IS487

Local Probe Studies in multiferroic

$AgCrO_2$

A.M.L.Lopes, G. Oliveira
Centro de Física Nuclear da Universidade de Lisboa, Portugal

J.P. Araujo, T.M.Mendonça
Instituto de Nanociência e Nanotecnologia, Universidade do Porto

V.Amaral
Departamento de Física e CICECO, Universidade de Aveiro

J.G. Correia,
Instituto Tecnológico e Nuclear, Portugal and ISOLDE CERN

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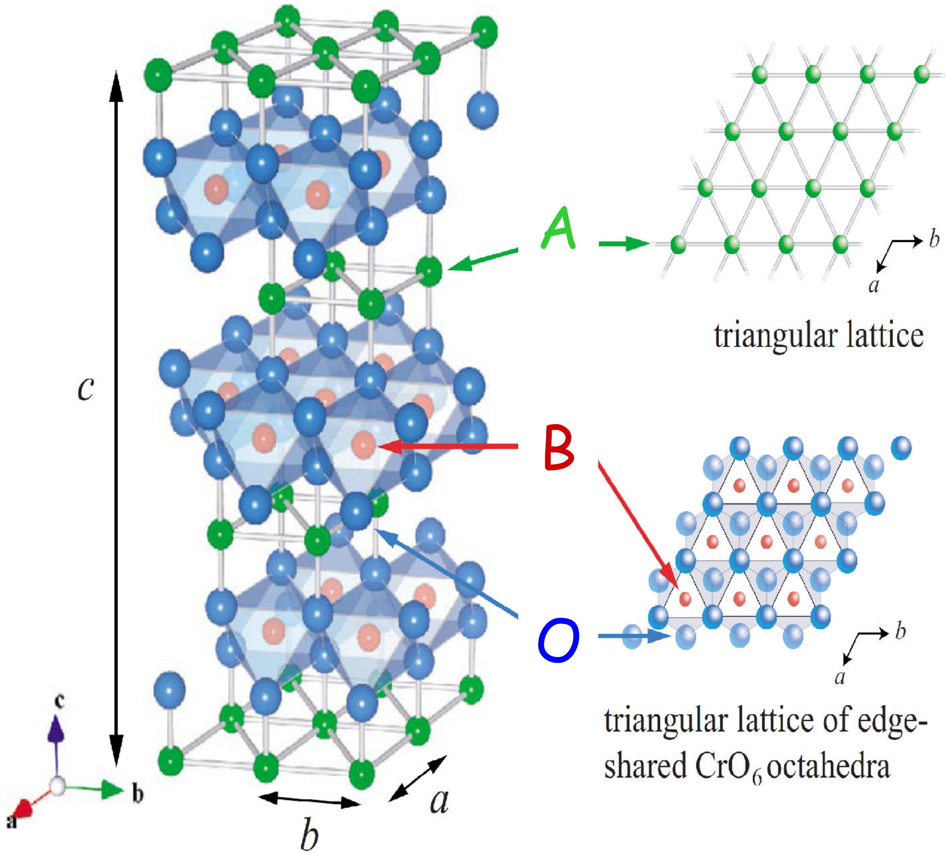
The Systems

SYSTEM: BUILDING BLOCKS

Delafossite ABO_2

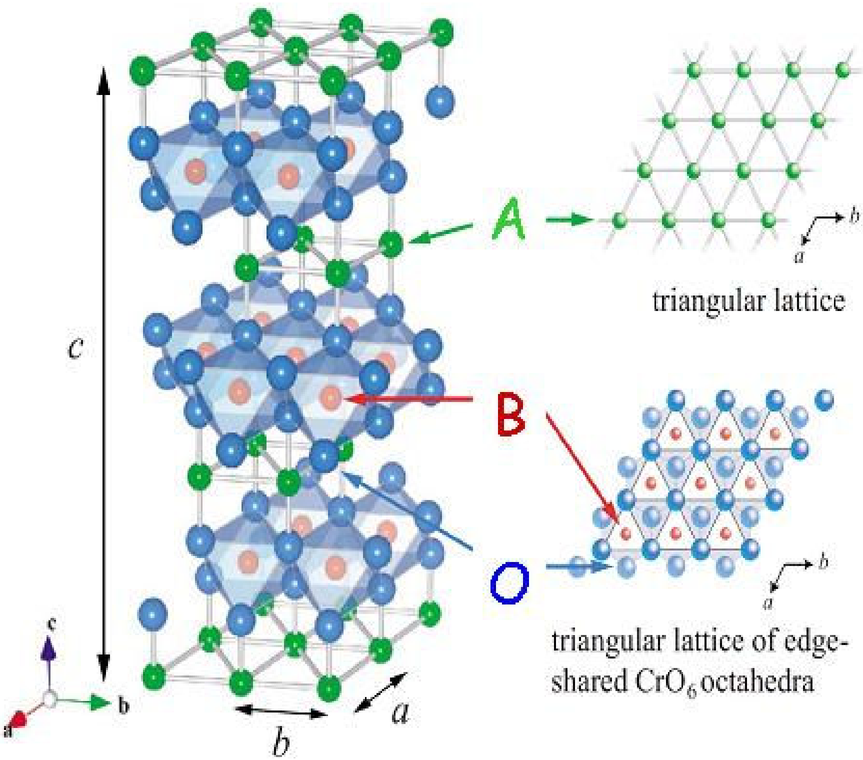


Building Blocks

- Rhombohedral lattice
- Triangular A-atom layers
- BO_2 sandwich layers
- B octahedrally coordinated
- Linear O–A–O bonds

SYSTEM: Materials and Properties

Delafossite ABO_2



Prototype Materials

- AgCrO2, CuCrO2, CuFeO2
- PdCrO2, PdCoO2, PtCoO2
- CuAlO2, CuGaO2, CuInO2

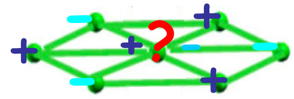
Properties

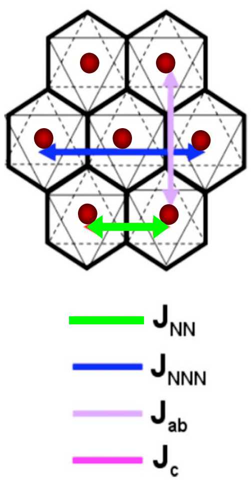
- semiconductors, AF interactions
- very good metals, highly anisotropic
- wide-gap semiconductors, p-type

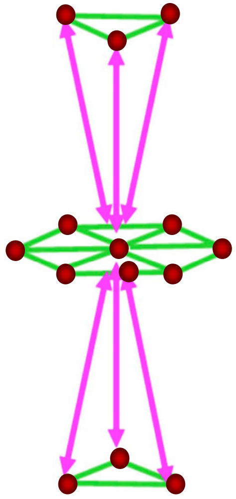
System: 2D (spin frustration)

$A^{1+}Cr^{3+}O^{2-}_2$ (A=Ag, Cu, Li, Na) magnetic structure (and ferroelectrics)

spins in a 2D triangular lattice antiferromagnet->**spin frustration**







J_{NN}>Jc <---> Cr-Cr intraplane AF magnetic interactions stronger then Cr-O-Ag-O-Cr interplane AF ones

↓

$ACrO_2$ quasi-2D lattice--> highly frustrated systems

At very low temperatures the system may presents a AF magnetic phase transition due to the interplane interactions.

Above T_N some authors claim that a 2D short range order exists

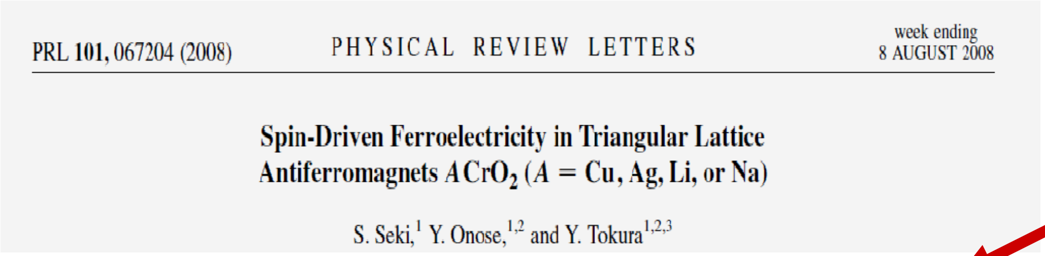
System: Interests and Issues

$ACrO_2$

Known, since some time, due to potential applications as transparent semiconductors

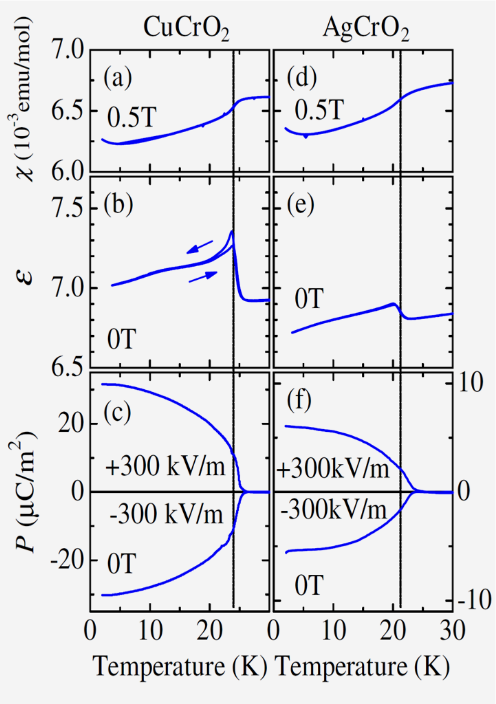
But very recently $ACrO_2$ systems gain renew interest due to the

discovery of ferroelectricity driven by magnetic ordering


PRL 101, 067204 (2008) PHYSICAL REVIEW LETTERS week ending 8 AUGUST 2008

Spin-Driven Ferroelectricity in Triangular Lattice Antiferromagnets $ACrO_2$ (A = Cu, Ag, Li, or Na)

S. Seki,[1] Y. Onose,[1,2] and Y. Tokura[1,2,3]



Boosting the search for multiferroicity in triangular lattice

Revival the interest in geometrically frustrated spin systems

Open new (reopen!) Issues…

- microscopic origin of magneto-electric coupling in triangular-lattice antiferromagnet
- frustration vs. long-range order
- 2D short range order

$AgCrO_2$

Synthesis and sample characterization

Synthesis and sample characterization

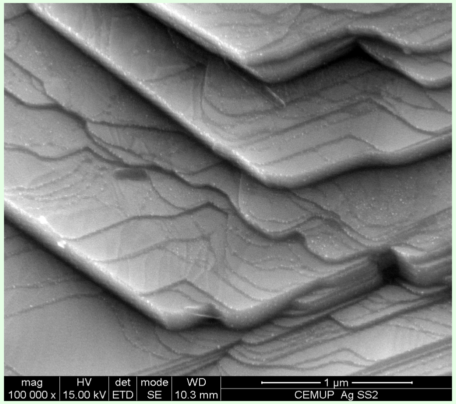
solid-state reaction

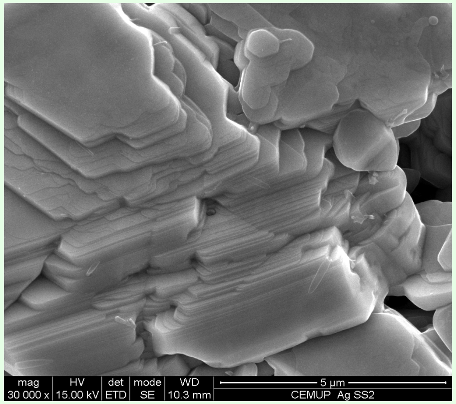
different annealing conditions

Calcination	TAG	Annealing #1 700°C	Annealing #2 900°C
500°C 12h Air	SS1	24h Air	24h Air 24h O_2 48h O_2
	SS2	12h O_2	12h O_2
	SS3	24h O_2	24h O_2 48h O_2

SEM images - sample morphology

Homogeneous sample with plateaus/layers due to the highly asymmetric crystallographic structure (c>>a=b)

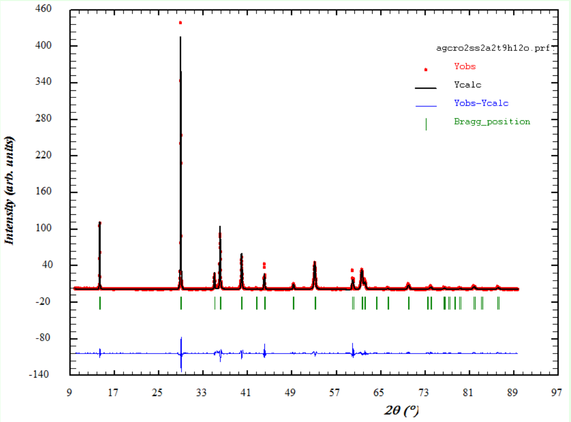




single phase-- Structural parameters:
a=b= 2.986 and c=18.506 Å

X-ray, Rhombohedric str.

(R-3m space group)



sol-gel combustion synthesis

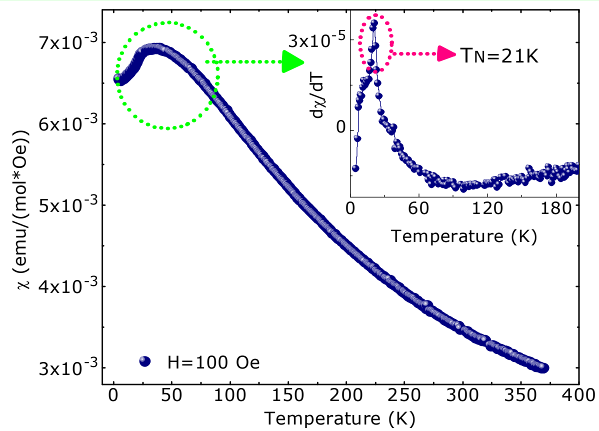
different complexant agents/combustion initiators

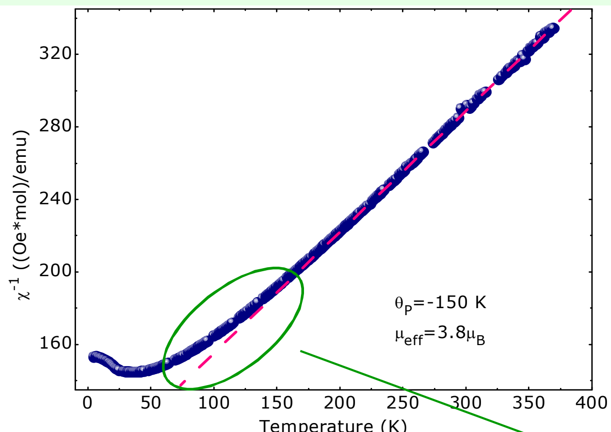
Process	TAG	Complexant Agent		pH	Calc.	Anneal. #1 700°C	Anneal. #2 900°C
Sol-gel + Microwave	SG1			4.2	X	24h Air	24h Air 48h O_2
	SG2	Urea	$(NH_2)_2CO$	4.7		24h Air	48h Air
Sol-gel	SG3.0			3.5	12h Air	24h O_2	24h O_2
	SG3.1						
	SG4	Urea+Citric Acid	$(NH_2)_2CO+C_6H_8O_7$	4.2			
	SG5	Urea+Ethylene Glycol	$(NH_2)_2CO+C_2H_6O_2$				
	SG6	Citric Acid	$C_6H_8O_7$				
	SG7	Ethylene Glycol	$(NH_2)_2CO$				
	SG8	Glycine	$C_2H_5NO_2$				

Synthesis and sample characterization

Magnetization

Clear transition @21K -> 3 dimensional magnetic order





-> Para to antiferromagnetic phase transition

Néel T-> TN=21K

Curie-Weiss T-> θp=-150K

-> Strong spin frustration as expected in triangular spin lattices

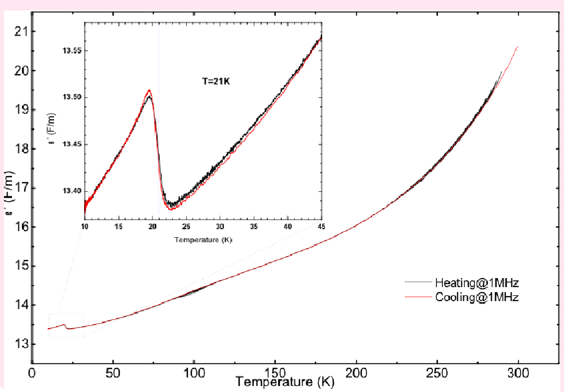
|θp|/TN=7

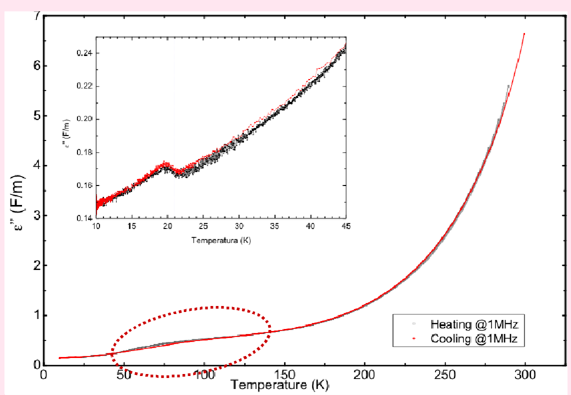
Below ~120K

-> χ-1 deviates from the Curie-Weiss linear regime!!

Real and imaginary dielectric constant

Sharp increase in the dielectric constant @ 21K -> ferroelectric transition





Ferroelectric transition simultaneously with the magnetic one.

Below ~100K

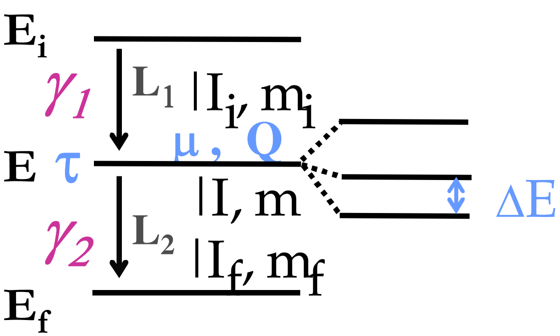
-> anomaly in ε`

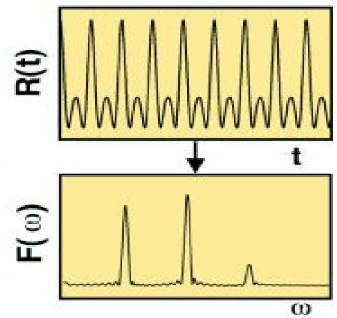
$^{111}In:AgCrO_2$

γ-γ PAC measurements

$^{111}In:AgCrO_2$ γ-γ PAC measurements

Hyperfine splitting → Electric field gradient / Magnetic hyperfine field

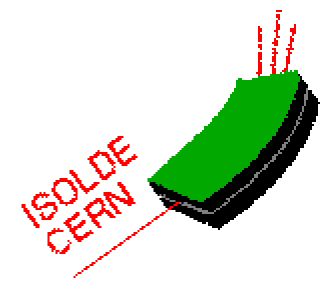




V_{zz} - EFG principal component

η - Asymmetry parameter

B_{hf} - Magnetic hyperfine field



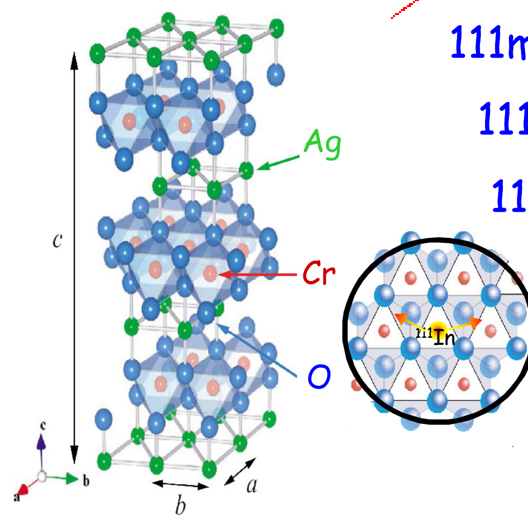
Samples implanted with 111In @ ISOLDE/CERN

E=60 keV, Dose < 10^{12} at/cm^2
111In--111Cd: I=5/2 and t1/2= 85 ns
Q=0.83 b and μ=-0.766 μn

Post-implant annealings @ T=700 °C in oxygen

Former studies in this and similar systems had proven that:

^{111}In goes only to the Cr site

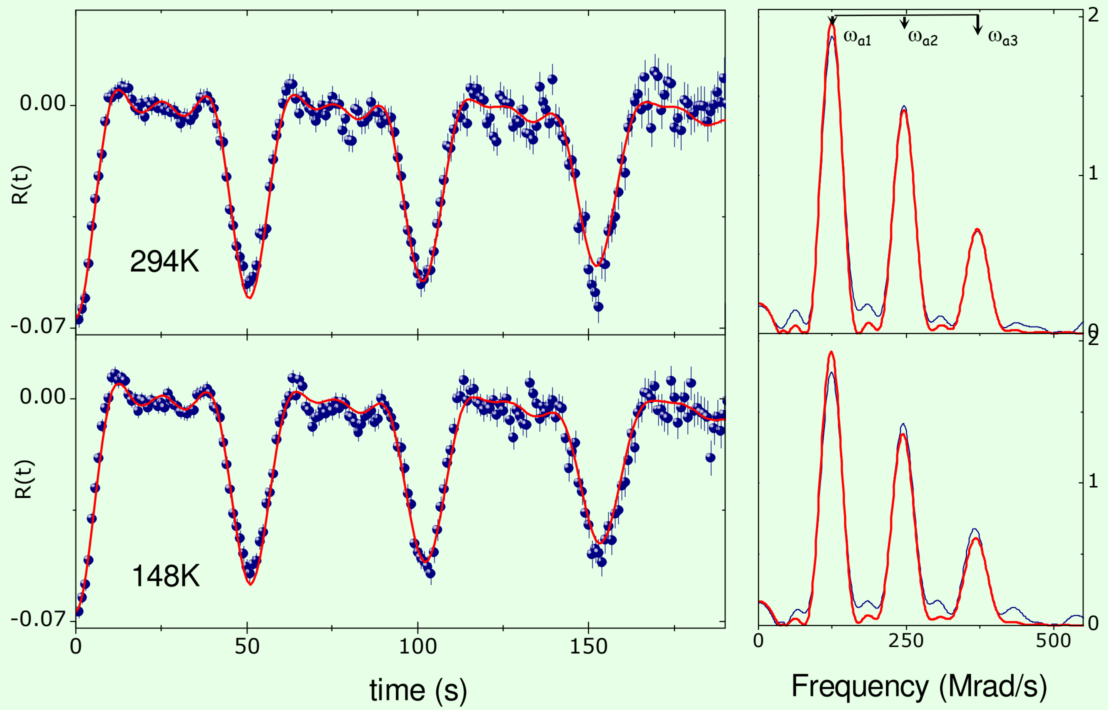


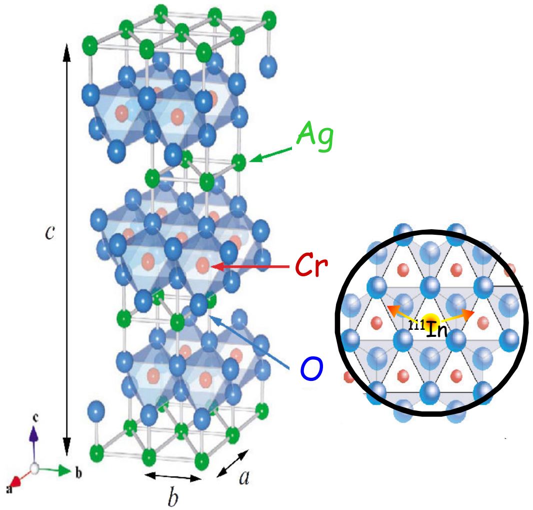
$^{111m}Cd:^{111}Cd$
$^{111}Ag:^{111}Cd$
$^{111}In:^{111}Cd$
$^{48}Cr:^{48}V$

$^{111}In:AgCrO_2$ γ-γ PAC measurements

PAC data @ RT and @ 148K

One single EFG corresponding to the Cr site





Quadrupole frequency

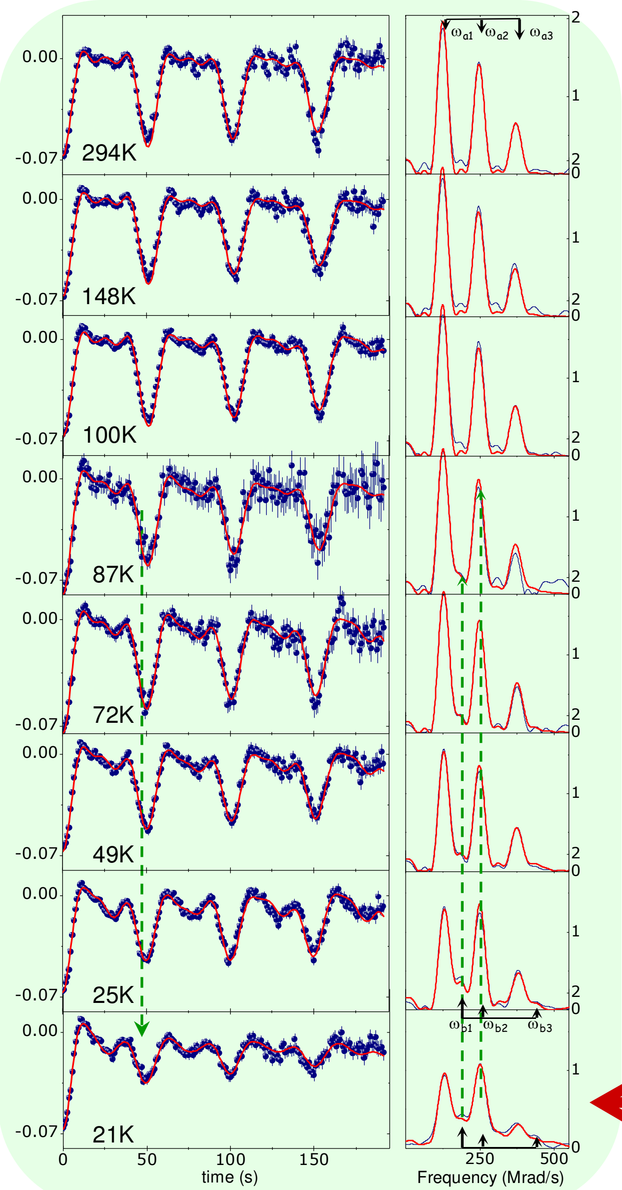
υ_Q=131 MHz

Asymmetry parameter

η~0

From 500K to ~100k: Only one EFG with almost temperature independent parameters

$^{111}In:AgCrO_2$ γ-γ PAC measurements



From 500K to ~100k only one EFG

Below 100k:

A second EFG with similar quadrupole frequency but higher asymmetry parameter appears

EFG1 --> υ_{Q1}=131 MHz and η_1~0

EFG2 --> υ_{Q2}=137 MHz and η_2~0.5

Two Cr local environments

Attenuation of both EFG --> Δ_1~1% and Δ_2~6%

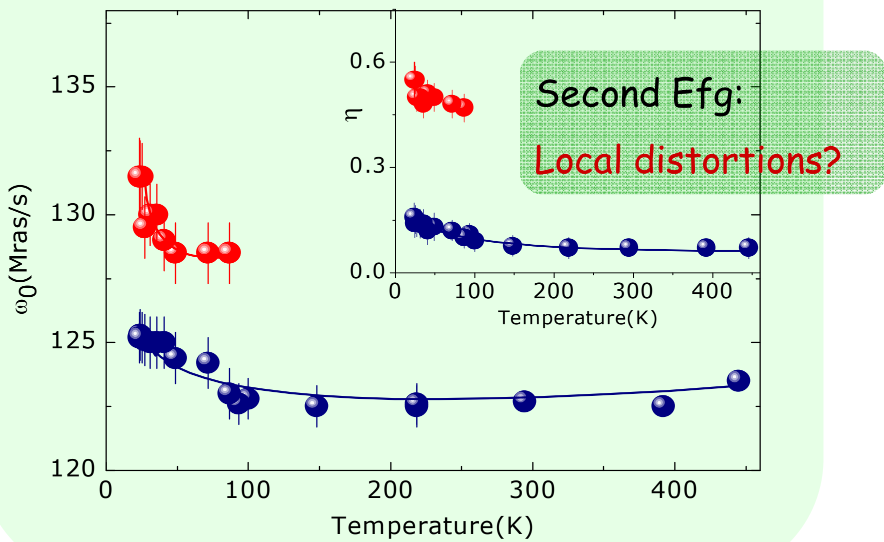
~constant in all temperature range

MHF is present at and below 21K

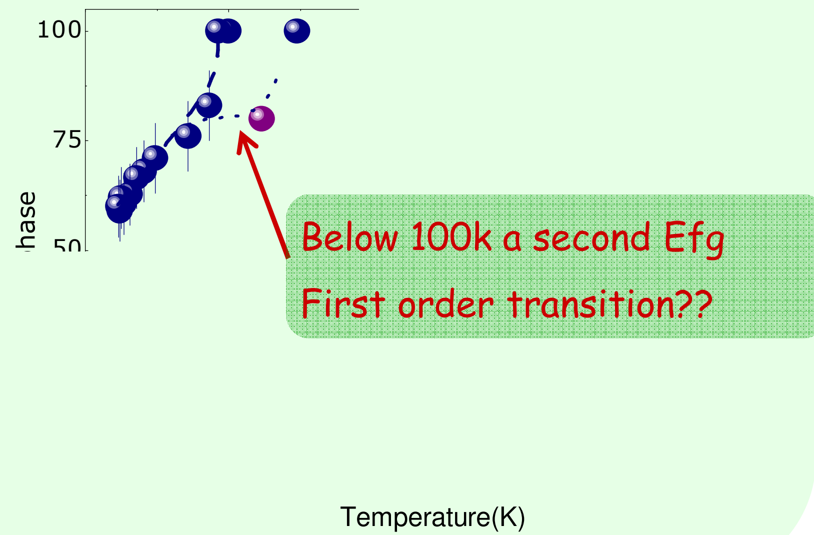
$^{111}In:AgCrO_2$ γ-γ PAC measurements

EFG parameters above T_N

Principal frequency and asymmetry parameters



% of each local environment

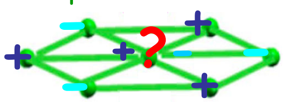


% of each local environment varies ~ linearly with temperature (no single activation process involved) Below T_N the process halts and the % of each LE ~ 50%

This transition occurs at ~ the same temperature where the reciprocal magnetic susceptibility starts deviating from the Curie-Weiss linear regime.

^{111}In:AgCrO$_2$ γ-γ PAC measurements

Cr spin frustration

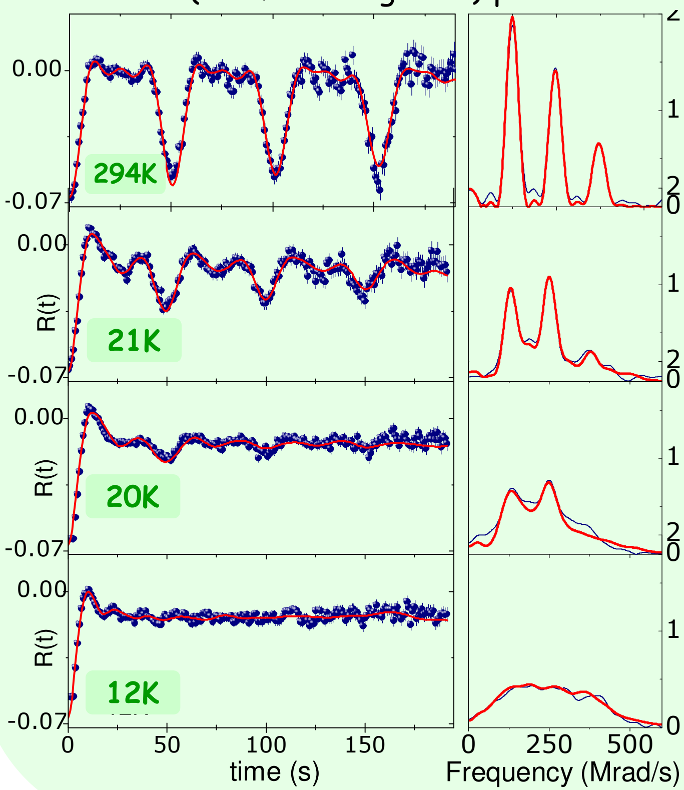


^{111}In, non magnetic, in the Cr triangular lattice should locally release the spin frustration. ^{111}In 1° neighbors can realize the antiferromagnetic order.

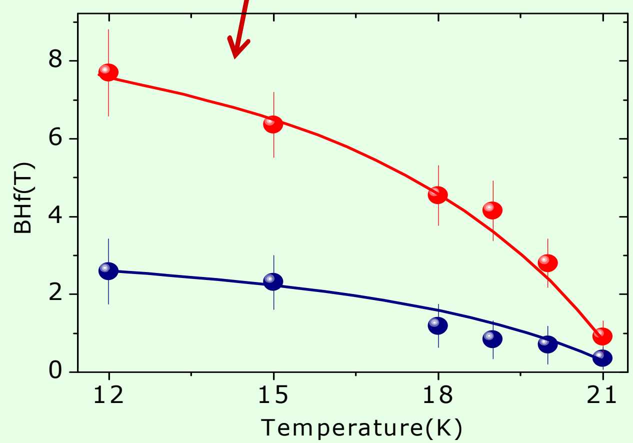
--> No contribution from the 1° Cr to the MHF but ...

PAC from 21K down to 12K

Below the (antiferromagnetic) phase transition

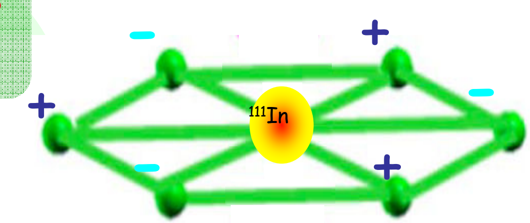


But...a relatively high MHF is observed!!!

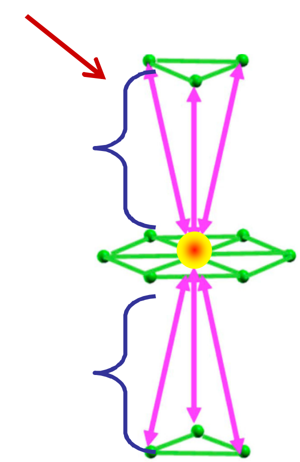


two MHF
two different EFG
→ different
Cr-O-Ag-O-Cr pathways?

no frustration



MHF -->2° Cr neighbors i.e., inter-plane interactions



Discussion

In the literature the non linear regime of the reciprocal susceptibility that is systematically observed in ACrO2 systems (Li, Ag, Cu, Pd…) is, up to now, ascribed to the development of 2D spin order.

Note that above T_N PAC shows:

-Pure EFG´s (no MHF) -No significant changes in $\Delta_{1,2}$ when approach T_N

No evidences for any kind of spin order

LiCrO2, local probe measurements just had shown that:

PHYSICAL REVIEW B 79, 184411 (2009)

μ^+SR investigation of local magnetic order in $LiCrO_2$

Jun Sugiyama,[1,*] Martin Månsson,[2] Yutaka Ikeda,[1,4] …

… internal magnetic field (H_{int}) can be explained by solely nuclear magnetic moments. This means that, contrary to previous suggestions by susceptibility and heat capacity measurements, no short-range order exists for $T \geq 62.5$ K. However, ZF-μ^+SR detected the change in H_{int} from a low-T static state to a high-T dynamic state at 115 K, most likely connected to a change in the position/motion of the Li ions.

μSR--> no EFG
PAC-- > EFG and MHF

Below 100K/above T_N:
We see no evidences for spin order and a 2° Cr local environment emerges.
Same phenomenology as in LiCrO2?
Ag atoms displacements?

Conclusions

-500K to ~100k a single Cr local environment

-Below 100k, two Cr local environments (similar frequency but higher asymmetry)

-Transition occurs @ the same T where the susceptibility deviate from the Curie-Weiss regime and an anomaly is observed in the dielectric constant

-No evidences for any kind of spin order above TN

-*Anomalies observed in the dielectric and magnetic measurements maybe explained by the existence of local distortions as measured by PAC e.g. Ag atoms displacements*

- Two MHF observed below TN. **MHF arises from inter-plane magnetic interactions**