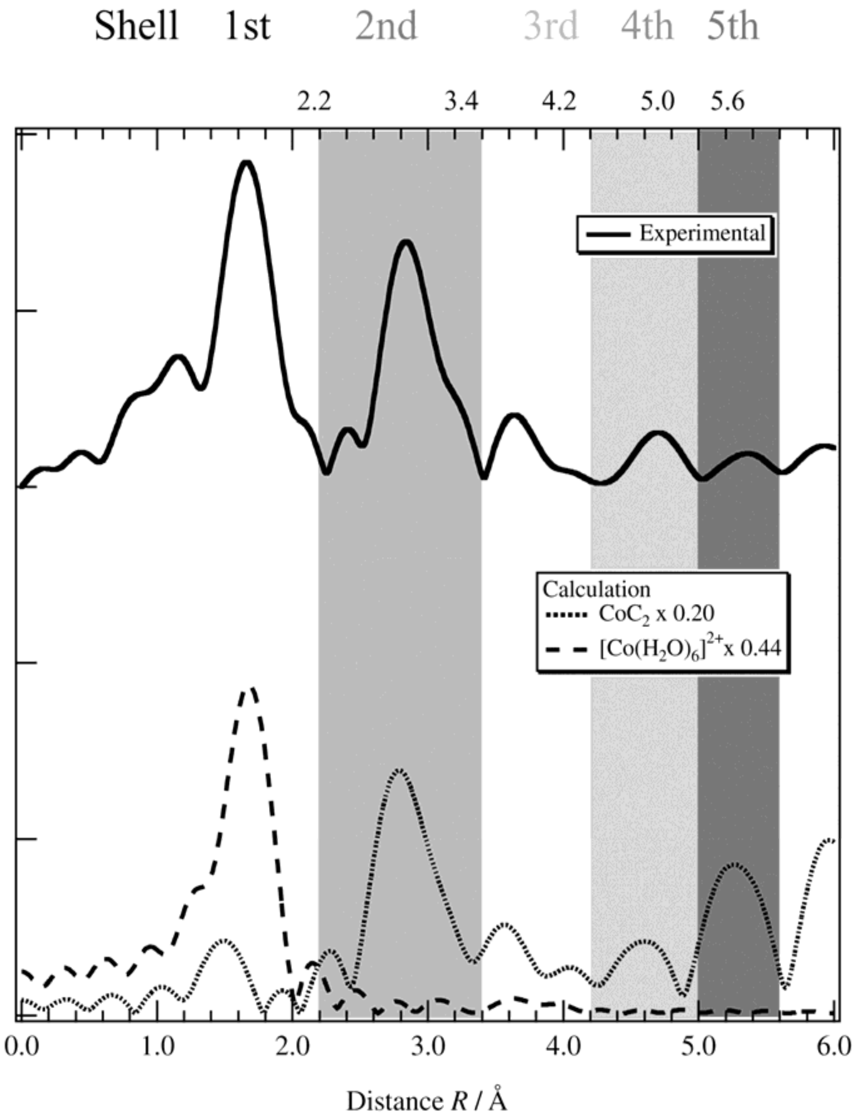
→ Orientation disorder of C_2^{2-}

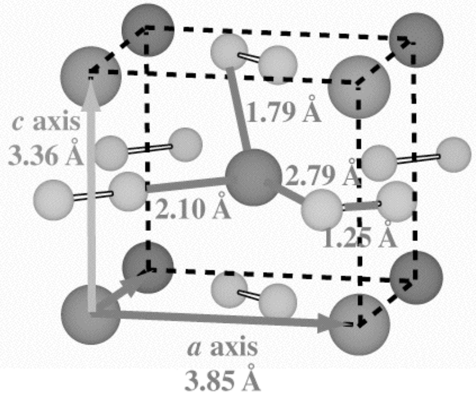
Sharp peaks → Large domain

Crystallite size > 45 nm
(Single domain particle)

Crystal structure of the hydrous CoC_2

EXAFS result



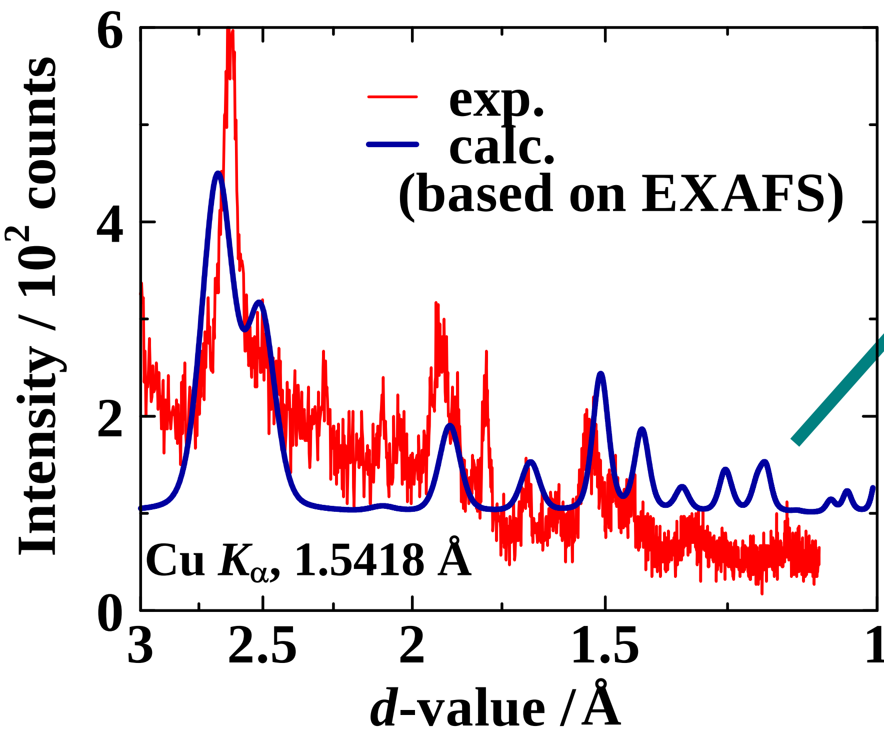


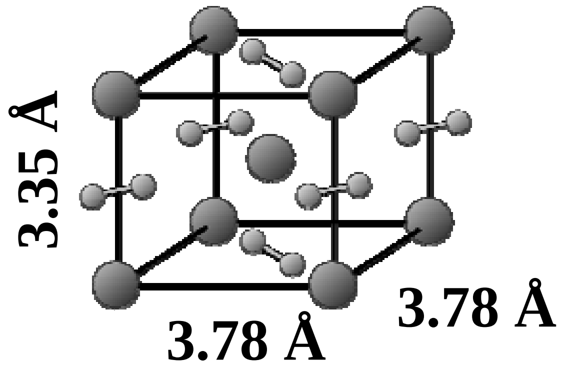
CoC_2	
空間群	正方晶系
	$P4_2/mnm$
a /Å	3.85
c /Å	3.36
V/ $Å^3$	49.8
Z	2
密度/g cm^{-3}	5.53

Structural model for calculated spectrum (MgC_2-type structure)

- **Tetragonal lattice**
- **C_2^{2-} dianions are ordered**
- **Co^{2+}–C_2^{2-}–Co^{2+} chain || *c*-axis**

XRD result of hydrous CoC_2



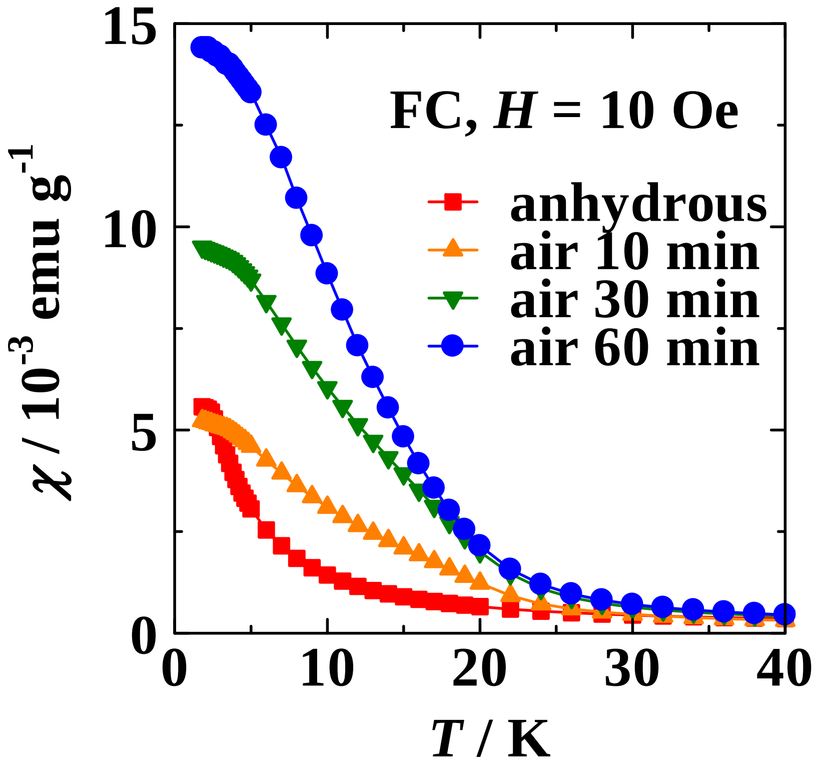


EXAFS spectrum is consistent with XRD pattern

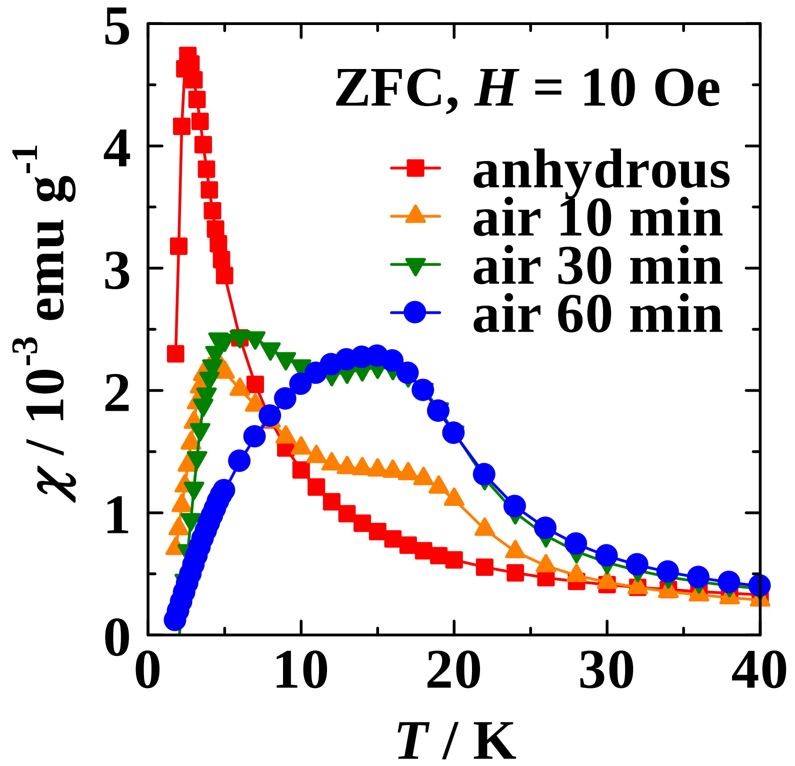
Broad peaks → small domain

Crystallite size: ~ 10 nm
(consistent with TEM images)

Susceptibility of the anhydrous and hydrous CoC_2



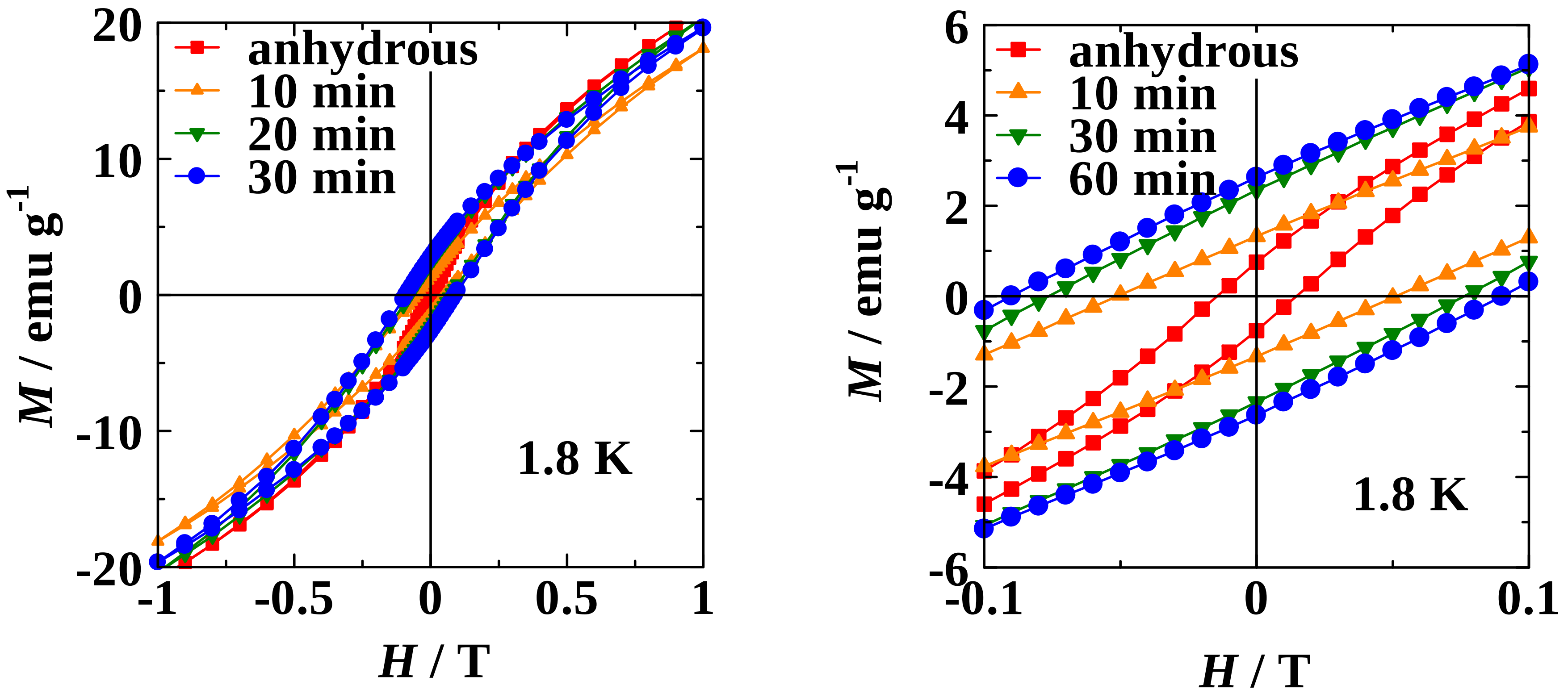
*FC: cooled with H = 10 Oe



Anhydrous CoC_2: Paramagnetic

Air-exposure induce the ferromagnetism

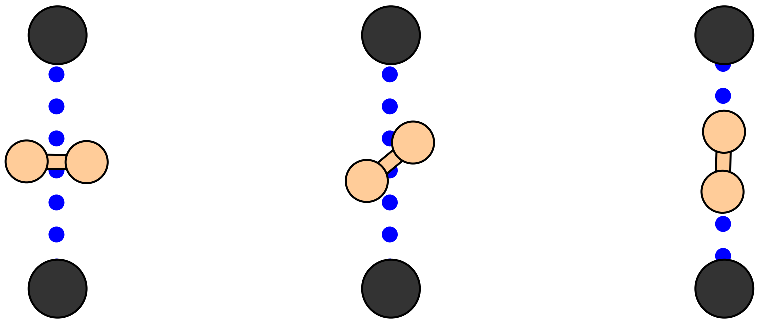
Magnetization curves of the anhydrous and hydrous CoC_2



Coercive force and remanent magnetization are raised by water absorption

Mechanism of the water-induced ferromagnetism

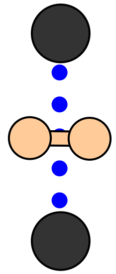
Possible Co^{2+}–C_2^{2-}–Co^{2+} configurations



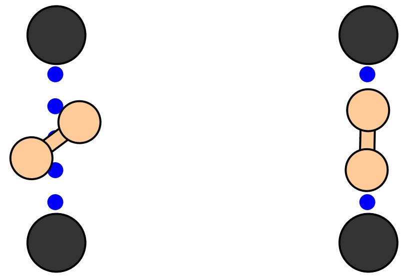
Perpendicula Intermediate Parallel

Hydrous CoC_2
(ferromagnetic)

Anhydrous CoC_2
(superparamagnetic)

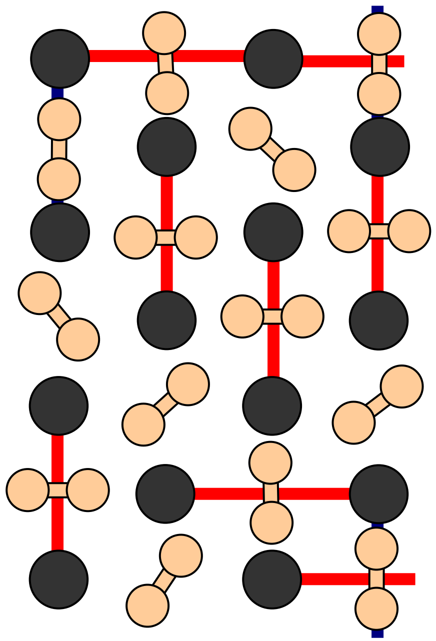


Ferromagnetic interaction

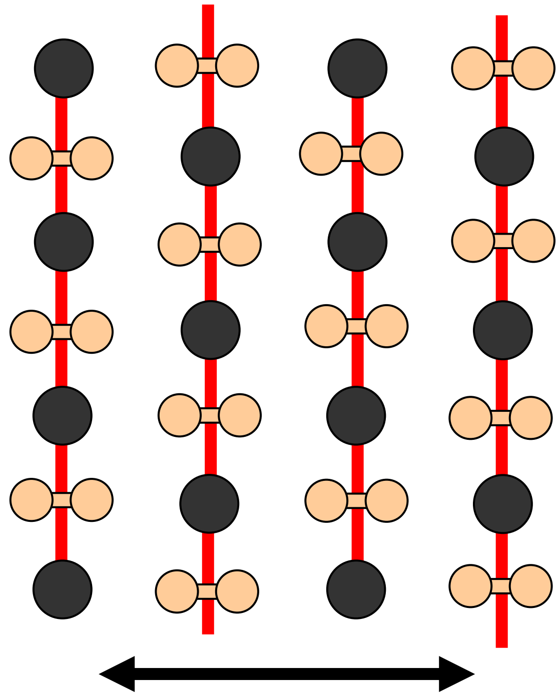


Weak interaction
(FM or AFM)

Schematic model of the influence of water absorption



Water absorption



Small superparamagnetic clusters

Expanded by water

C_2^{2-}

Co^{2+}

Ferromagnetic configuration (strong)

Large ferromagnetic domain

Ferromagnetism!

Summary

	Anhydrous CoC2	Hydrous CoC_2
Lattice:	Cubic	Tetragonal
Orientation of C_2^{2-}:	Disordered	Ordered
Magnetism:	Superparamagnet	Ferromagnet
Structural domain:	Large (~ 50 nm)	Small (~ 10 nm)

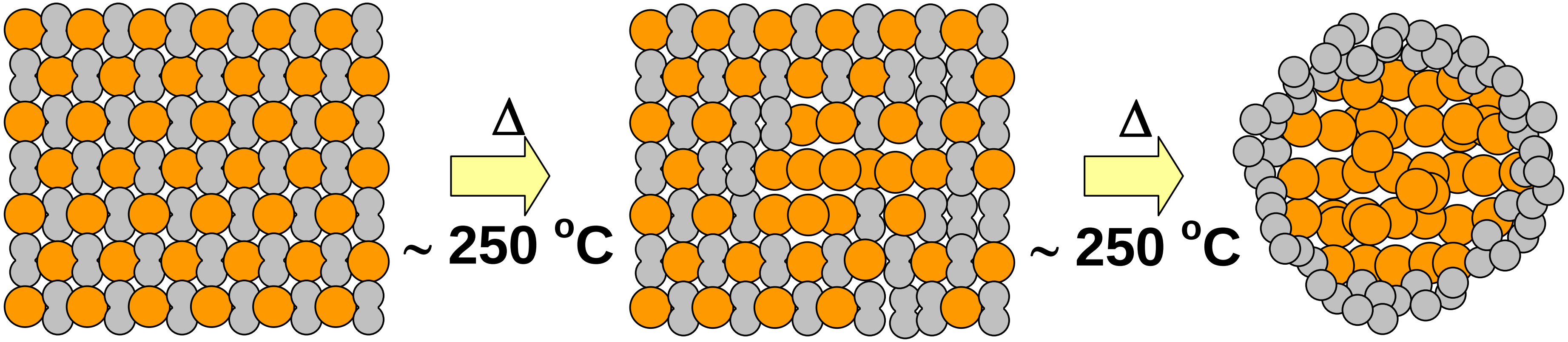
Water-absorption induce the orientation ordering of C_2^{2-}

↓

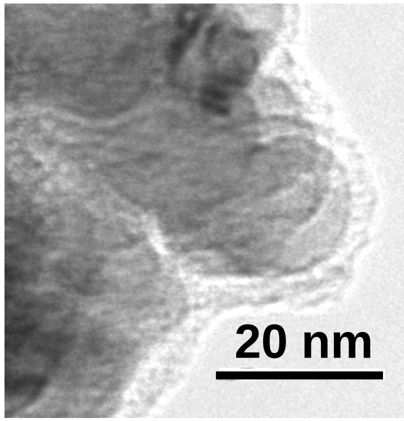
Water-induced ferromagnetism

The other feature of MC_2 compound –easy synthesis of nanoalloy–

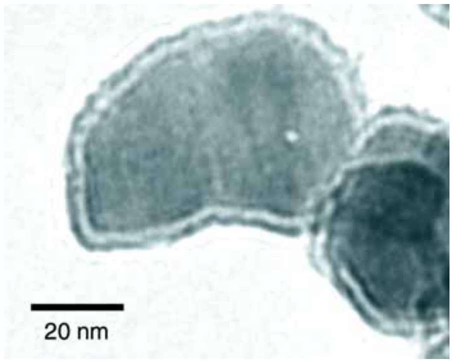
Heating the MC_2 compounds gives "carbon-coated metal nanoparticle"



MC_2 — MC_2 + C + metal — Carbon-coated metal (5 - 20 nm)



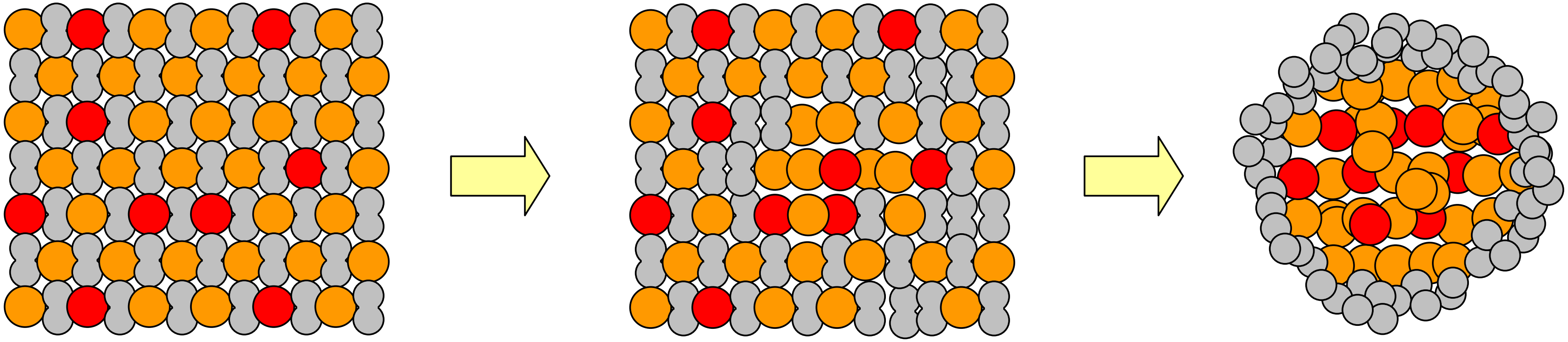
cf. Co@C



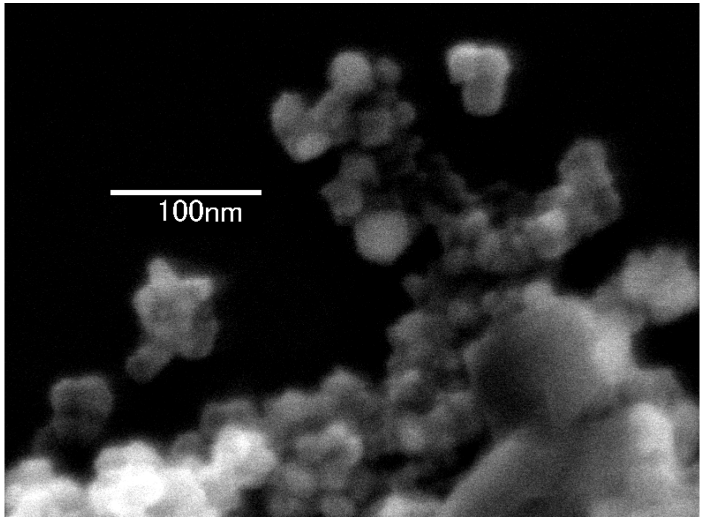
cf. Fe@C

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

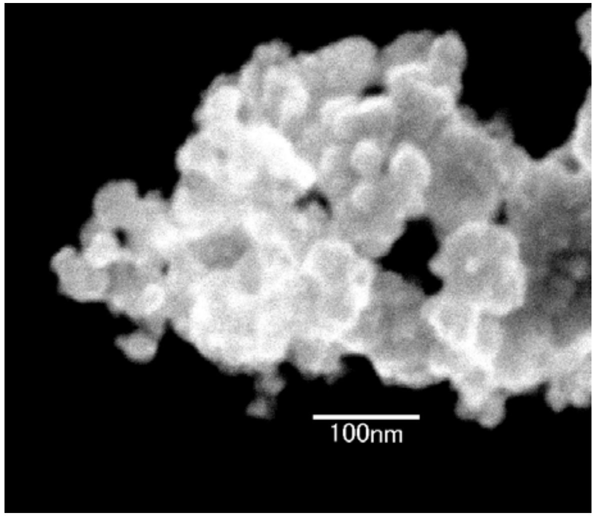
If the mixture of MCl_2 and $M'Cl_2$ is used for synthesis, nanoalloy can be easily obtained only by heating!



$M_xM'_{1-x}C_2$ **Carbon-coated alloy**



FeCo@C
Fe:Co ~ 1:1



NiPd@C
Ni:Pd ~ 1:1