



# **Experimental techniques**

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Indo – French School and Conference on the "Magnetism of Molecular Systems" 28<sup>th</sup> November



**Magnetic Materials and Switches Lab** 



- 1) Introduction
- 2) Molecular Magnetic Materials (MMM)
- 3) Magnetic Measurement Techniques
- a) SQUID Magnetometers; b) PPMS Susceptometer
- 4) DC Measurement techniques
- a) Usual DC and RSO; b) Solution; c) Horizontal and
- Vertical Rotators; d) (Photo)magnetic measurements
- 5) AC Measurement techniques

#### Acknowledgements

#### IISc Start-up Grant Solid State and Structural Chemistry Unit

Prof. Rodrigue Lescouëzec Dr. Hab. Rodolphe Clérac Dr. Hab. Yves Journaux Dr. Yangling Li Prof. Miguel Julve Prof. Francisco Lloret Dr. Pierre Dechambenoit Prof. Corine Mathonière Dr. Matias Urdampilleta Mr. Mathieu Rouzières Dr. Eric Rivière





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## **"Definition "**

Molecular Magnetism (MM) can be defined, according to Prof. O. Kahn, as a discipline, which designs, synthesizes, studies and applies molecular magnetic materials with new but predictable properties at the crossroads of quantum theory, chemistry, physics and biology.<sup>1</sup>

[1] O. Kahn, O. *Molecular Magnetism*, New York: VCH, **1993**; b) D. Gatteschi, R. Sessoli, R. J. Villain *Molecular nanomagnets*. Oxford: Oxford University Press, **2006**.

# Molecular (Magnetic) Materials

"Molecular magnetism is the research field devoted to the design, the synthesis, the study and the use of molecular magnetic materials with new original and predictable properties"



Prof M. Verdaguer, Emeritus professor Université Pierre et Marie Curie

## Molecular Magnets...

# Nano-Magnets (SMMs and SCMs)

#### Switchable Materials

#### Multi-functional Materials



#### What is SQUID?



#### Superconducting Quantum Interference Device



SQUID magnetometers, UPMC, Paris-6



MPMS 3\_ Quantum Design's

#### **Comparison SQUID/PPMS for DC and AC magnetic measurements**

Measurement type	MPMS SQUID- XL	PPMS VSM	PPMS ACMS	MPMS 3 SQUID-VSM
DC; M=f(H)	-7 – 7 T	-7 – 7 T	-7 – 7 T	-7 – 7 T
DC; M=f(T)	1,8 – 400 K (10 K / min)	4 (2) – 350 K (20 K / min)	3 (2) – 325 K	1,8 – 400 K
AC M=f(T,F, H)	A < 3.5 Oe and F =0.1 – 1,000 Hz		A ≤ 10 Oe and F=10 – 10,000 Hz	A < 3,5 Oe and F =0.1 - 1000 Hz
Sensibility (emu)	≈10 <sup>-7</sup> for DC ≈3,3 10 <sup>-8</sup> for AC	< 10 <sup>-6</sup>	≈2,5 10 <sup>-5</sup>	≈10 <sup>-8</sup> for VSM
Comments	Slow H variation; Very slow AC measurement T very stable	Very fast H Variation* Difficult to stabilize at T=2 K	Fast AC measurement; Difficult to stabilize at T=2 K	Advantages SQUID + PPMS

\*For a hysteresis loop with  $H_{max}$ = 5T and  $\Delta H$  = 0.25 T, it takes 30 min on VSM and > 3 h on SQUID-XL

Slide Courtesy Dr. Yangling Li



#### **SQUID Magnetometer**



#### Reference : Magnetic Property Measurement System (MPMS-XL) hardware Reference Manual

#### **DC measurement on SQUID**



Reference : Magnetic Property Measurement System (MPMS-XL) hardware Reference Manual

#### **DC measurement on SQUID**



#### **DC measurement on SQUID**











SQUID Magnetometer, KIT, Germany







SQUID Magnetometer, KIT, Germany

#### Before Sample Preparation: Some essential tools







Glass rod

good quality analytical balance







ceramic knife



ceramic tweezer



Ceramic scissors

## **Centering of Sample**



## **Centering of Sample**



## Problem due to loss of SQUID tuning



#### SQUID Magnetometer, CRPP, Bordeaux

## **Restoring SQUID tuning**

		SQUID Tuning	×I			
MM4	_89_a1.rs		-			
	0.004	Current Tune Value Maximum Value				
	0.002	Drive 10.98 % Tune 11.37 %				
oltage 1 Fit	Automatic Tuning					
Detrended V g Detrended	0	Start     Stop     Max Drive     33     %       Max Tune     27     %				
Long L		Manual Tuning     Tune				
	-0.002	Up Slow Up Slow				
		Stop Fast Stop Fast				
	-0.004 2.2	Down 0.00 % Set Down 0.00 % Set				
		OK Cancel				

#### SQUID Magnetometer, CRPP, Bordeaux

# Good Magnetic Data

Obviously, you need good measurements!!!

What are the possible sources of errors when you measure magnetic properties?

There are five traditional source of errors which one can finds in the scientific articles and most of the magnetochemists have made one of these mistakes at least once

#### -Ferromagnetic impurity

- -Loss of solvent molecules
- -Orientation of the microcrystals under magnetic field
- -Saturation effect
- -Diamagnetic correction

Slide Courtesy Dr. Hab. Yves Journaux

## Ferromagnetic impurity

#### The enemy of the magneto-chemist

#### The metallic spatula !!!!





#### good tools



Your sample is polluted with a ferromagnetic impurity !!!!

Slide Courtesy Dr. Hab. Yves Journaux

#### Presence of a ferromagnetic impurity (magnet)

 $B = \mu_0 [H + M] \quad with \ M = \chi . H$ 

*x* = *M* / *H* without ferromagnetic impurity

At low field, the magnetic susceptibility  $\boldsymbol{\chi}$  does not depend on the magnetic field

with Ferromagnetic impurity

$$M_{measured} = \chi_{true}. H + M_{impurity}$$

$$\chi_{measured} = \chi_{true} + M_{impurity} / H$$

with a ferromagnetic impurity magnetic susceptibility  $\chi$  depends on the magnetic field Slide Courtesy Dr. Hab. Yves Journaux

#### The first thing to do, is to check the field-dependent magnetization at 100 K



## **Loss of Solvent Molecules**

#### Presence of the solvent molecules in the crystal structure



#### Molecular compounds are fragile



## **Sample Loading and Purging**

When you introduce your sample in the SQUID. You put it in the sample loading chamber.

"The standard sample loading technique is the presence of a vacuum atmosphere inside the sample loading space. When the system is purged, the sample space goes through a series of pump/purge cycles using the FLUSH valve to pump out the sample space and the VENT valve to back fill with helium gas."

For molecular compounds, there is great risk to loose the crystallization solvent molecules!!!

## **Loss of Solvent Molecules**



With crystallization solvent molecules this sample exhibit an antiferromagnetic ordering at low temperature



Without crystallization solvent molecules sample shows a ferromagnetic ordering at 14 K The crystallization solvent molecules control the intermolecular interaction

In most cases the loss of crystallization solvent molecules lead to intermolecular antiferromagnetic interaction and could mask the interesting magnetic properties like slow relaxation of magnetization in case of Single Molecule Magnets

To be sure about the magnetic data, it is a good practice to perform a TGA (thermogravimetry) or DTA (Differential Thermal Analysis) experiment before measuring the sample in the SQUID magnetometer, in order to see the possible solvent loss around room temperature

#### Orientation of the microcrystals under magnetic field





The micro crystals are oriented by the magnetic field. Now the sample is no longer being randomly oriented. A majority of micro crystals have their easy axis // to the magnetic field Slide Courtesy Dr. Hab. Yves Journaux

### Orientation of the microcrystals under magnetic field

 $E = -M \cdot H = -\chi$ . H<sup>2</sup> to minimize its energy, the crystal will orient itself in order to have the largest  $\chi$  value



#### To avoid the orientation of the microcrystal

You have to block the microcrystals!!!

Slide Courtesy Dr. Hab. Yves Journaux

#### To block the crystals, several solutions are possible

-Parafilm -Araldite -Viscous liquid But with this kind of solution it is difficult to correct the diamagnetic contribution of these supplementary materials

# easy solution but not very safe

Slide Courtesy Dr. Hab. Yves Journaux





#### **Blocking the microcrystals using Viscous liquid**

SQUID Magnetometer data, CRPP, Bordeaux

## **Saturation Effect**

In a SQUID magnetometer (DC measurement), the susceptibility is obtained by  $\chi_M = M_M / B$ 

 $\chi_{M}$  is calculated as the slope of the red line (secant line) which has nothing to do with the real value of  $\chi_{M}$ .

 $\chi_M$  at 1 T is given by the slope of **the green line** (tangent line)



However, we are interested in the value of  $\chi_M$  at B=0, which is the slope of the pink line (linear part of the M=f(B) curve)

#### At low temperature, measurements have to be done at low field

Slide Courtesy Dr. Hab. Yves Journaux

## **Diamagnetic corrections**

Crude data must be corrected for

-Diamagnetism of the sample holder

-diamagnetism of the sample

-TIP contribution



 
 χ<sub>M</sub>T uncorrected
 χ<sub>M</sub>T overcorrected
 χ<sub>M</sub>T corrected
 χ<sub>M</sub>T corrected

for a weakly coupled system a bad diamagnetic correction could lead to anapparent ferro or ferrimagnetic interactionSlide Courtesy Dr. Hab. Yves Journaux
## **Diamagnetic corrections**

To find the right correction for the diamagnetism

You have to have a good law  $\chi_{dia}$ =f(T,H) for the diamagnetism of the sample holder We use  $\chi_{nac}$ = A(H) T + B(H)/T +C(H)/T<sup>2</sup>

#### For the sample

The ideal solution is to have the measurements for an isomorphic compound containing non-magnetic metal ions like Zn(II)

Calculate the diamagnetism of the sample using Pascal's constants,

A good approximation is given by  $\chi_M dia \approx \{M_{mol}/2\}^* 10^{-6}$ 

Slide Courtesy Dr. Hab. Yves Journaux

## **Diamagnetic corrections**

Actually you do not need to correct the data for the diamagnetism of the sample.

In fact, it would be better to add a Constant term to the theoretical law

 $\chi_{M} = f(J_{i}, D_{i}, g_{i}, T) + C_{dia}.10^{-6}$ 

and check afterwards if the  $C_{dia}$  value is reasonable

The *C*<sub>dia</sub> term contains both the diamagnetic and the TIP contributions

**TIP** : temperature independent paramagnetism

## **Diamagnetic corrections of the bag**



SQUID Magnetometer data, KIT, Germany

							SK.N	/1_149_Xd.dc
	L 🕖 🕅	I IV - III - III	<b>T</b>	<b>B 2</b>	📐 <u>ष</u>			
	Time	Comment	Field (Oe)	Tempere	Long(emu)	Long Sd Dev	Long Arithm	Long Reg Fit
	1.5700+.00		500.00	100.05	0.776.45.05	0.0000	7.0000	0.00405
	1.53620+09		500.00	109.95	0.57646-05	0.0000	3.0000	0.99495
1	1.53820+09		500.00	107.86	8.5043e-05	0.0000	3.0000	0.99562
Z	1.5382e+09		500.00	105.81	8.5477e-05	0.0000	3.0000	0.99490
3	1.5382e+09		500.00	103.75	8.5817e-05	0.0000	3.0000	0.99428
4	1.5382e+09		500.00	101.78	8.7192e-05	0.0000	3.0000	0.99569
5	1.5382e+09		500.00	99.728	8.8529e-05	0.0000	3.0000	0.99155
6	1.5382e+09		500.00	97.785	8.9166e-05	0.0000	3.0000	0.99580
7	1.5382e+09	0	500.00	95.771	9.0567e-05	0.0000	3.0000	0.99598
8	1.5382e+09		500.00	93.733	9.1144e-05	0.0000	3.0000	0.99414
9	1.5382e+09		500.00	91.711	9.2576e-05	0.0000	3.0000	0.99573
10	1.5382e+09		500.00	89.708	9.3603e-05	0.0000	3.0000	0.99340
11	1.5382e+09		500.00	87.758	9.5090e-05	0.0000	3.0000	0.99344
12	1.5382e+09		500.00	85.745	9.7302e-05	0.0000	3.0000	0.99545
13	1.5382e+09		500.00	83.769	9.7134e-05	0.0000	3.0000	0.99725
14	1.5382e+09		500.00	81.748	9.8978e-05	0.0000	3.0000	0.99735
15	1.5382e+09		500.00	79.711	0.00010036	0.0000	3.0000	0.99609
16	1.5382e+09		500.00	77.743	0.00010071	0.0000	3.0000	0.99290
17	1.5382e+09		500.00	75.707	0.00010270	0.0000	3.0000	0.99514
18	1.5382e+09		500.00	73.750	0.00010500	0.0000	3.0000	0.99540
19	1.5382e+09		500.00	71.784	0.00010630	0.0000	3.0000	0.99664
20	1.5382e+09		500.00	69.740	0.00010805	0.0000	3.0000	0.99716
21	1.5382e+09		500.00	67.733	0.00011048	0.0000	3.0000	0.99751
22	1.5382e+09	0	500.00	65.733	0.00011099	0.0000	3.0000	0.99557

#### Magnetic moment vs Temperature

SQUID Magnetometer data, UPMC, Paris-6

Comment	Time S	Tempere	Magned	Range	Pressu(Torr)	Measure	Measuumber	Motorp. (C)	Temp.	Field Scode)	Chambcode)	Chambp (K)	Redire State	Rotati (deg)	Rotator state
C0	α	2	в	C4	C	C6	0	C8	(9	C10	a	C12	C13	C14	C15
	3.7494e+09	249.91	2499.6	1.0000	6.0766	-1.0000e+08	1.0000	29.326	1.0000	1.0000	1.0000	249.91	0.0000	249.91	9.9492e-44
	3.7494e+09	250.11	2499.6	1.0000	6.0767	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	250.20	0.0000	250.09	9.9492e-44
	3.7494e+09	254.18	2499.6	1.0000	6.0795	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	254.33	0.0000	254.14	9.9492e-44
	3.7494e+09	258.12	2499.6	1.0000	6.0838	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	258.28	0.0000	258.07	9.9492e-44
	3.7494e+09	262.04	2499.6	1.0000	6.0893	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	262.19	0.0000	261.99	9.9492e-44
	3.7494e+09	265.97	2499.6	1.0000	6.0973	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	266.12	0.0000	265.93	9.9492e-44
	3.7494e+09	269.91	2499.6	1.0000	6.1063	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	270.04	0.0000	269.90	9.9492e-44
	3.7494e+09	273.94	2499.6	1.0000	6.1181	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	274.11	0.0000	273.93	9.9492e-44
	3.7494e+09	277.87	2499.6	1.0000	6.1309	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	278.04	0.0000	277.81	9.9492e-44
	3.7494e+09	281.76	2499.6	1.0000	6.1465	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	281.91	0.0000	281.71	9.9492e-44
	3.7494e+09	285.72	2499.6	1.0000	6.1664	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	285.85	0.0000	285.71	9.9492e-44
	3.7494e+09	289.71	2499.6	1.0000	6.1957	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	289.85	0.0000	289.68	9.9492e-44
	3.7494e+09	293.69	2499.6	1.0000	6.2319	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	293.87	0.0000	293.64	9.9492e-44
	3.7494e+09	297.60	2499.6	1.0000	6.2749	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	297.76	0.0000	297.55	9.9492e-44
	3.7494e+09	301.54	2499.6	1.0000	6.3271	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	301.68	0.0000	301.52	9.9492e-44
	3.7494e+09	305.54	2499.6	1.0000	6.3844	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	305.70	0.0000	305.50	9.9492e-44
	3.7494e+09	309.44	2499.6	1.0000	6.4464	-1.0000e+08	1.0000	29.326	2.0000	1.0000	1.0000	309.60	0.0000	309.39	9.9492e-44
	3.7494e+09	313.35	2499.6	1.0000	6.5135	-1.0000e+08	1.0000	29.326	2.0000	1.0000	1.0000	313.51	0.0000	313.30	9.9492e-44
	3.7494e+09	317.31	2499.6	1.0000	6.5846	-1.0000e+08	1.0000	29.326	2.0000	1.0000	1.0000	317.48	0.0000	317.25	9.9492e-44
	3.7494e+09	321.23	2499.6	1.0000	6.6616	-1.0000e+08	1.0000	29.326	2.0000	1.0000	1.0000	321.35	0.0000	321.21	9.9492e-44
	3.7494e+09	325.23	2499.6	1.0000	6.7317	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	325.38	0.0000	325.18	9.9492e-44
	3.7494e+09	329.14	2499.6	1.0000	6.8027	-1.0000e+08	1.0000	28.837	2.0000	1.0000	1.0000	329.30	0.0000	329.08	9.9492e-44

#### SQUID-VSM data, IISc, Bangalore

#### Magnetic moment vs Temperature Data from VSM



Magnetic susceptibility vs Temperature

	FeTpCovimBF4DRIED_a13.r														
	<b>L</b> () ()	I II.	<b>P D</b>	<b>B</b> 🔀	🛕 🔟										
	Time (0	Comment	Field (Oe)	Tempere	Long(emu)	Long Sd Dev	Longt (cm)	Long 0d	Long Arithm	Long Reg Fit	Long Ractor				
0	1.4825e+09		0.62804	100.04	-3.6648e-06	6.1532e-08	0.0000	0.0000	2.0000	0.96614	1.8250				
1	1.4825e+09		49.660	100.03	1.3416e-05	1.1775e-07	0.0000	0.0000	2.0000	0.97973	1.8250				
Z	1.4825e+09	1	99.798	100.02	3.0147e-05	8.8269e-08	0.0000	0.0000	2.0000	0.97670	1.8250				
3	1.4825e+09		150.06	100.02	4.7152e-05	9.9945e-10	0.0000	0.0000	2.0000	0.97720	1.8250				
4	1.4825e+09		199.98	100.01	6.4091e-05	8.6343e-08	0.0000	0.0000	2.0000	0.97755	1.8250				
5	1.4825e+09	1	250.23	100.01	8.1053e-05	3.8547e-08	0.0000	0.0000	2.0000	0.97743	1.8250				
6	1.4825e+09		300.25	100.00	9.7872e-05	2.5973e-08	0.0000	0.0000	2.0000	0.97775	1.8250				
7	1.4825e+09	[	400.57	100.00	0.00013183	5.5144e-08	0.0000	0.0000	2.0000	0.97764	1.8250				
8	1.4825e+09		500.71	100.00	0.00016550	1.0957e-07	0.0000	0.0000	2.0000	0.97777	1.8250				
9	1.4825e+09	1	600.97	100.00	0.00019943	8.1564e-08	0.0000	0.0000	2.0000	0.97773	1.8250				
10	1.4825e+09		701.28	99.998	0.00023311	1.0955e-07	0.0000	0.0000	2.0000	0.97781	1.8250				
11	1.4825e+09		801.36	99.999	0.00026686	1.2128e-07	0.0000	0.0000	2.0000	0.97781	1.8250				
12	1.4825e+09	1	901.56	99.997	0.00030052	1.5613e-07	0.0000	0.0000	2.0000	0.97791	1.8250				
13	1.4825e+09		1002.0	99.999	0.00033426	1.9030e-07	0.0000	0.0000	2.0000	0.97793	1.8250				
14	<b>A</b>														

#### Magnetic moment vs field

SQUID Magnetometer data analysis, CRPP, Bordeaux



SQUID Magnetometer data analysis, CRPP, Bordeaux

### **Spin Crossover or Spin-transition**



Atkins P. W. Physical chemistry. **1994** 221. Slichter C. P. J. Chem. Phys. **1972**, *56*, 2142.

#### Spin Crossover or Spin Transition Electron-Transfer-Coupled Spin Transition



SQUID Magnetometer data analysis, CRPP, Bordeaux

#### Spin Crossover or Spin Transition Electron-Transfer-Coupled Spin Transition



### Spin Crossover or Spin Transition Electron-Transfer-Coupled Spin Transition



SQUID Magnetometer data analysis, CRPP, Bordeaux

#### **Magnetic Measurements: Thermal Quenching**





#### **Magnetic measurement in solution**





SQUID Magnetometer data, CRPP, Bordeaux

#### Magnetic measurement: crystals kept in the mother liquor



SQUID Magnetometer data, CRPP, Bordeaux

#### 1st Measurement: Irradiation vs Time



## 1st measurement: kinetic of the irradiation



# 2nd measurement: Relaxation of the photoinduced metastable state



## Depending upon the sample weight



Abhishake Mondal\_Thesis, 2013, UPMC-Paris-6

Photomagnetic measurement on a single crystal



size: 1.5 x 1.5 x 1 mm<sup>3</sup>, wt: 0.5 mg

Abhishake Mondal\_Thesis, 2013, UPMC-Paris-6

## Photomagnetic measurement on a single crystal



## Heating after irradiation: 0.5 K/min



SQUID Magnetometer data analysis, UPMC, Paris-6

# Light induced thermal hysteresis effects



Abhishake Mondal\_Thesis, 2013, UPMC-Paris-6

Inorg. Chem. **1998,** 37, 4432

### **Reverse Photomagnetism: OFF Mode**



Abhishake Mondal\_Thesis, 2013, UPMC-Paris-6

# On/off repeatable photo(magnetic) switch {Fe<sup>III</sup><sub>2</sub>-Co<sup>II</sup><sub>2</sub>} ⇔ {Fe<sup>III</sup><sub>2</sub>-Co<sup>III</sup><sub>2</sub>}



J. Am. Chem. Soc. 2013, 135, 1653

Abhishake Mondal\_Thesis, 2013, UPMC-Paris-6

#### **Other Measurement Techniques: Single-Crystal X-ray diffraction**

## On/off photo-switch : in a single crystal $Fe^{\parallel}_{2}-Co^{\parallel}_{2} \Leftrightarrow Fe^{\parallel}_{2}-Co^{\parallel}_{2}$



#### **Other Measurement Techniques: Reflectivity measurements**





#### AC susceptibility measurement using SQUID and PPMS

 $\chi = dM/dH$ 

 $B = B \downarrow 0 + B \downarrow 1 \cos(t)$ 

 $\chi = \chi' - i\chi''$ 

Superconducting Quantum Interference Device (SQUID)

**Real part** 

 $\chi \uparrow' = \chi \cos(\varphi)$ 

Reflects sensitivity of the material to H applied

Physical Properties Measurement System (PPMS)

**Imaginary part** 

$$\chi f'' = \chi \sin(\varphi)$$

Reflects dissipation, energy lost, absorption of energy

SQUID Magnetometer and PPMS Susceptometer, CRPP, Bordeaux

#### **AC Susceptibility**



Slide courtesy Dr. Hab. Rodolphe Clérac

#### AC measurement on SQUID – two points measurements



Two properties measured in AC mode  $M_{ac}$  and phase shift,  $\phi$ 

- M' (in phase) =  $M_{ac} \cos (\phi)$
- M "(out of phase)=  $M_{ac}$  Sin ( $\phi$ )
- $X' = X \cos (\phi)$  and  $X'' = X \sin (\phi)$

Slide Courtesy Dr. Yangling Li

800

AC signal extraction

#### AC susceptibility measurement using SQUID

● ● ● AM Ni2_a1.ac																					
	m o n	h ng .m l		<b>A</b> 'z	10 131																
	Time	Comment	Field (Oe)	Tempere	m' (emu)	m' Scad Dev	m" (emu)	m" Scd Dev	Amplit(emu	) Amplitd Dev	Phase (deg)	Phased Dev	Regression Fi	t Drivee (Oe	) Wavey (Hz	) Steps Cycle	Blocks	Scansemen	t Clockuenc	y Amplifier Gain	AC Filt
-		i ci		i Co	1.9	i G	LO	i cz		102	(CTA)		(CIZ)	ius.	1363.9	(LIS)	CID		((C18)		0.00
	1.45290+09		0.0000	15.005	6.0202e-06	4.9617e-08	-5.6042e-08	1.1511e-08	6.02040-06	4.9507e-08	-0.53336	0.11394	0.96086	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
1	1.4529e+09		0.0000	14.497	6.2862e-05	4.3870e-08	2.6738e-08	8.2096e-08	6.2862e-06	4.3520e-08	0.24370	0.74996	0.82088	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
2	1.4529e+09		0.0000	14.000	6.5657e-06	5.7577e-08	-9.6766e-08	4.4435e-08	6.5664e-06	5.8225e-08	-0.84436	0.38030	0.87671	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
3	1.4529e+09		0.0000	13.500	6.9017e-06	4.0601e-08	6.1174e-09	8.8077e-09	6.9017e-06	4.0593e-08	0.050785	0.073420	0.88425	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.0004
- 4	1.45296+09		0.0000	13.000	7.1537e-06	6.7430e-08	-1.35250-08	9.6713e-08	7.1537e-06	6.7611e-08	-0.10834	0.77360	0.68918	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
5	1.4529e+09		0.0000	12.501	7.6384e-05	1.5678e-07	-7.0424e-08	9.4412e-08	7.6388e-06	1.5764e-07	-0.52823	0.69749	0.89001	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
6	1.4529e+09		0.0000	11.999	8.1850e-06	3.4296e-08	4.1590e-08	1.4156e-07	8.1851e-06	3.3585e-08	0.29113	0.99209	0.90189	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
7	1.4529e+09		0.0000	11,500	8.5420e-06	6.7623e-09	-3.5339e-09	9.3255e-08	8.5420e-06	6.7334e-09	-0.023712	0.62551	0.91803	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
8	1.4529e+09		0.0000	11.001	9.0324e-06	3.6253e-08	-7.7692e-08	2.9697e-08	9.0328e-06	3.5996e-08	-0.49280	0.19033	0.91836	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.0001
9	1.4529e+09		0.0000	10.498	9.7175e-06	1.7631e-07	-3.4693e-08	1.1369e-08	9.7176e-06	1.7635e-07	-0.20456	0.063319	0.93118	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
19	1.4529e+09		0.0000	9.9999	1.0359e-05	1.2565e-07	-5.4337e-08	2.2464+-08	1.0359e-05	1.2577e-07	-0.30054	0.12061	0.93563	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
11	1.4529e+09		0.0000	9.4976	1.1055e-05	5.7623e-10	5.5024e-08	1.0417e-09	1.1055e-05	5.8137e-10	0.28518	0.0053843	0.94495	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
12	1.4529e+09		0.0000	8.9990	1.1892e-05	1.3152e-07	8.8929e-08	1.5605e-07	1.18920-05	1.3034e-07	0.42846	0.75658	0.95350	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
13	1.45290+09		0.0000	8.4986	1.27510-05	2.2075e=08	-6.9146e-08	2.9716e-09	1.2731e-05	2.2059e-08	-0.31119	0.013919	0.95998	3.0000	199.89	958.00	2.0000	2.0000	4.0000	1.0000	0.000
14	1.4529e+09		0.0000	8.0000	1.3905e-05	3.7013e-08	1.3327e-08	3.0660e-08	1.3905e-05	3.6983e-08	0.054916	0.12649	0.96488	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
15	1.4529e+09		0.0000	7.4986	1.5091e-05	7.5102e-09	2.8443e-08	3.4359e-08	1.5091e-05	7.5746e-09	0.10799	0.13040	0.96917	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
16	1.4529e+09		0.0000	6.9993	1.6262e-05	9.1913e-09	-8.1038e-08	1.0382e-07	1.6263e-05	9.71120-09	-0.28552	0.36559	0.97407	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
17	1.4529e+09		0.0000	6.4996	1.7902e-05	1.7768e-07	2.2250e-08	1.3317e-07	1.7902e-05	1.7785e-07	0.071212	0.42552	0.97906	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
18	1.4529e+09		0.0000	5.9998	1.9571e-05	3.2814e-06	-1.3570e-07	1.0927e-07	1.9571e-05	3.3571e-08	-0.39725	0.31922	0.98248	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
19	1.4529e+09		0.0000	5.4995	2.1474e-05	8.1841e-08	1.3219e-07	1.5059e-08	2.1474e-05	8.1747e-08	0.35270	0.041523	0.98396	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
20	1.4529e+09		0.0000	4.9995	2.4011e-05	1.8977e-07	6.0200e-08	3.2245e-08	2.4012e-05	1.8969e-07	0.14365	0.078080	0.98847	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
21	1.4529e+09		0.0000	4.4988	2.6836e-05	1.3486e-07	-9.8183e-08	4.2770e-08	2.6836e-05	1.3470e-07	-0.20963	0.092381	0.99012	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
22	1.4529e+09		0.0000	3.9970	3.0495e-05	8.1109e-09	7.1537e-08	7.1203e-10	3.0495e-05	8.1083e-09	0.13441	0.0013735	0.99191	3,0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
23	1.4529e+09		0.0000	3.4980	3.48668-05	1.2332e-07	4.6583e-07	9.3668e-09	3.4869e-05	1.2343e-07	0.76545	0.012683	0.99447	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
24	1,4529e+09		0.0000	2,9989	4.0105e-05	6.2557e-08	2.5631e-06	2.5030e-08	4.0187e-05	6.0833e-08	3.6567	0.041302	0.99571	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
25	1.45296+09	-	0.0000	2.5001	4.0716e-05	3.9950e-09	7.8396e-06	7.6535e-08	4.1464e-05	1.0545e-08	10.899	0.10489	0.99633	3.0000	199.89	938.00	2.0000	2.0000	4.0000	1.0000	0.000
26	1.4529e+09		0.0000	2 0000	3 7205e-05	1.1046e-08	7 1586e-06	9.0378e-08	3 7888e-05	2 79218-08	10.891	0.13106	0.99574	3.0000	199.89	938.00	2 0000	2 0000	4,0000	1.0000	0.000

#### SQUID Magnetometer data analysis, CRPP, Bordeaux

## **PPMS data treatment**

	0										AM Ni2_B1										
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1	Comment	Time S	Tempere	Magned	Frequy (Hz)	Amplie (Oe) M	4-DC (emu)	M-Std(emu)	M' (emu)	M"' (emu)	Moment (emu)	Phase (deg)	Calcoil' (emu)	Calcoil" (emu)	Calcoil (emu)	CC Ph (deg)	Count	Gain	Measure Type	Elapsed (sec	) Samplr (c
		3.2937e+07	15.004	0.037000	1000.0	9.9994	T	0.082311		1	1		1	1		1	1	125.00	1.0000	0.0000	-0.29313
1		3 29378+07	15.013	0.037000	10.000	6.0013		31272e-07	1.3181e-05	9.7036e-07	1.3217e-05	4,210.4	1.4928e-08	2.2305e-11	1.4928e-08	0.085611	3200.0	5.0000	5.0000	13,497	-0.29313
2		3.2937e+07	15.014	0.037000	30.000	6.0013		2.7670e-07	1.4040e-05	-1.2801e-07	1.4040e-05	-0.52240	1.4922e-08	5.9940e-12	1.4922e-08	0.023016	4800.0	5.0000	5.0000	13,497	-0.29313
3		3.2937e+07	15.012	0.037000	60.000	6.0012		7.7553e-08	1.4004e-05	-9.7183e-09	1.4004e-05	-0.039761	1.4929e-08	1.3918e-13	1.4929e-08	0.00053414	4800.0	5.0000	5.0000	13.497	-0.29313
4		3.2937e+07	15.009	0.037000	100.00	6.0012		4.9844e-08	1.4019e-05	-1.3385e-07	1.4020e-05	-0.54703	1.4932e-08	-1.1339e-11	1.4932e-08	-0.043510	4000.0	5.0000	5.0000	13.497	-0.29313
5		3.2937e+07	15.008	0.037000	150.00	6.0011		2.1754e-08	1.3610e-05	-1.8560e-07	1.3612e-05	-0.78127	1.4925e-08	-3.2536e-11	1.4925e-08	-0.12490	6000.0	5.0000	5.0000	13.497	-0.29313
6		3.2937e+07	15.007	0.037000	200.00	6.0010		1.9351e-08	1.4035e-05	2.1641e-08	1.4035e-05	0.088350	1.4925e-08	-4.7864e-11	1.4925e-08	-0.18375	4000.0	5.0000	5.0000	13.497	-0.29313
7		3.2938+07	15.007	0.037000	300.00	6.0007		2.2447e-08	1.4010e-05	-1.8482e-09	1.4010e-05	-0.0075583	1.4925e-08	-7.9101e-11	1.4925e-08	-0.30367	6000.0	5.0000	5.0000	13.497	-0.29313
8		3.2938+07	15.006	0.037000	400.00	6.0002		1.0912e-08	1.3943e-05	5.3320e-08	1.3943e-05	0.21911	1.4926e-08	-1.0872e-10	1.49276-08	-0.41734	4000.0	5.0000	5.0000	13.497	-0.29313
9		3.2938e+07	15.006	0.037000	600.00	5.9989		1.2257e-08	1.3975e-05	1.3184+-08	1.3975e-05	0.054053	1.4935e-08	-1.7010e-10	1.4936e-08	-0.65255	6000.0	5.0000	5.0000	13.497	-0.29313
10		3.2938+07	15.005	0.037000	800.00	6.0012		6.0471e-09	1.3972e-05	1.9419e-08	1.39726-05	0.079636	1.4941e-08	-2.3193e-10	1.4943e-08	-0.88933	2666.0	5.0000	5.0000	13.497	-0.29313
11	-	3.2938e+07	15.006	0.037000	1000.0	5.9988		6.6535e-09	1.3941e-05	5.6084e-08	1.3941e-05	0.23049	1.4946e-08	-2.9487e-10	1.4949e-08	-1.1302	3333.0	5.0000	5.0000	13.497	-0.29313
12	-	3.2938e+07	15.004	0.037000	1200.0	2.9979		1.0892e-08	6.9508e-06	5.4902e-08	6.9510e-06	0.45255	1.4924e-08	-3.6791e-10	1.4928e-08	-1.4122	4000.0	5.0000	5.0000	13.497	-0.29313
13		3.2938e+07	15.004	0.037000	1500.0	2.9994		8.2410e-09	6.9698e-06	1.6602e-08	6.9698e-06	0.13648	1.4924e-08	-4.6425e-10	1.4931e-08	-1.7818	5000.0	5.0000	5.0000	13.497	-0.29313
14		3.2938+07	15.004	0.037000	2000.0	3.0019		6.7756e-09	6.9631e-06	2.4793e-08	6.9631e-06	0.20401	1.4919e-08	-6.2470e-10	1.4932e-08	-2.3977	4000.0	5.0000	5.0000	13.497	-0.29313
15		3.2938+07	15.005	0.037000	3000.0	3.0020		6.4149e-09	6.9491e-06	3.3770e-08	6.9492e-06	0.27843	1.4906e-08	-9.4562e-10	1.4936e-08	-3.6300	6000.0	5.0000	5.0000	13.497	-0.29313
16		3.2938++07	15.004	0.037000	4000.0	2.9999		4.4454e-09	6.9273e-06	2.5859e-08	6.9273e-06	0.21388	1.4886e-08	-1.2641e-09	1.4940e-08	- 4.8536	5714.0	5.0000	5.0000	13.497	-0.29313
17		3.2938+07	15.003	0.037000	5000.0	0.99989		4.1146e-09	2.3069e-06	3.3642e-09	2.3069e-06	0.083555	1.4863e-08	-1.5869e-09	1.4948e-08	-6.0940	4545.0	5.0000	5.0000	13.497	-0.29313
18		3.2938e+07	15.003	0.037000	6000.0	1.0005		5.0114e-09	2.3109e-06	-7.7236e-09	2.3109e-06	-0.19150	1.4837e-08	-1.9044e-09	1.4959e-08	-7.3142	5454.0	5.0000	5.0000	13.497	-0.29313
19		3.2938+07	15.003	0.037000	8000.0	1.0000		1.4844e-09	2.3058e-06	-7.5598e-09	2.3058e-06	-0.18785	1.4781e-08	-2.5261e-09	1.4995e-88	-9.6982	6153.0	5.0000	5.0000	13.497	-0.29313
20		3.2939+07	15.001	0.037000	10000	1.0004		1.9217e-09	2.3018e-06	-1.5635e-08	2.3019e-06	-0.38917	1.4711e-08	-3.1691e-09	1.5049e-08	-12.157	5882.0	5.0000	5.0000	13.497	-0.29313
21		3.2939+07	14.007	0.037000	10.000	6.0013		4.9950e-07	1.5471e-05	-6.9448e-07	1.5487e-05	-2.5702	1.4903e-08	1.5635e-11	1.4903e-08	0.060110	3200.0	5.0000	5.0000	13.497	-0.29313
22		3.2939e+07	14.008	0.037000	30.000	6.0013		3.5684e-07	1.5318e-05	-2.3782e-08	1.5318e-05	-0.088957	1.4921e-DB	8.2645e-12	1.4921e-08	0.031735	4800.0	5.0000	5.0000	13.497	-0.29313
23		3.2939#+07	14.009	0.037000	60.000	6.0012		8.8672e-08	1.5384e-05	4.2570+-08	1.5384e-05	0.15854	1.4931e-08	-7.2444e-13	1.4931e-08	-0.0027800	4800.0	5.0000	5.0000	13.497	-0.29313
24		3.2939++07	14.010	0.037000	100.00	6.0012		2.3721e-08	1.5306e-05	6.0380e-08	1.5306e-05	0.22603	1.4932e-08	-1.1422e-11	1.4932e-08	-0.043828	4000.0	5.0000	5.0000	13.497	-0.29313
25		3.2939e+07	14.010	0.037000	150.00	6.0011		2.0029e-08	1.5364e-05	2.9322e-08	1.5364e-05	0.10935	1.4924e-08	- 3.2084e-11	1.49246-08	-0.12318	6000.0	5.0000	5.0000	13.497	-0.29313
26		3.2939e+07	14.009	0.037000	200.00	6.0010		2.1429e-08	1.5379e-05	1.6630e-08	1.5379e-05	0.061957	1.4925e-08	-4.7626e-11	1.49268-08	-0.18282	4000.0	5.0000	5.0000	13.497	-0.29313
27		3.29396+07	14.009	0.037000	300.00	6.0007		2.7606e-08	1.5363e-05	1.3833e-08	1.5363e-05	0.051591	1.4925e-08	-7.9114e-11	1.4925e-08	-0.30371	6000.0	5.0000	5.0000	13.497	-0.29313
28	-	3.2939++07	14.009	0.037000	400.00	6.0002		1.6951e-08	1.5356e-05	1.1159e-08	1.5356e-05	0.041635	1.4927e-08	-1.0874e-10	1.4927e-08	-0.41736	4000.0	5.0000	5.0000	13.497	-0.29313
29	-	3.2940++07	14.009	0.037000	600.00	5.9989		1.6185e-08	1.5334e-05	2.9843+-08	1.5334e-05	0.11151	1.4935e-08	-1.7009e-10	1.4936e-08	-0.65246	6000.0	5.0000	5.0000	13.497	-0.29313

#### PPMS Susceptometer AC data, CRPP, Bordeaux



Slide courtesy Dr. Hab. Rodolphe Clérac



Slide courtesy Dr. Hab. Rodolphe Clérac





Slide courtesy Dr. Hab. Rodolphe Clérac
#### **AC susceptibility measurement**



$$\chi' = \frac{(\chi_{\rm isoT} - \chi_{\rm adia}) \left( (2 \pi)^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right) (\nu \tau)^{1-\alpha} + 1 \right)}{(2 \pi)^{2-2\alpha} (\nu \tau)^{2-2\alpha} + 2^{2-\alpha} \pi^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right) (\nu \tau)^{1-\alpha} + 1} + \chi_{\rm adia} \quad \chi'' = \frac{(2 \pi)^{1-\alpha} \cos\left(\frac{\pi \alpha}{2}\right) (\nu \tau)^{1-\alpha} (\chi_{\rm isoT} - \chi_{\rm adia})}{(2 \pi)^{2-2\alpha} (\nu \tau)^{2-2\alpha} + 2^{2-\alpha} \pi^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right) (\nu \tau)^{1-\alpha} + 1}$$

#### Fitting all data with generalized Debye model for each temperature

## **AC susceptibility measurement**

#### **Cole-Cole fittings**



Т (К)	а	<b>C</b> <sub>0</sub>	C <sub>inf</sub>
3.5	0.29047	7.2219	4.7438
4.0	0.32745	6.2401	3.918
4.5	0.29051	5.4031	3.4138
5.0	0.25752	4.7544	3.0251
5.5	0.21007	4.2307	2.7428
6.0	0.15537	3.8083	2.5375
6.5	0.094651	3.4630	2.3897
7.0	0.0705	3.1842	2.2393
7.5	0.11309	2.9616	2.0441

Generalized Debye fits (solid lines) of the Cole-Cole experimental plots for a polycrystalline sample at 0 Oe at different temperatures.



Horizontal Sample Rotator for MPMS

#### Using a Single Crystal



Perspective view (left) and side view (right) of a typical single crystal of  $PPh_4[Fe(Tp)(CN)_3] \cdot H_2O$  together with selected crystallographic axes and directions.

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Fe<sup>3+</sup> magnetic susceptibility ellipsoid obtained from PND within its coordination octahedron at 2 K. The local easy magnetization axis ( $\chi_1$ ) is nearly parallel to the  $\chi_3$ pseudo-axis (in red) of the molecule.





EPR spectra recorded at 9.42 GHz (X-band) on a powder sample of  $PPh_4[Fe{Tp}(CN)_3]$  in the temperature range [5-50 K].





View of the magnetic ellipsoid in projection along the magnetic axis  $\chi_1$ .

## 

Magnetic axes of the crystal  $\chi_{m1}$ ,  $\chi_{m2}$  and  $\chi_{m3}$ , determined by PND at 2 K, in the monoclinic crystallographic basis set ( $\beta = 100,34^{\circ}, \phi_1 = 1,8^{\circ}$  et  $\phi_3 = 91,8^{\circ}$ ).

#### **Using a Single Crystal**



Magnetic susceptibility as a function of the rotation angle around an axis perpendicular to **a**-axis and [0,1,1] directions (at 2 K and 5 K, under 1 T). The  $\phi = 0$  angle corresponds to an orientation where the **a**-axis is parallel to the applied magnetic field.

**Using a Single Crystal** 



Magnetization curves at 2 K for three directions of the applied magnetic field **B**, in the range [0-7 T].

# THANK YOU FOR YOUR ATTENTION

## In life, nothing should be feared

everything is to be understood ...

Marie Curie