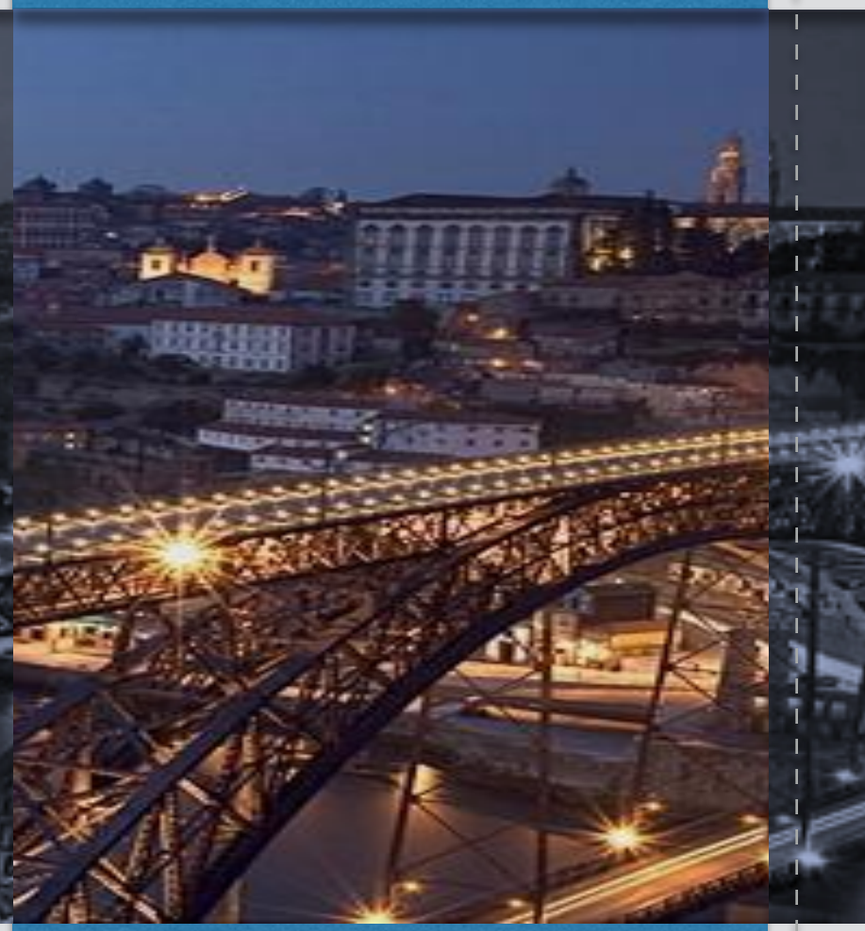
Dynamic off-centering of Cr^{3+} ions and short-range magneto-electric clusters in $CdCr_2S_4$.

25-27 November 2013 ISOLDE Workshop, CERN



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[3]**CICECO** and Departament of Physics, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[4]**ORNL**, P.O. Box 2008, MS6475, Oak Ridge, Tennessee 37831-6475, USA
[5]**APS** - Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
[6]**C²TN**, Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobabela LRS, Portugal

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C.T. Sousa[1]
Y. Ren [5]
V.S.Amaral[3]
J.G. Correia [6]
J.P. Araújo [1]
A.M.L. Lopes [2]

Outline

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- Motivation
- General Aspects – $CdCr_2S_4$
- Macroscopic Structure
  - Local Atomic Probe Characterization
    - Electric Field Gradient – PAC
    - Atomic displacements – PDF
  - Magnetic/Electric Properties
- Summary

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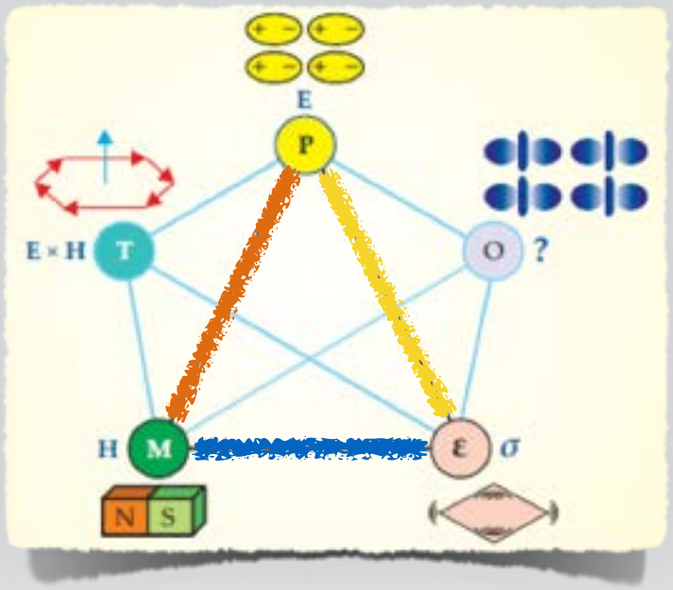
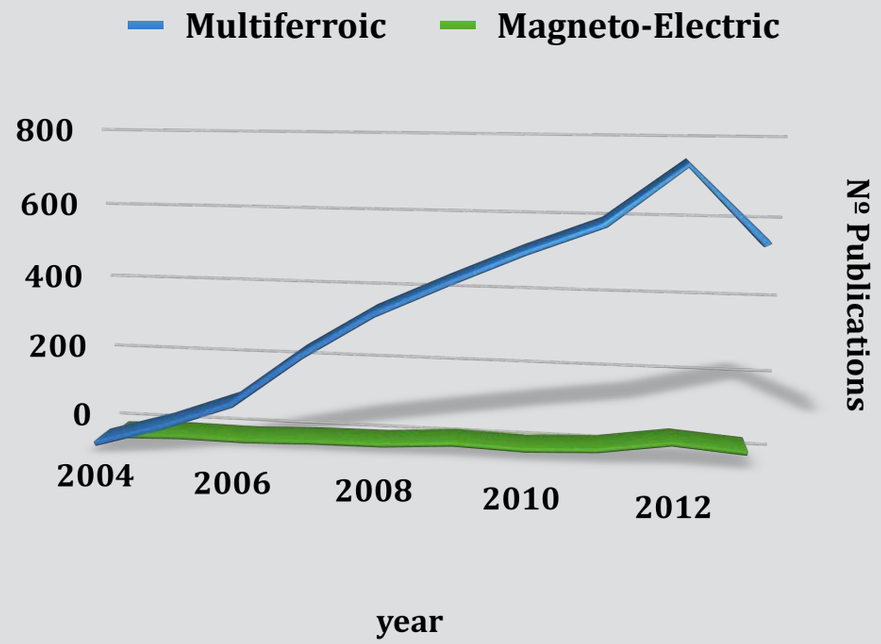
Motivation

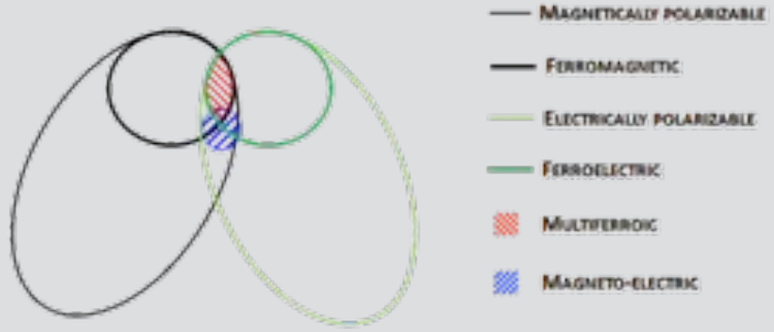
Multiferroics





Ferroic Orders: ferromagnetism (M), ferroeletricity (P), and ferroelasticity ($\mathcal{E}$), ...

Solid state systems exhibiting simultaneous (anti) ferroelectric ((A)FE) and (anti) ferromagnetic ((A)FM) orders - Multiferroics;



Maximization of the (A)FE-(A)FM coupling

possibility to manipulate the magnetic degrees of freedom electrically or vice-versa;

Possible applications: new non-volatile memories with magnetic/ electric Read/ Write;

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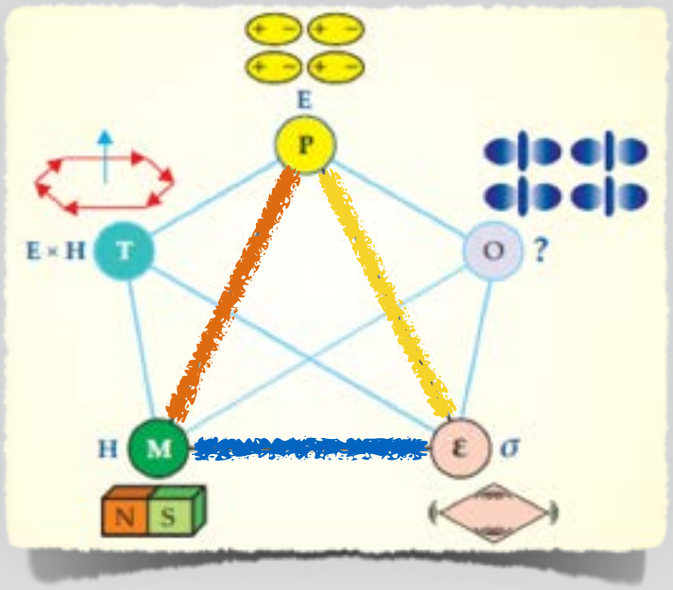
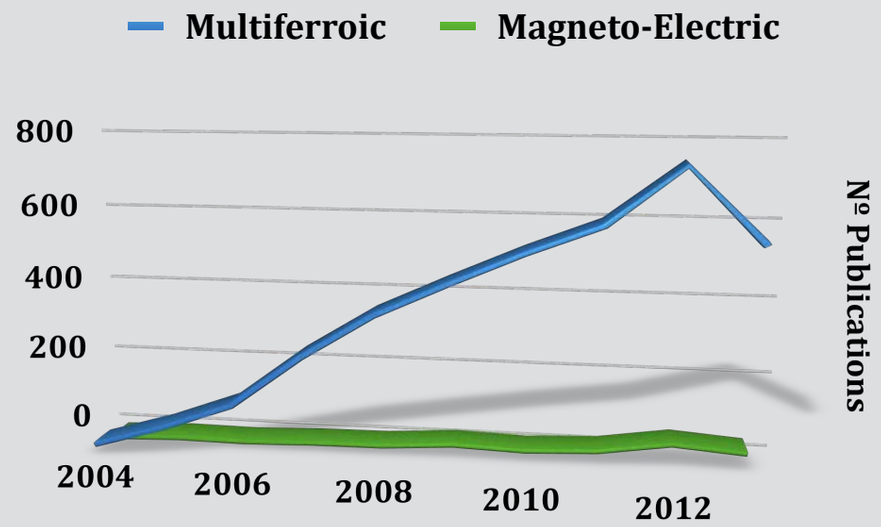
Multiferroics





Ferroic Orders: ferromagnetism (M), ferroeletricity (P), e ferroelasticity (ε)

PHYSICAL REVIEW B 84, 045106 (2011)

Phonon anomalies and possible local lattice distortions in giant magnetocapacitive $CdCr_2S_4$

V. Gnezdilov, [1] P. Lemmens, [2] Yu. G. Pashkevich, [3] Ch. Payen, [4] K. Y. Choi, [5] J. Hemberger, [6] A. Loidl, [6] and V. Tsurkan [6,7]

nature REVIEWS

Multiferroic and magnetoelectric materials

W. Eerenstein[1], N. D. Mathur[1] & J. F. Scott[2]

Contents lists available at SciVerse Scie...

of Magnetism and Magnetic Materials

...urnal homepage: www.elsevier.com/locate/jmmm

PHYSICAL REVIEW B 86, 064408 (2012)

Multiferroicity in geometrically frustrated α-MCr_2O_4 systems (M = Ca, Sr, Ba)

Li. Zhao, Tian-Wey Lan, Kuen-Jen Wang, Chia-Hua Chien, Tsu-Lien Hung, Jiu-Yong Luo, Wei-Hsiang Chao, Chung-Chieh Chang, Yang-Yuan Chen, and Maw-Kuen Wu*

Magnetic couplings in the quasi-2D triangular Heisenberg antiferromagnets ...-ACr_2O_4 (A=Ca, Sr, Ba)

...amay [b], G. André [b]

PHYSICAL REVIEW B 84, 014434 (2011)

Local distortions in multiferroic $AgCrO_2$ triangular spin lattice

A. M. L. Lopes, [1,*] G. N. P. Oliveira, [1] T. M. Mendonça, [2] J. Agostinho Moreira, [2] A. Almeida, [2] J. P. Araújo, [2] V. S. Amaral, [3] and J. G. Correia [1,4]

Possible applications: ...ad/ Write;

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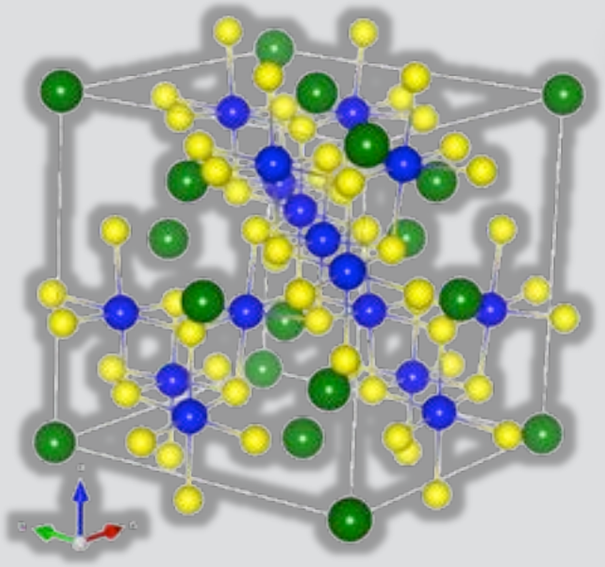
Crystal Structure



AB_2X_4

Relaxor-like ferroelectric

local distortions

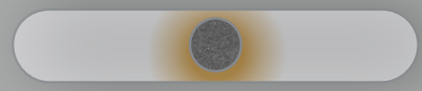
disorder

short and long-range orders

$CdCr_2S_4$

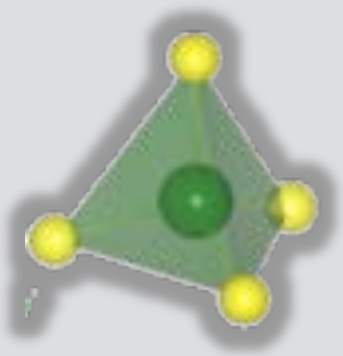
- Spinel Family:
- ACr_2X_4, A=Cd, Hg, Co, Fe; e X=S, Se, O
-- Cubic Face Centered packing
- A Coordenated tetrahedrically
- B Coordenated octahedrically

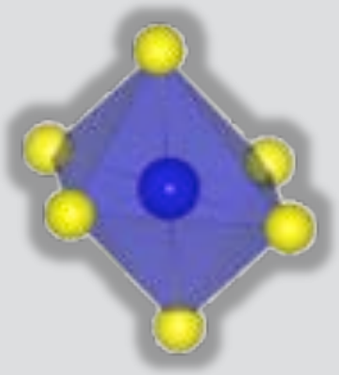
synthesised in closed quartz ampule



800ºC 10^{-5} torr 2 months

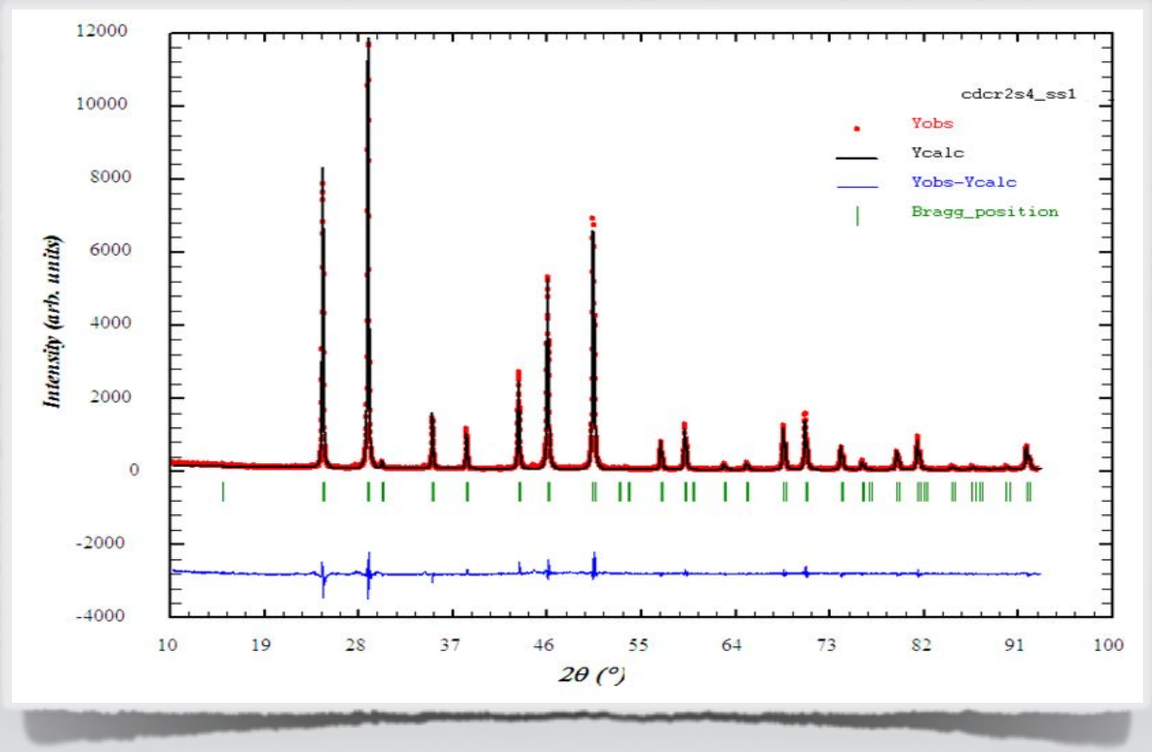
A site Cd^{2+} B site Cr^{3+}





CdS_4 CrS_6

Spinel Cubic structure: Fd-3m



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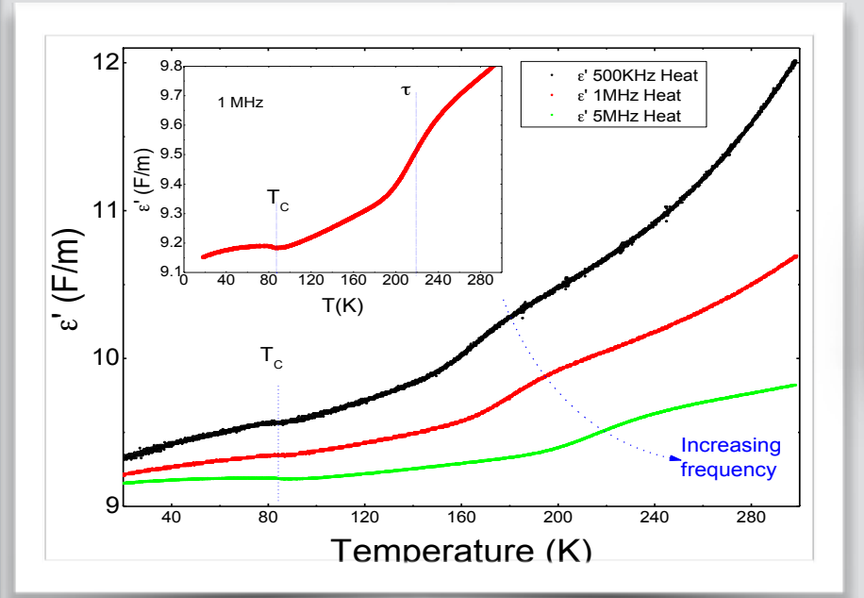
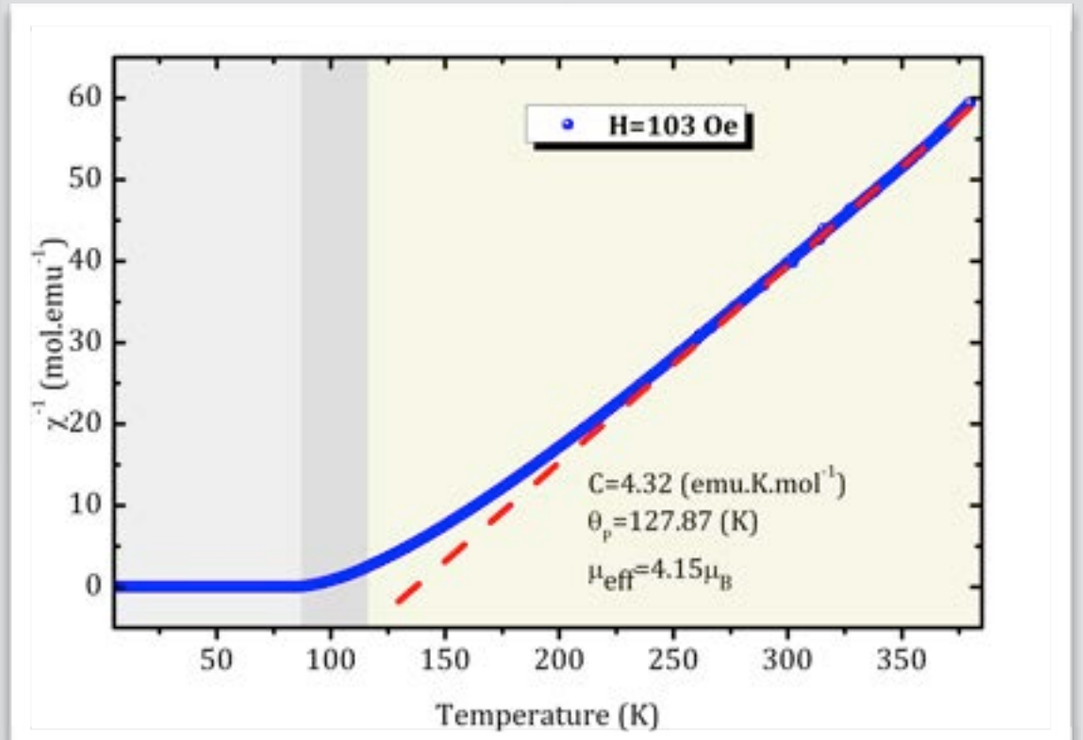
Magnetic and Electric

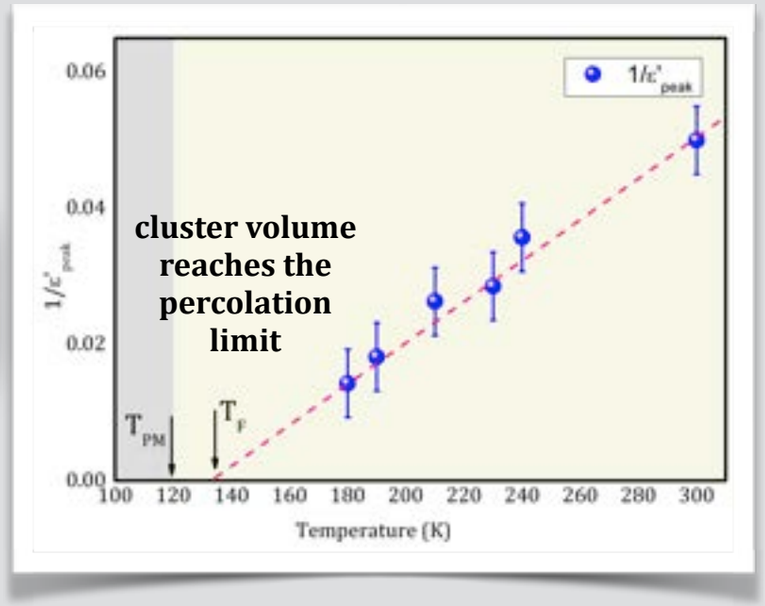


Temperature dependence of complex dielectric constant. The $CdCr_2S_4$ sample was measured to a frequency of 500 KHz, 1 and 5 MHz.

Small increase @ 86K -> above ferroelectric transition



Relaxor like behavior



Vogel-Fulcher Law representation of the reciprocal dielectric constant maximum peak position as a function of temperature.

~~Space group - ferroelectric order~~

Fd-3m to the F4$^-$3m noncentrosymmetric space group, which permits the existence of electric dipoles.

discovery of phonon anomalies at T_F < 130 K suggests that the electronic polarizability is enhanced by the Cr-S distance and respective bond hybridization.

Phase Transition	Para/Ferromagnetic
Curie T	-> T_C=86 K
Curie-Weiss T	-> θ_p=128 K

Temperature dependence of χ^{-1} measured on heating and with H=103 Oe.

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T

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(c)

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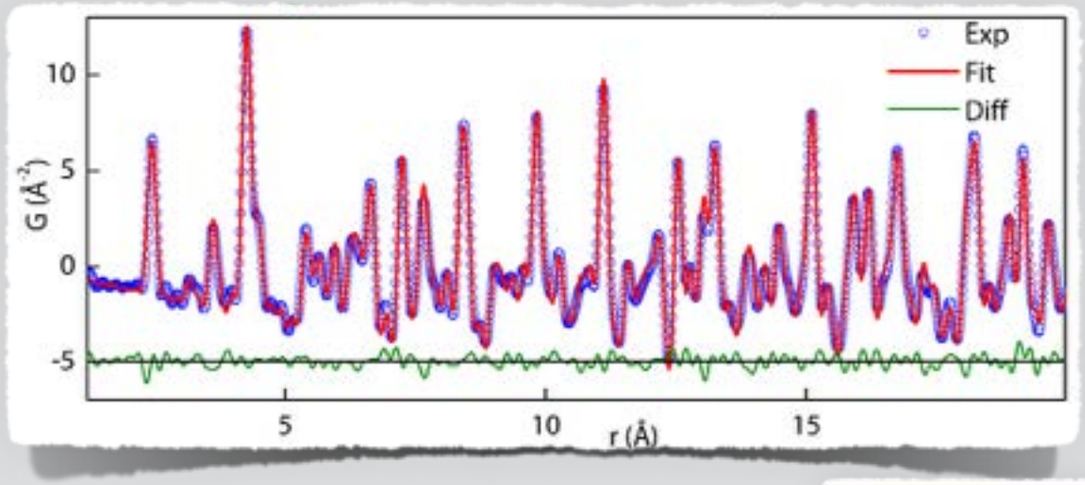
Pair Distribution Function



The PDF results at 80 K of the spinel $CdCr_2S_4$ structure (blue dots), as a solid red line (fit), with the difference curve (green) offset for clarity.

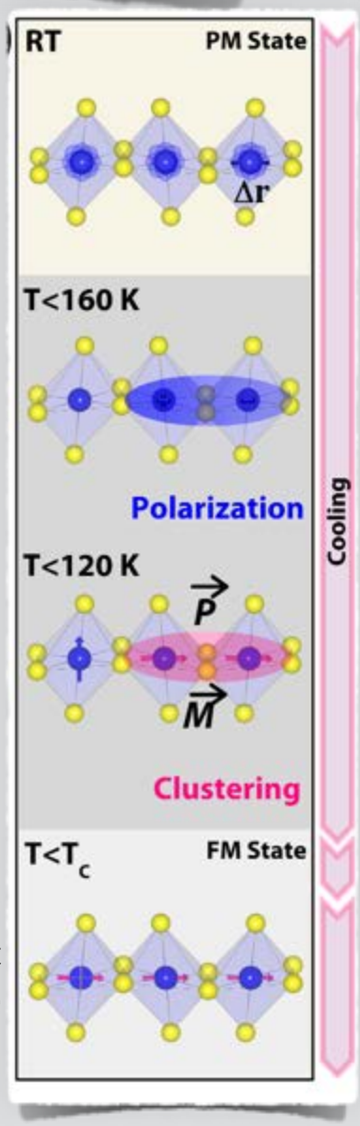
T > 130 K-negative thermal expansion regime

T < 130 K-positive thermal expansion regime

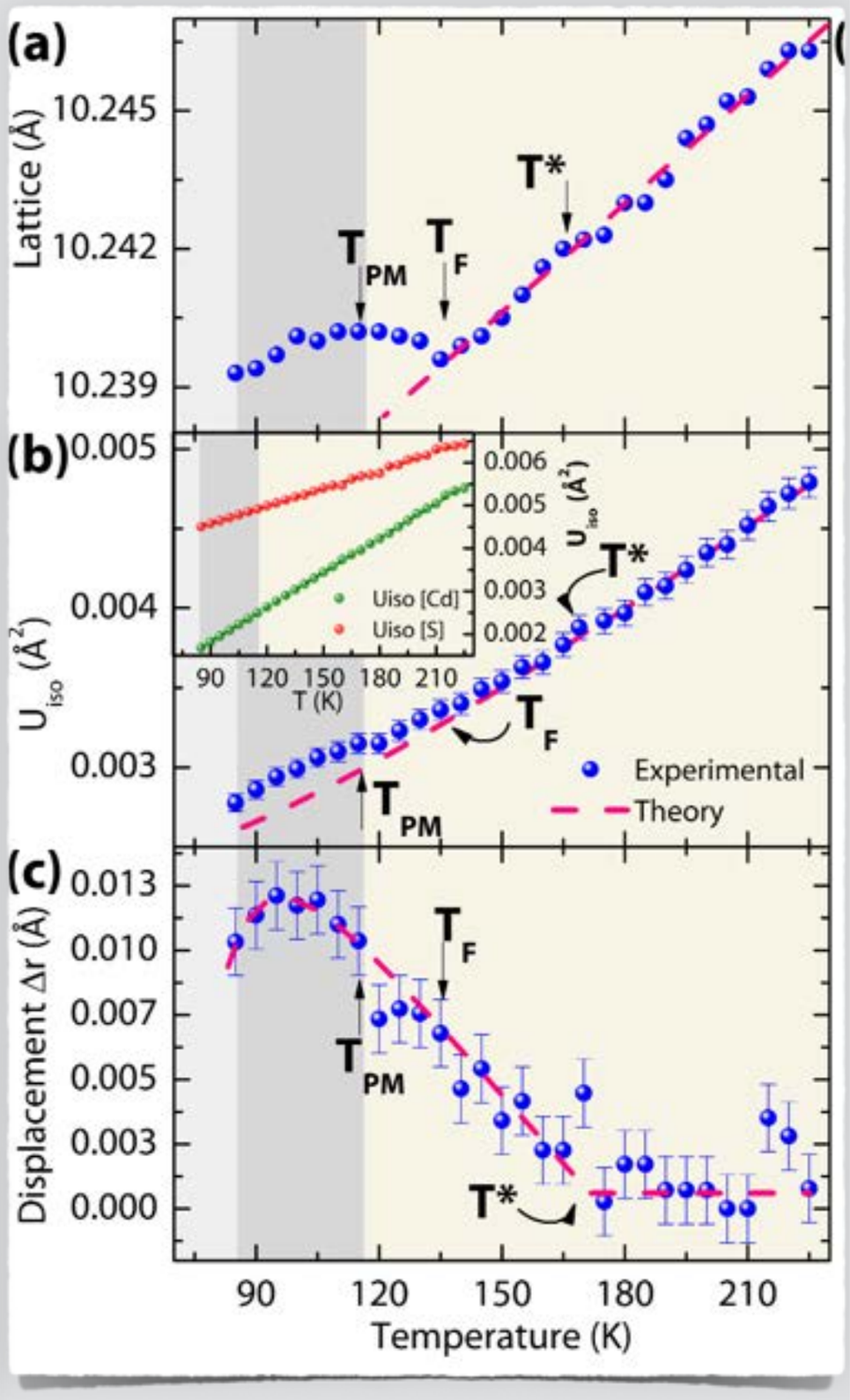
T_{PM} ~115K - negative thermal expansion regime

Amplitude of the Cr local off-centering.

$\Delta r_{max} < 0.012$ Å



Schematic representation of the local environment of Cr^{3+} as a function of temperature based on our findings.



(a) The temperature-dependent lattice parameters. (b) Isotropic ADPs of the Cr atom; inset: isotropic ADPs of the Cd and S atoms. (c) Amplitude of the local Cr off-centering. (d)

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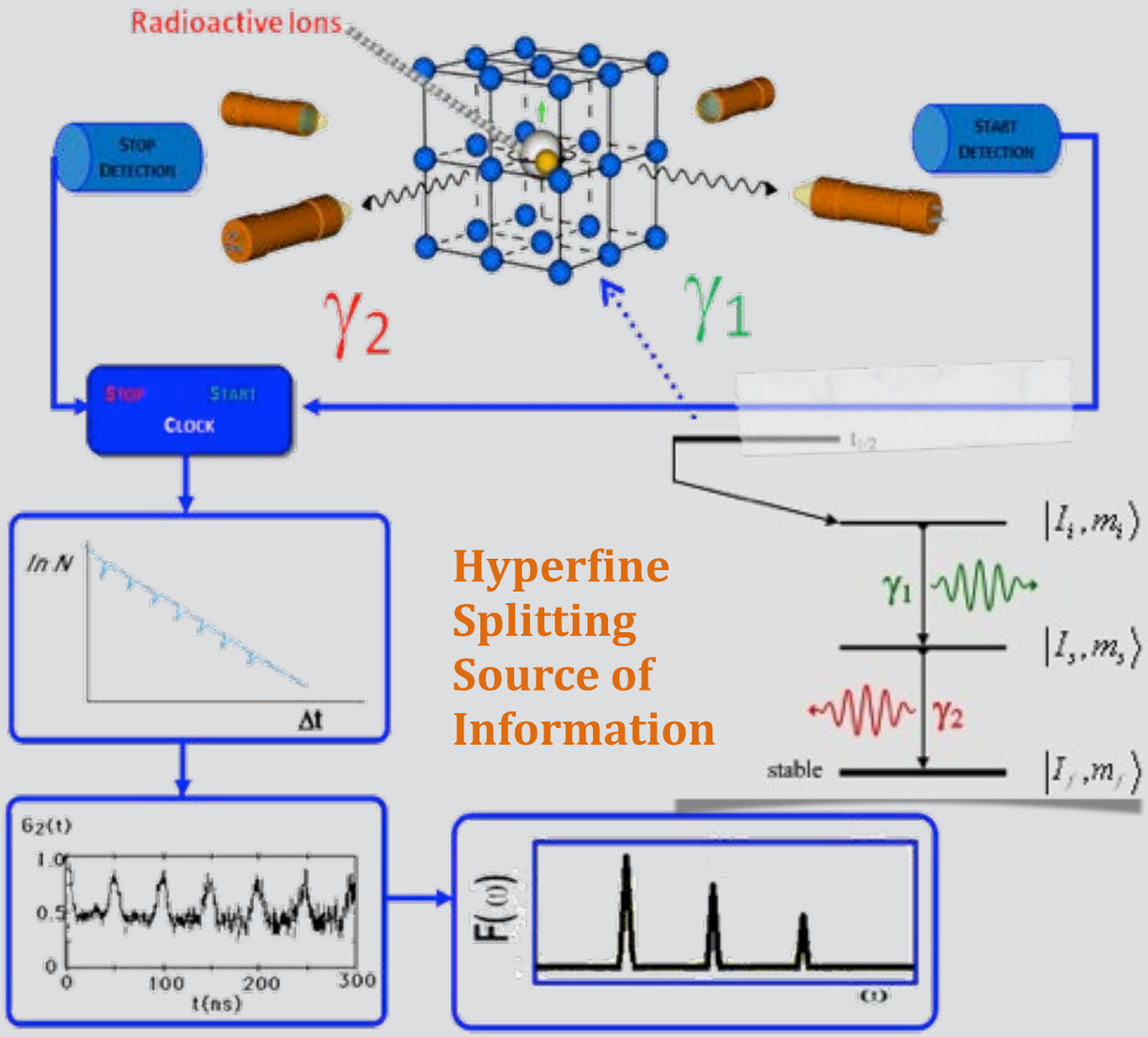
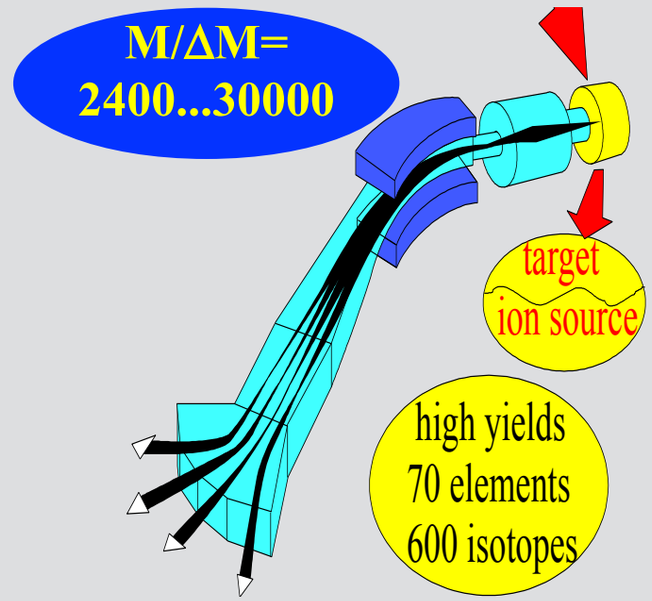
Perturbed Angular Correlation



Hyperfine Splitting Source of Information



Probe implanted at ISOLDE/CERN
^{111}In and ^{117}Ag implanted

	$CdCr_2S_4$
$^{111}In \rightarrow ^{111}Cd$	Cr/Cd Site
$^{117}Cd \rightarrow ^{117}In$	Cd Site

colocar decay scheme

Quadrupolar Frequency

$$\nu_Q = \frac{\left(eQV_{zz}\right)}{h}$$

Asymetry Parameter

$$\eta = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

EFG

V_{zz} - EFG Main component
η - Asymmetry parameter
B_{hf} - Magnetic hyperfine field

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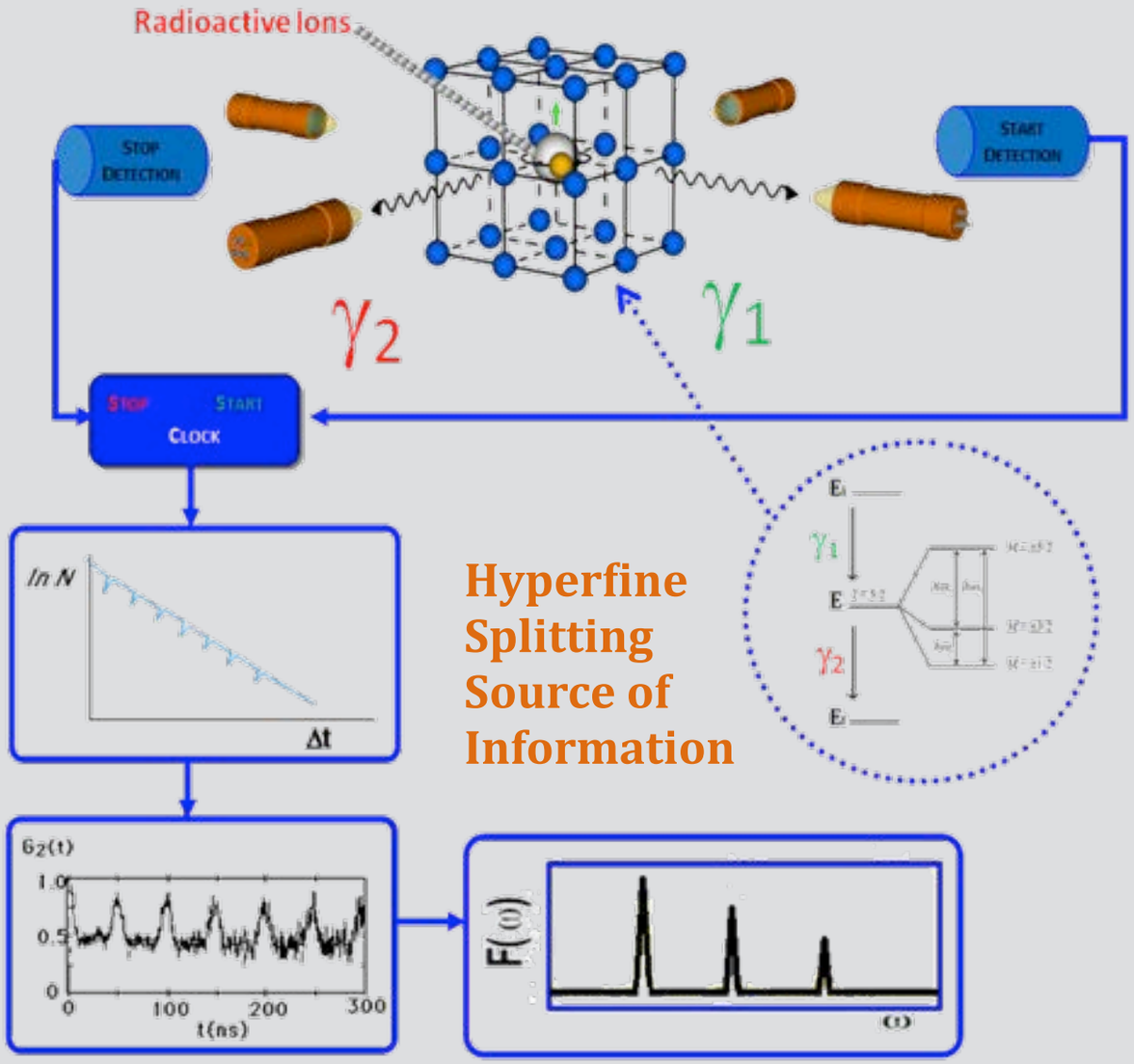

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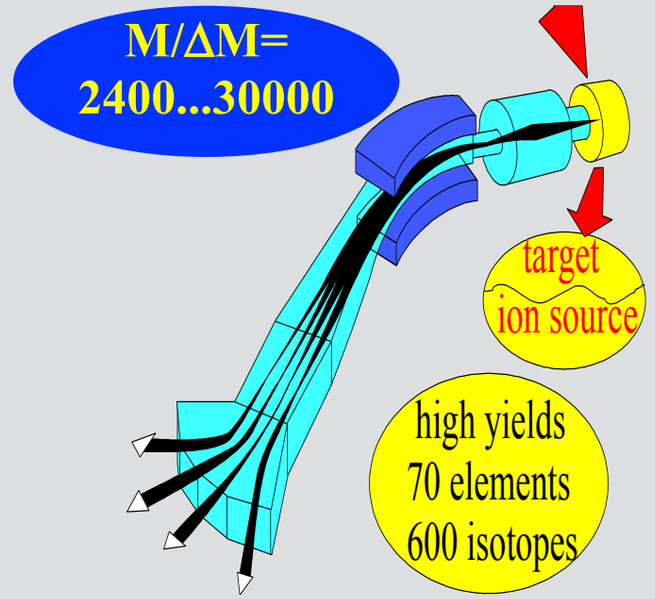

Probe implanted at ISOLDE/CERN
^{111}In and ^{117}Ag implanted

	$CdCr_2S_4$
$^{111}In \rightarrow ^{111}Cd$	Cr/Cd Site
$^{117}Cd \rightarrow ^{117}In$	Cd Site

Quadrupolar Frequency

$$\nu_Q = \frac{(eQV_{zz})}{h}$$

Asymmetry Parameter

$$\eta = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

EFG

V_{zz} - EFG Main component
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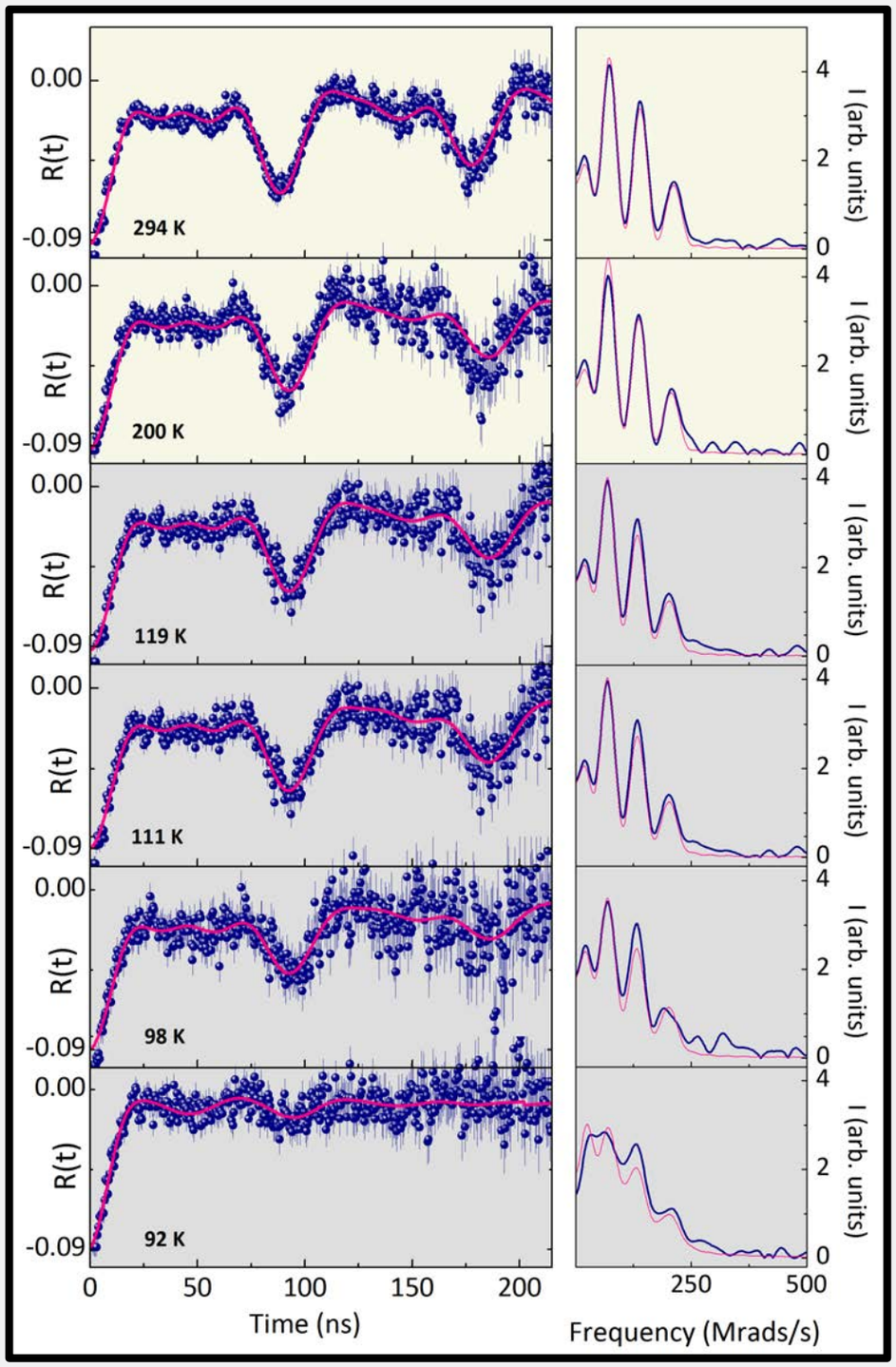
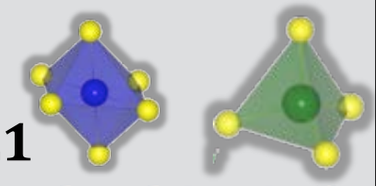


Representative R(t) functions, correspondent fits and respective Fourier transform.

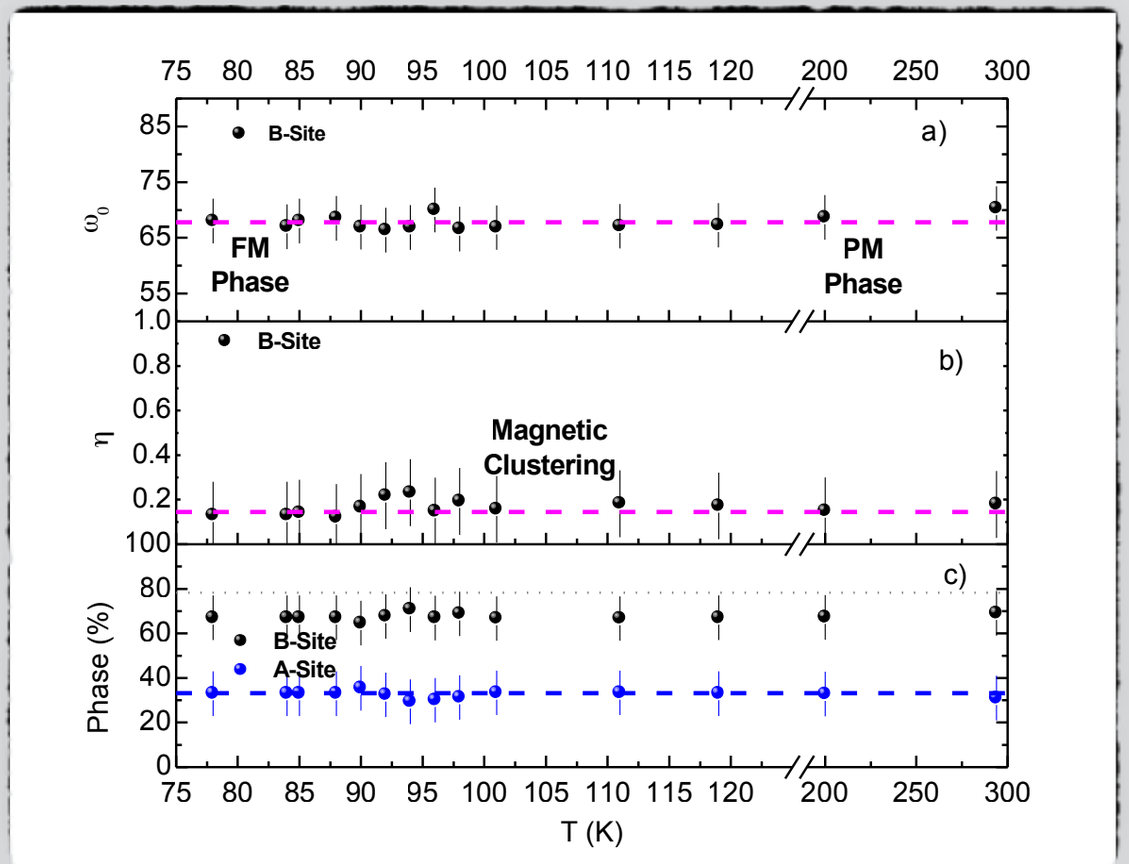
AFTER IMPLANTATION ANNEALING
15 MIN T=500 °C VACUUM

2 Local Environments



EFG_1 --> ν_{Q1}=72 MHz and η=0.1

EFG_2 --> ν_{Q2}=0 MHz (Probe @ Cd cubic site)



EFG temperature dependence parameters in the $CdCr_2S_4$ system, the fraction of each EFG (bottom), asymmetry parameter (middle) and fundamental frequency (top).

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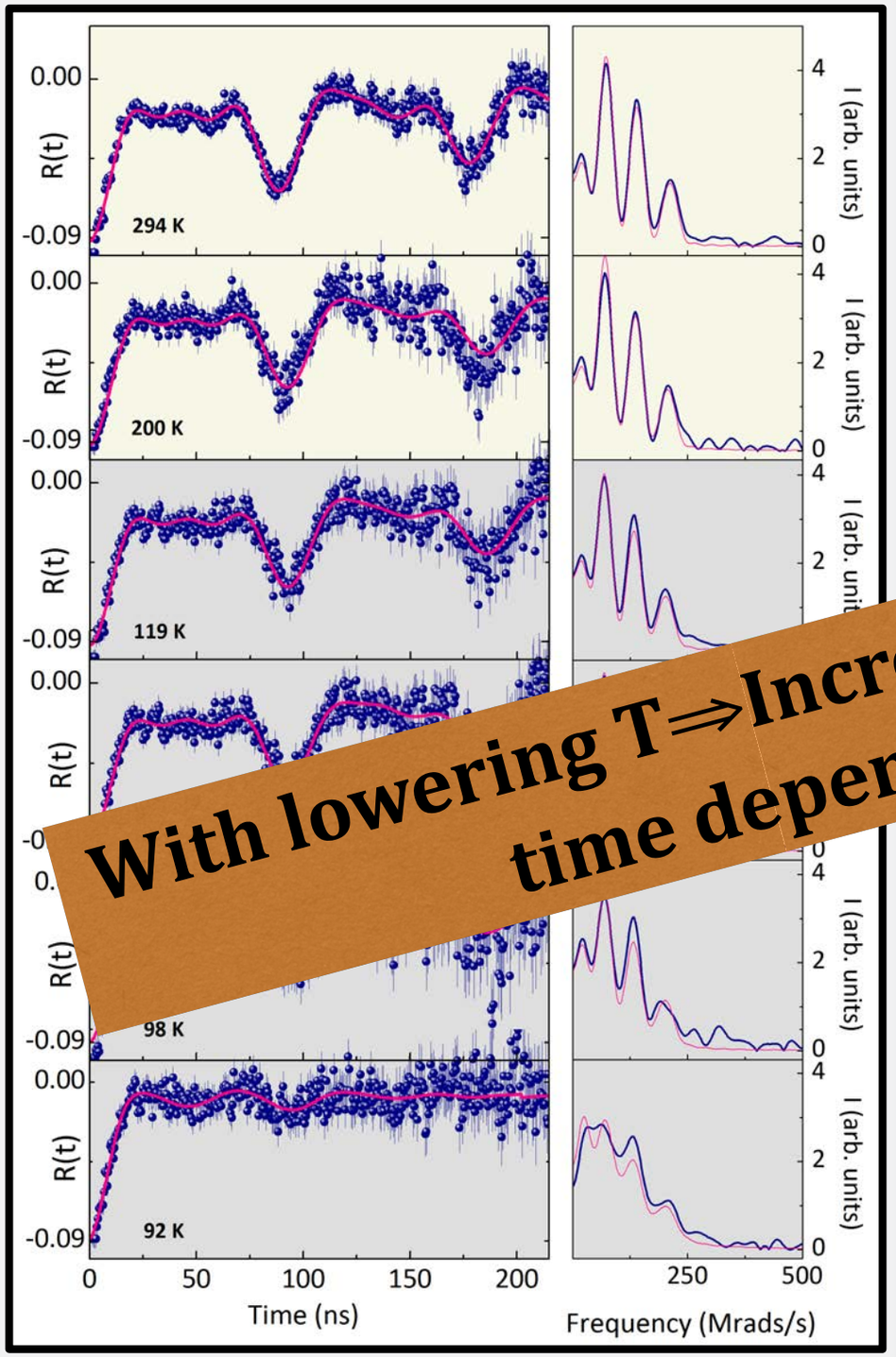
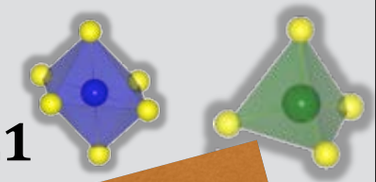


Representative R(t) functions, correspondent fits and respective Fourier transform.

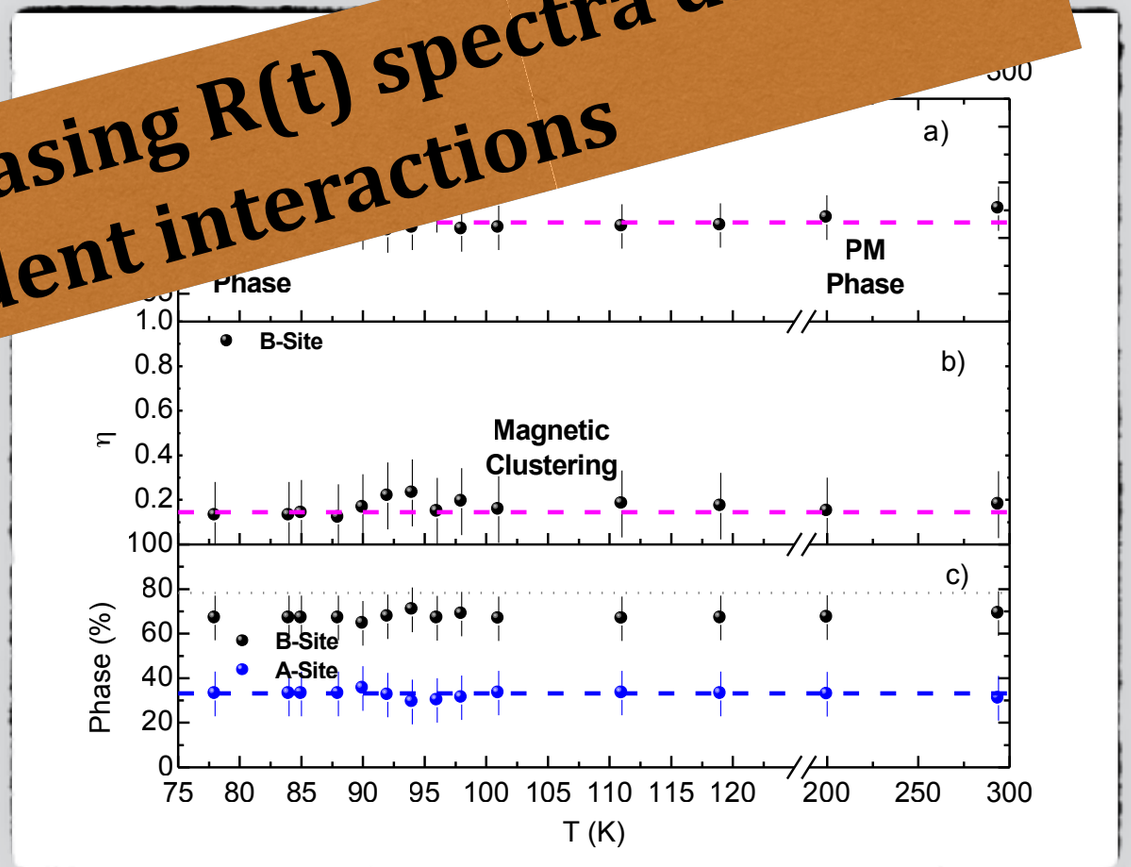
After implantation Annealing
15 min T=500 °C vacuum

2 Local Environments



EFG_1 --> ν_{Q1}=72 MHz and η=0.1
EFG_2 --> ν_{Q2}=0 MHz (Probe @ C… …te)

With lowering T⇒Increasing R(t) spectra damping time dependent interactions



EFG temperature dependence parameters in the $CdCr_2S_4$ system, the fraction of each EFG (bottom), asymmetry parameter (middle) and fundamental frequency (top).

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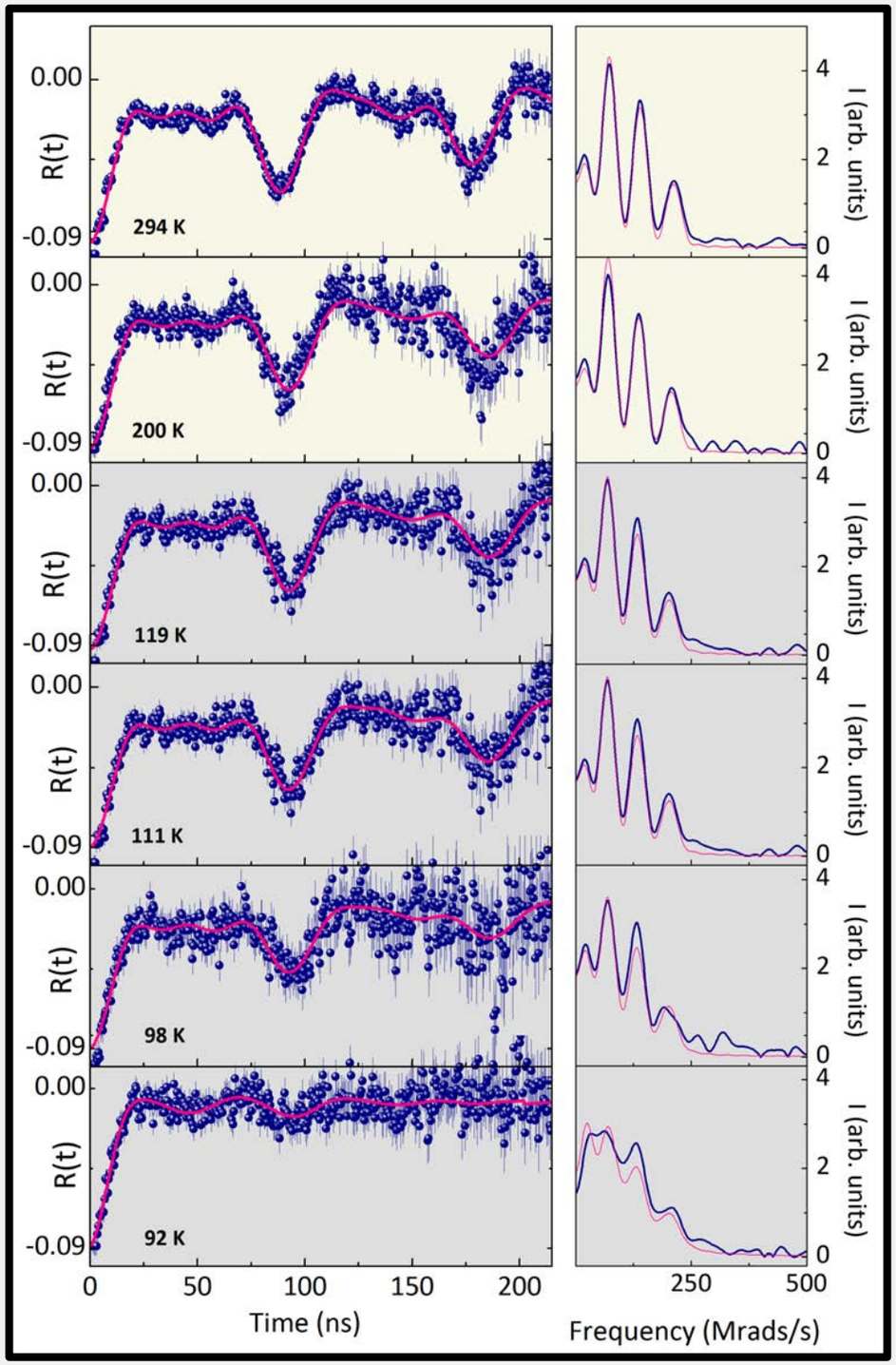

Representative R(t) functions, correspondent fits and respective Fourier transform.

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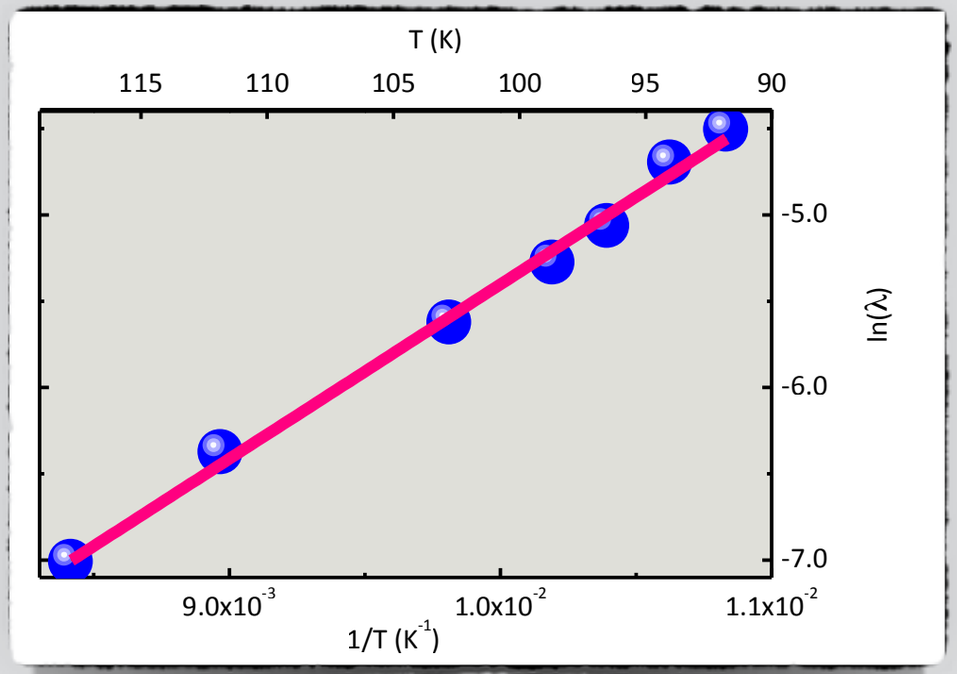

From 119K to 92K:
Dynamic Attenuation is observed (λ)
Slow thermally activated process

Activation Energy (E_a)=0.1 eV

$$\lambda_1 = \lambda_\infty e^{\frac{E_a}{KT}}$$

Cr ions oscillate between equivalent potential energy minima towards an order-disorder-type phase transition

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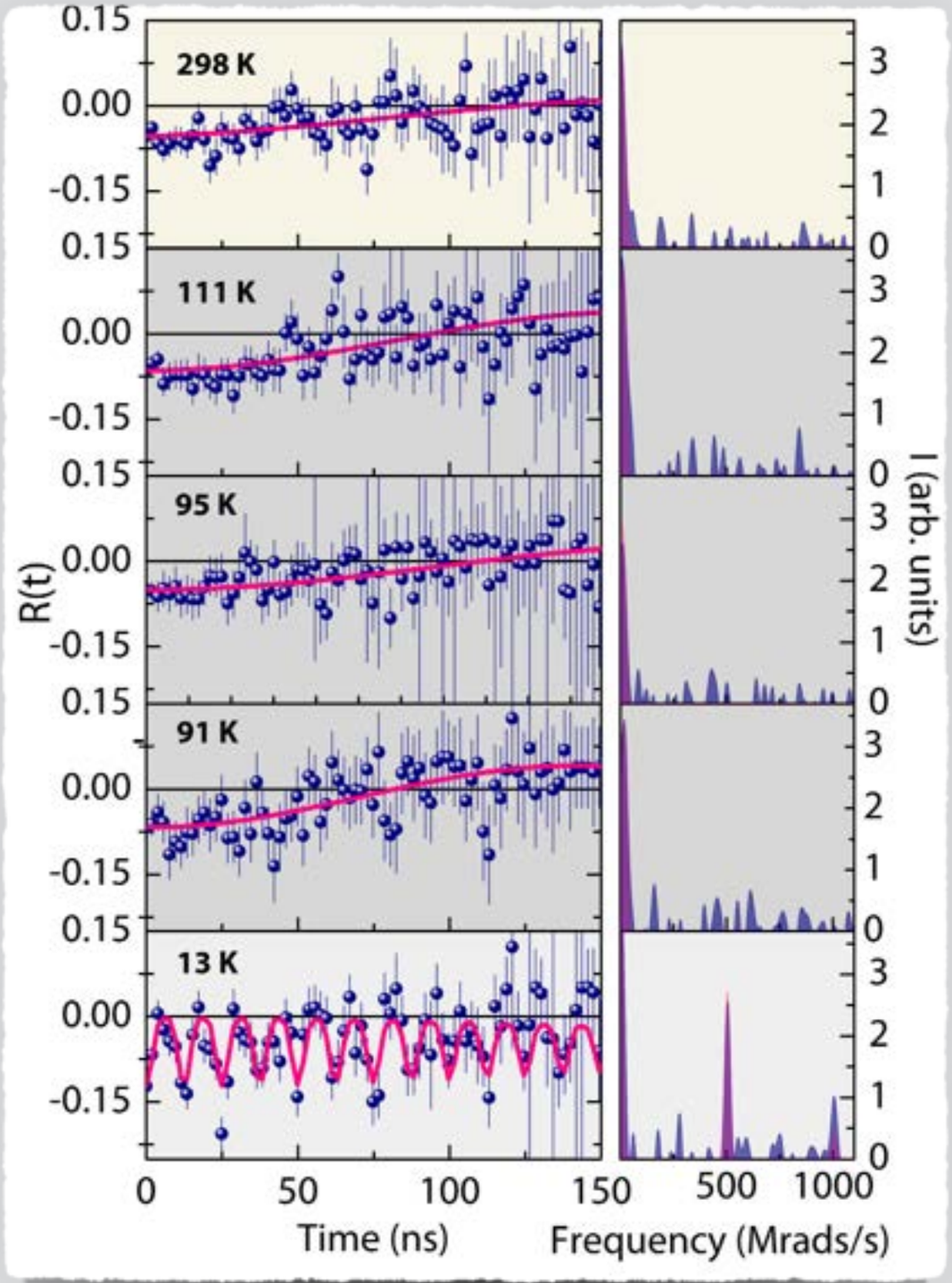
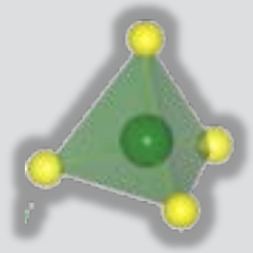


Representative R(t) functions, corresponding fits, and respective Fourier transform taken at different temperatures for the ^{117}Cd probe.

Paramagnetic Region

1 Local Environment



A site Cd^{2+}

No "exponential" damping of the R(t)

$EFG_{Cd} \rightarrow \nu_Q \simeq 0$ MHz

Ferromagnetic Region

High Larmor frequency is observed

local distortions of the magnetic ion Cr^{3+}. And macroscopically?

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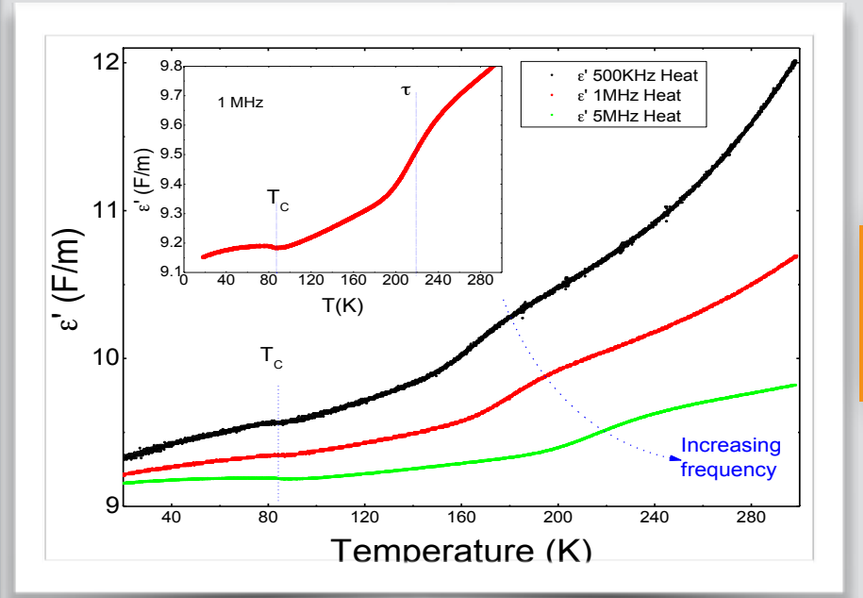
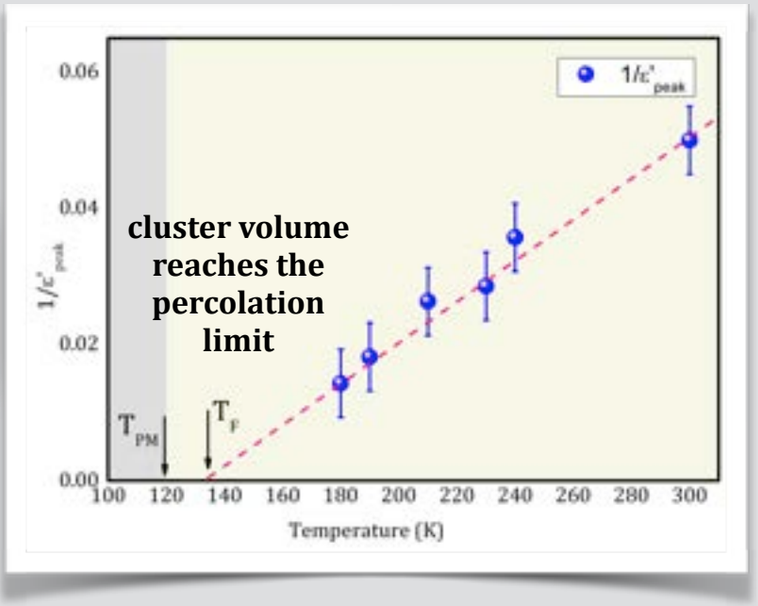


Temperature dependence of complex dielectric constant. The $CdCr_2S_4$ sample was measured to a frequency of 500 KHz, 1 and 5 MHz.

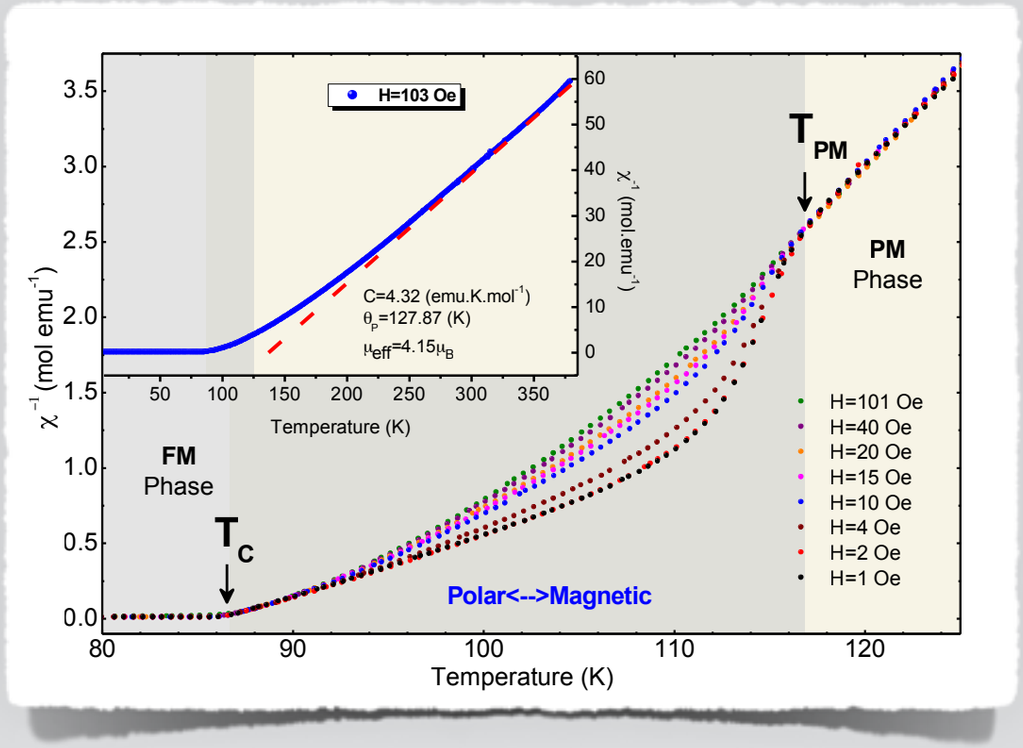
Small increase @ 86K -> above ferroelectric transition

Relaxor like behavior



Vogel-Fulcher Law representation of the reciprocal dielectric constant maximum peak position as a function of temperature.

Phase Transition Para/Ferromagnetic
Curie T -> T_C=86 K
Curie-Weiss T -> θ_p=128 K



Below 116 K
short-range magnetic clusters
H>100 Oe cluster destruction

Temperature dependence of χ^{-1} measured on heating and with H=103 Oe.

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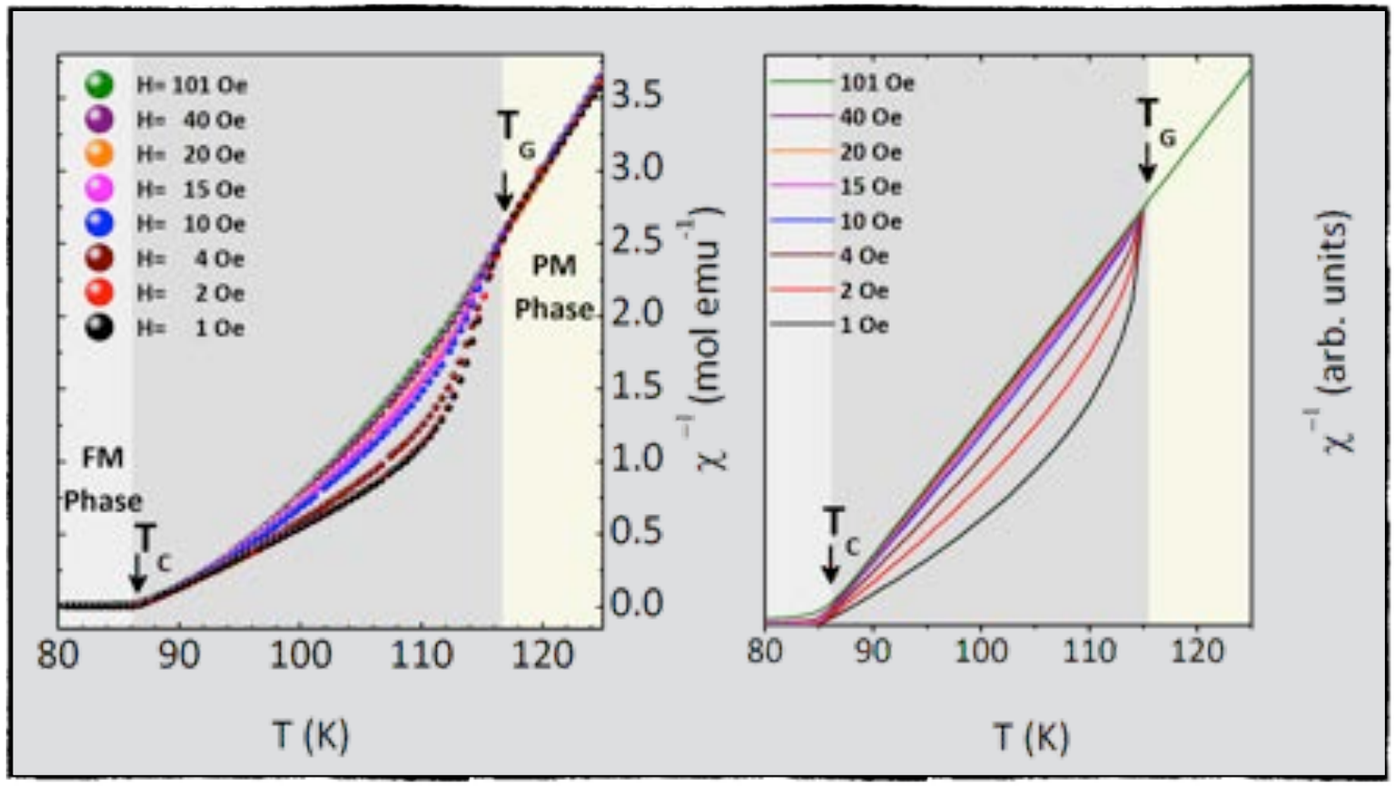
Magnetic - Theoretical Model



Landau Thermodynamic Model

Inverse magnetic susceptibility resulting from theoretical calculations of the Landau theory of phase transitions considering linear magneto electric coupling

$$G = \frac{1}{2}A\left(T - T_C\right)M^2 + \frac{1}{4}BM^4 + \frac{1}{2}A'\left(T - T_{PM}'\right)P^2 + \frac{1}{4}B'P^4 - MH - PE - \alpha PM$$

Short range magnetic cluster (SRMC) in the PM regime
Linear correlation between electric and magnetic degrees of freedom

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Cr^{3+} dynamic off-centering is intrinsically entangled to the formation of local dipoles, which are responsible for the observed magnetic correlations between adjacent Cr^{3+} neighbors.

PAC/ε' (T)

polar nanoclusters

PDF/PAC

Cr^{3+} dynamic off-centering

M(T)

Cr^{3+} - Cr^{3+} magnetic correlations

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Dynamic off-centering of Cr^{3+} ions and short-range magneto-electric clusters in $CdCr_2S_4$

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Thank You

Thank you for the attention.
Any questions?