

Hyperfine Interactions Laboratory

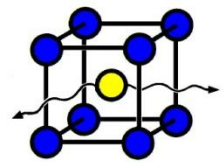


Temperature dependence of the magnetic hyperfine field at ^{111}Cd in ZnO doped with Co.

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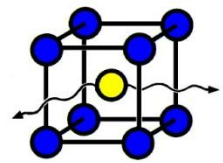
Introduction

Semiconductor oxides doped with 3d ions are good candidates to produce Diluted magnetic semiconductor (DMS) material for spintronics

Thomas Dietl , *et al. Science* 287, 1019 (2000) – *calculated that ZnO doped with 5% of Mn would present T_C above room temperature.*

Yuji Matsumoto, *et al. Science* 291, 854 (2001) – *measured magnetization in TiO₂ doped with 7% Co. Results showed $T_C > 400$ K and saturated magnetization = $0.32 \mu_B$*

ZnO, In₂O₃, TiO₂, SnO₂, SnO, etc. are wide band-gap semiconductor oxides, which have been reported to show ferromagnetic ordering when doped with transition metal elements



Introduction

Almost all papers which have reported the occurrence of ferromagnetism in ZnO doped with different transition elements observed it by magnetization measurements.

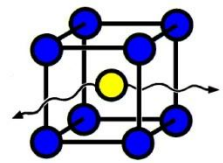
Several papers have, however, reported that samples of ZnO doped with transition metal elements do not show magnetism.

Magnetic ordering observed:

- Only in nano-structured thin films,
- not in bulk samples,
- only in small fraction of samples (2% to 3%)
- It is likely due to defects (oxygen vacancies).

Magnetic ordering not observed:

- magnetism could come from impurities in samples,
- defects in samples are difficult to control.



Introduction

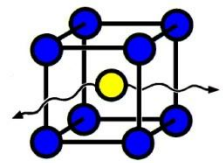
Latest explanation about this controversy is that:

**Bad samples
show
magnetism**

**Good samples
don't show
magnetism**

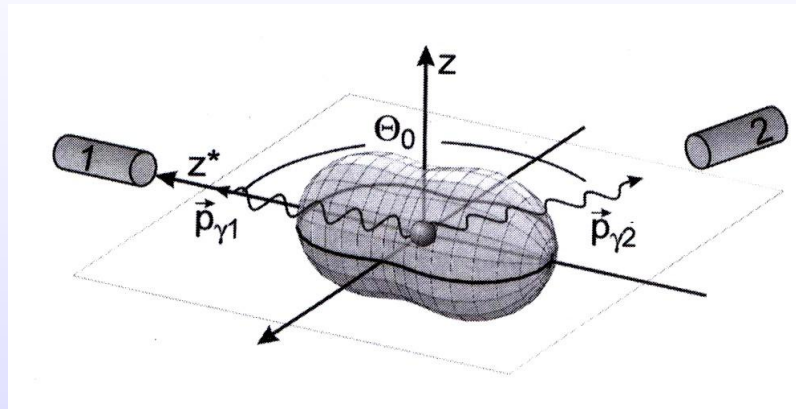
An investigation of doped ZnO samples using a very sensitive local technique would help to understand the occurrence of magnetism in these materials.

In this work perturbed angular correlation (PAC) technique was used to investigate the electric quadrupole interactions during preparation of ZnO samples doped with Co as well as to study the temperature dependence of the magnetic hyperfine field (B_{hf}) in one of them.



PAC method

PAC measures the time dependence of the γ -ray emission pattern. This evolution in time is caused by hyperfine interactions

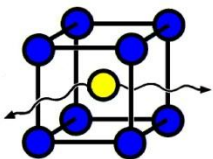


The angular distribution of the emission pattern is given by the correlation function

$$W(\theta, t) = 1 + A_{22}G_{22}(t)P_2(\cos\theta)$$

Hyperfine interactions cause a precession of the emission pattern described by the perturbation factor

PAC method

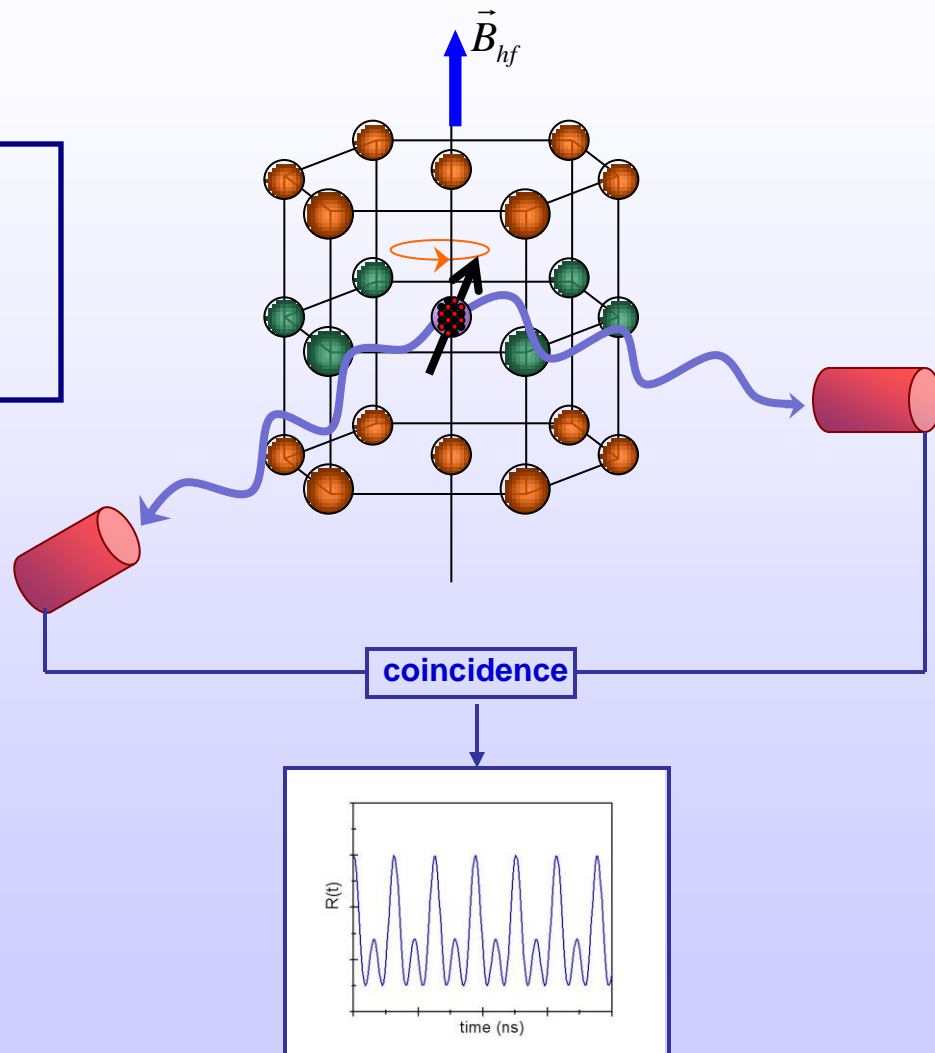


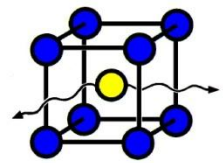
Magnetic interaction:

$$\omega_L = -g \frac{\mu_N}{\hbar} B_{hf}$$

Electric quadrupole interaction:

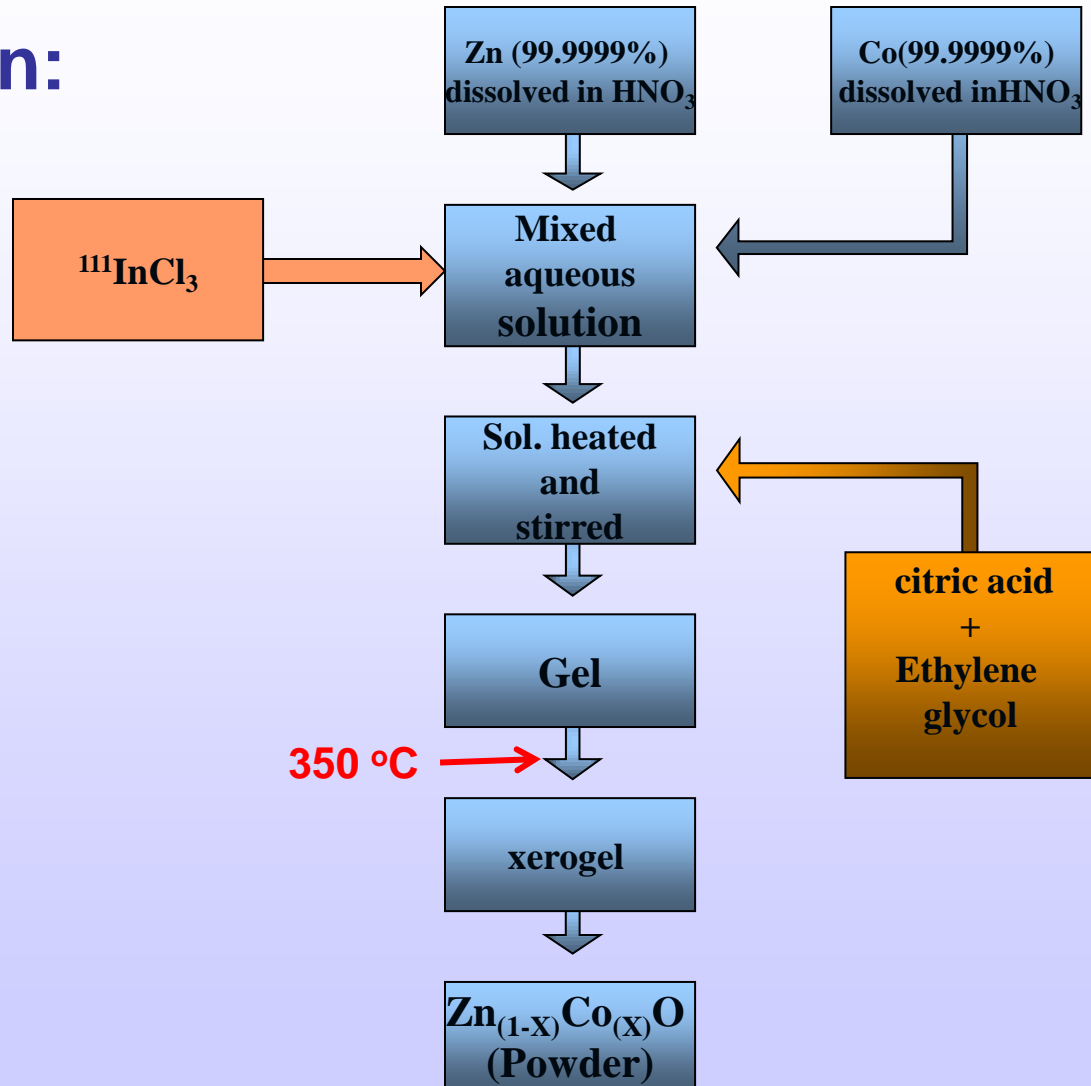
$$\omega_Q = \frac{eQV_{zz}}{4I(2I - 1)\hbar}$$

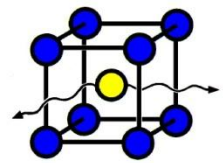




Experimental

Sample preparation:



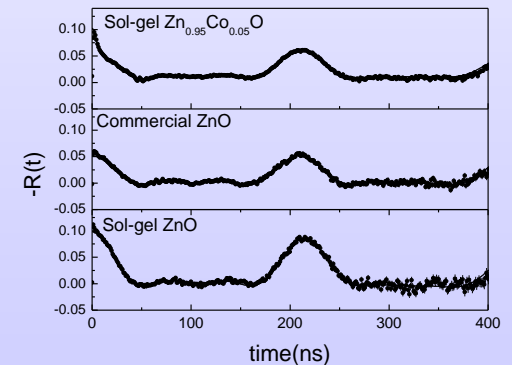
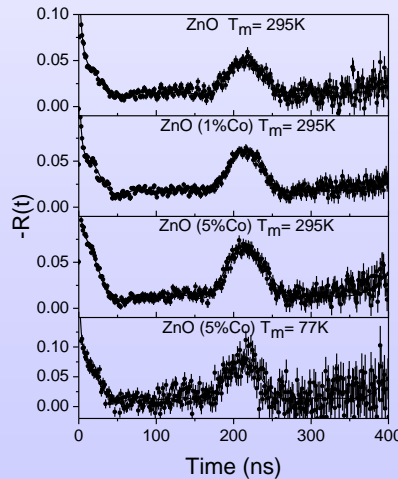
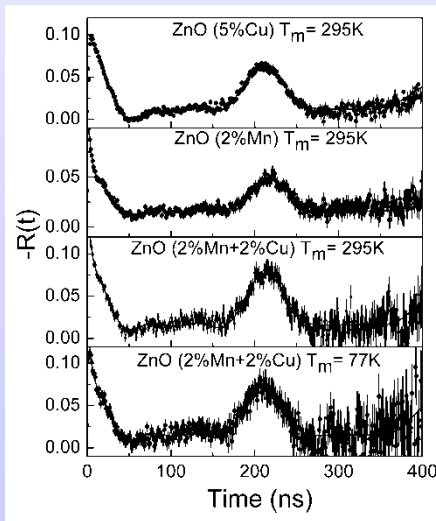
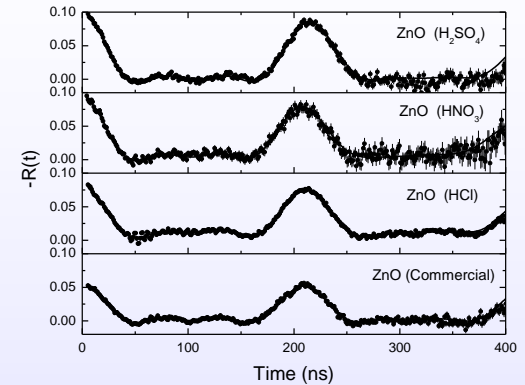


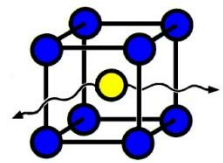
Results

Twelve samples of pure ZnO: $\langle \nu_Q \rangle = 31.9(3)$ MHz

several samples of ZnO doped with different concentrations of Co, Mn, Cu:

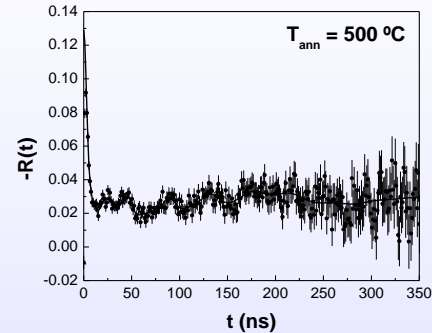
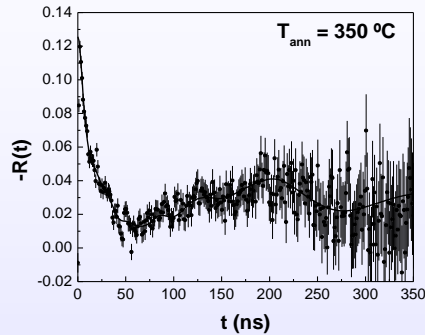
$$\nu_Q \sim 32(4) \text{ MHz}$$





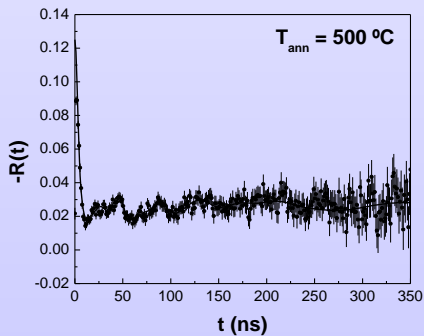
Results

ZnO doped with 10% of Co

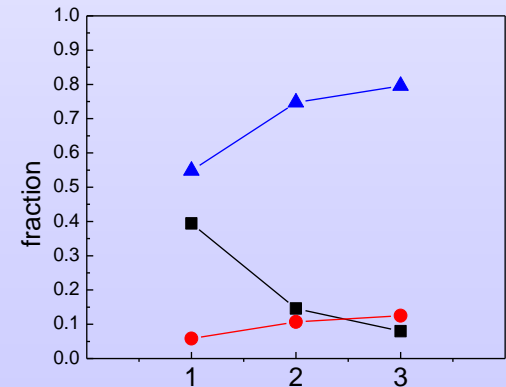


1 - Xerogel: after first annealing at 350 °C

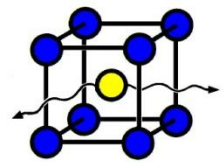
2 - annealing at 500 °C in flowing N₂



- $\nu_{Q1} = 31 \text{ MHz}$, $\eta_1 = 0.3$, $\delta_1 = 9\%$, $f_1 = 8\%$
- $\nu_{Q2} = 150 \text{ MHz}$, $\eta_1 = 0.2$, $\delta_1 = 7\%$, $f_1 = 12.5\%$
- ▲ $\nu_{Q3} = 190 \text{ MHz}$, $\eta_1 = 0$, $\delta_1 = 58\%$, $f_1 = 79.6\%$



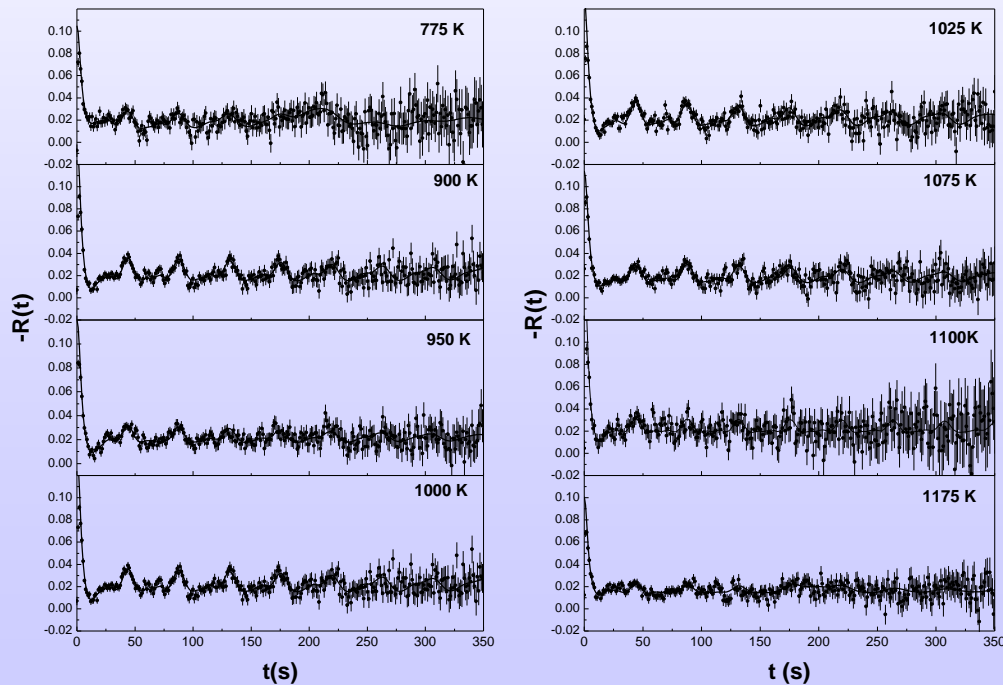
3 - pellet: annealing at 500 °C in N₂



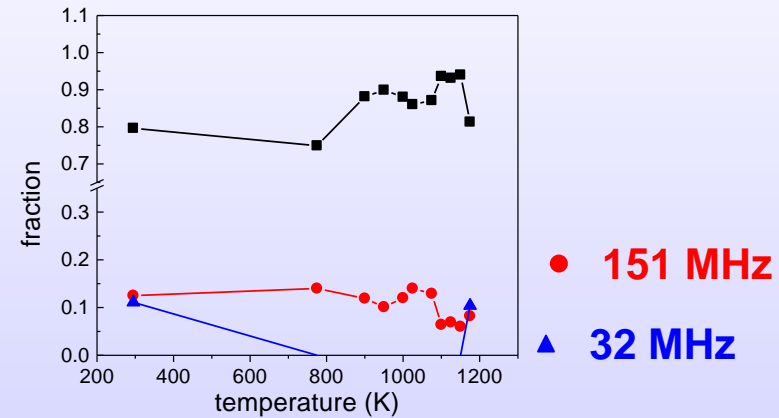
Results

Sample sealed in a quartz ampoule at 2×10^{-2} mbar

Sample measured at different temperatures from ~ 500 °C to ~ 900 °C

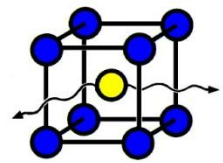


■ broad-distribution ν_Q



● 151 MHz

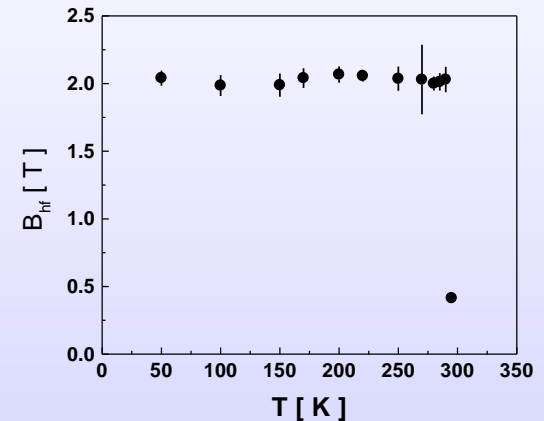
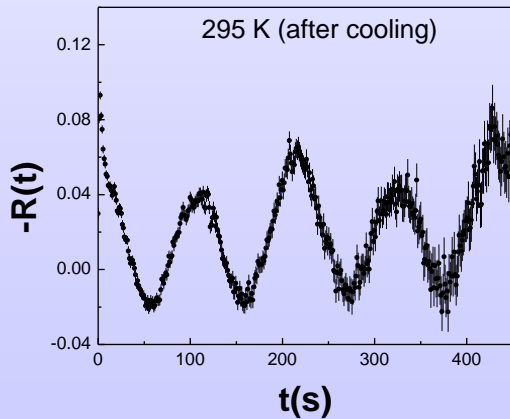
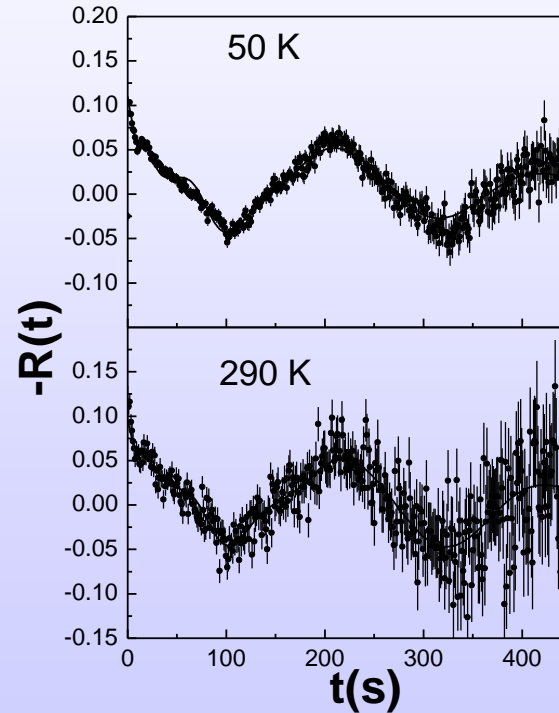
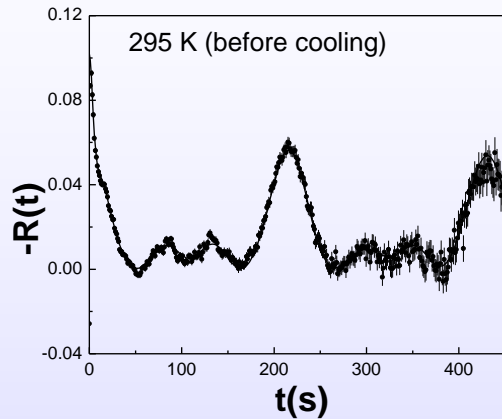
▲ 32 MHz



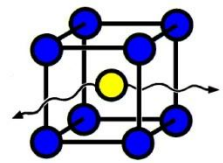
Results

quartz ampoule was broken: sample measured at room temperature

Sample measured from 50 K to 295 K

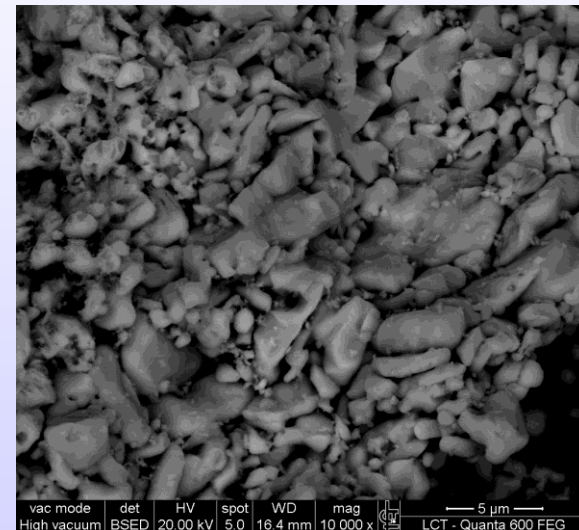
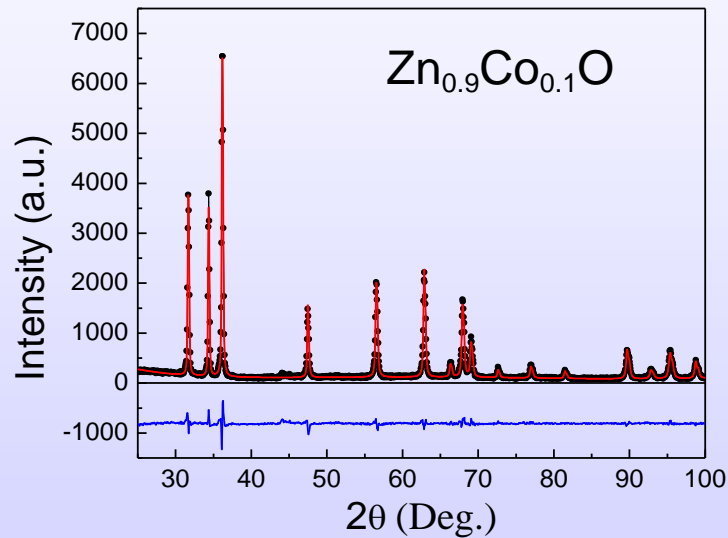


- $B_{hf} \sim 2T$
- First order transition
- Unusual magnetic behavior

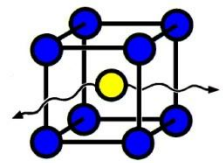


Results

Sample quality checked by X-ray diffractometry, SEM and EDS



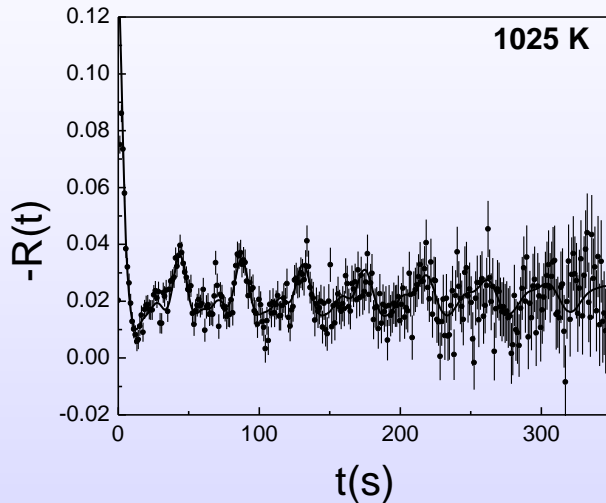
Good bulk sample showing magnetism!



Conclusion

Key to understand the occurrence of magnetism:

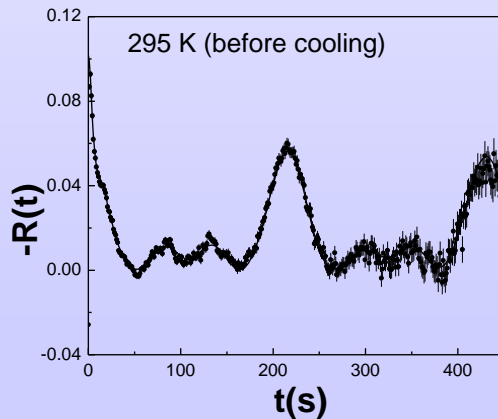
Explanation of the probe environment corresponding to $\nu_Q = 151$ MHz



In_2O_3 ? $\nu_{Q1} = 155$ MHz $\eta = 0$ (29%)
 $\nu_{Q2} = 119$ MHz $\eta = 0.71$ (71%)
 [S. Habenicht *et al.* Z. Phys. B101(1996)187]

Co_2O_3 ? $\nu_Q = 146$ MHz $\eta = 0.15$
 [Z. Inglot *et al.* J. Phys.:condens. Matt. 3(1991)2137]
 $T_N = 40$ K

CoO ? $\nu_Q = 0$
 $T_N = 298$ K $B_{hf}(4K) = 17.7$ T
 [H. H. Rinneberg, D. A. Shyrley, Phys. Rev. 13(1976)2138]



$\text{In} - \text{V}_{\text{ox}}$? $\nu_Q = 185$ MHz $\eta = 0.1$ in $\text{ZnO} + \text{Zn}$
 [S. Deubler *et al.*, Nucl. Instrum. Meth. B63(1992)223]

In near interstitial Zn ?
 $\nu_Q = 170$ MHz $\eta = 0.12$ in $\text{ZnO} + \text{Zn}$
 [R. Wang *et al.*, J. Solid State Chem. 122(1996)166]

