From ferrimagnetic to spin glass behavior and back in lamellar Mn oxides undoped and doped with Co

Andrés Rosales Rivera (arosalesr@unal.edu.co)
Departamento de Física y Química
Laboratorio de Magnetismo y Materiales Avanzados
Universidad Nacional de Colombia, Sede Manizales, Colombia

5th Workshop on Statistical Physics-UN-UniAndes-Abril 2026 Bogotá, Colombia

This work is made in collaboration with the Profs:

Oscar Giraldo,
UN, Sede Manizales
Manizales, Colombia

Mónica Gómez
Universidad Católica de Pereira
Pereira, Colombia

Nayda Arias
USACA, Cali
Colombia

Diego Muraca
Unicamp, Campinas, SP
Brasil

Plan

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Background: Weiss’ Magneton – Néel – Controversy – Ferrimagnetism of two sub-lattices (Néel) – Spin Glass –Frustrate Antiferromagnets of more of two sub-lattices (J. R. López de Almeida),

Possible reconciliation Inverse Susceptibility Curve -Weiss´ Magneton - Ferrimagnetism of more of two sub-lattices?

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Introduction-Background-Motivation

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Lamellar Mn Oxides

Synthesis

Characterization: Structural, Chemical, Thermal, Magnetic

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Results, Discussion, Interpretation

Summary, Comments no Conclusions, Perspectives

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Acknowledgements

Introduction – Background - Motivation

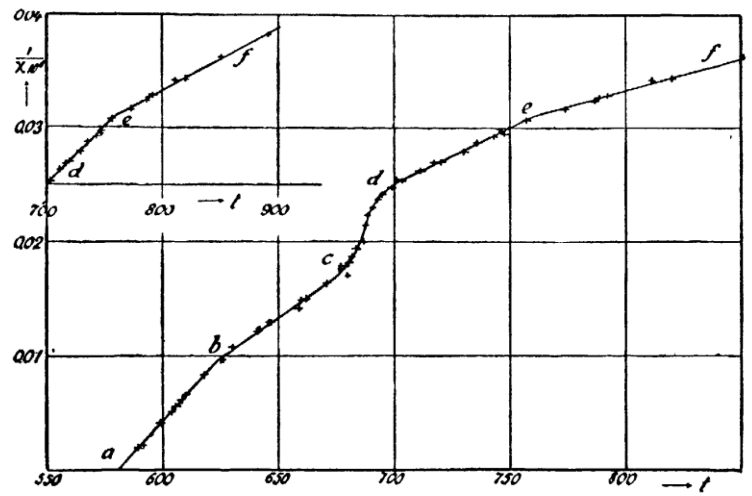
Weiss' Magneton: The Sin of Pride or a Venial Mistake?
Pierre Quédec. http://www.jstor.org/stable/27757606 .

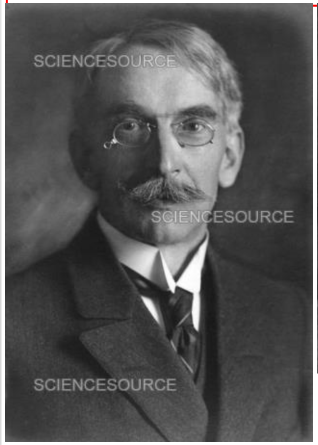
P. Weiss: **CR, 152 (1911), 367-369. 3:**
$\boldsymbol{\chi^{-1}}$ ***vs. T*** curve (inverse susceptibility) on several different materials, and to postulate the existence of an elementary quantity called the Weiss magneton.

Curie law: **χ = C/*T*, C is the Curie constant**

P. Langevin: **C∝ μ², μ** shares units with the magnetic moment but does not represent an intrinsic magnetic moment. (Annales de chimie et de physique, 8:5 (1905), 70-127)

P. Weiss (1911)*: $\boldsymbol{\chi^{-1}}$ vs. *T curve of different materials at high temperature splits into distinct straight line segments, each corresponding to a substantial temperature interval. From slope of these straight lines, Weiss determined a different value for ***C and thus for μ (Weiss´ magneton):*** **HIGHLY CONTROVERSIAL INTERPRETATION¡¡¡**
P. Weiss: CR, 152 (1911), 367-369. 3. P. Weiss, phys., 5:1 (1911), 900-912, 965-988.





Pierre Weiss

Louis Neel

L. Néel (1948):
shows that the curve of the inverse susceptibility versus temperature is continuous and smooth one, rather than a series of several straight lines as earlier interpreted by Weiss (1911).

Néel:
Ferrimagnetism
Two sublattices
Eq. (1)

$$\frac{1}{\chi} = \frac{T + \left(\frac{C}{\chi_0}\right)}{C} - \frac{b}{T - \theta_f}$$

J. R. L. de Almeida. Eur. Phys. J. B 13, 289{295 (2000). Strongly frustrated random antiferromagnets. Antiferromagnetic structures of more of two sublattices. A high dimensionality calculation (Weiss like) has been carried out for antiferromagnetism(AFM) in structures with many sublattices. By allowing quenched disorder in the exchange interactions our results clearly exhibit the interplay between the effects of lattice frustration and disorder on the system's properties.

Introduction – Background – Motivation

Some characteristics

Octahedron: MO_6

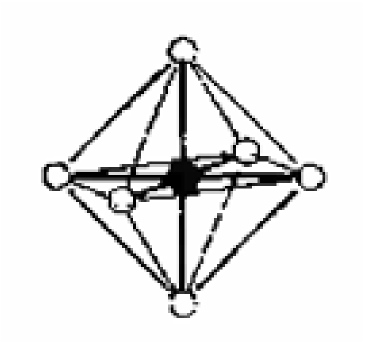
Sheets: MO_2

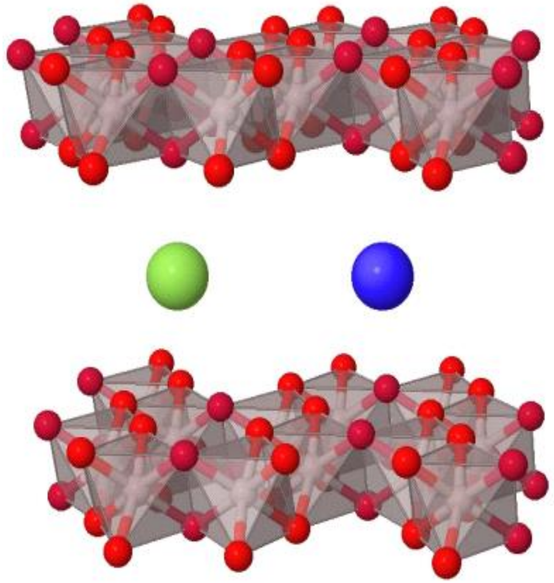
M: Ion metal in octahedral site (Mn,Co) ●

A = Na, K 🟢

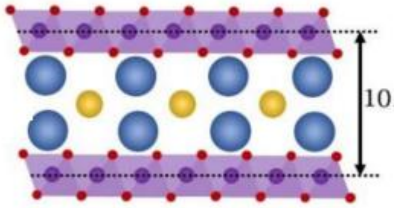
Oxigen: 🔴

H_2O: 🔵

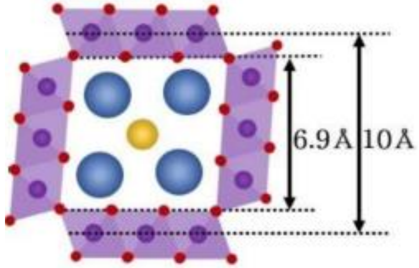




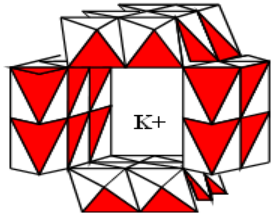
Lamellar Mn oxides



Buserite



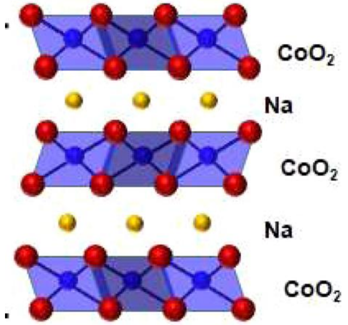
Todorokite

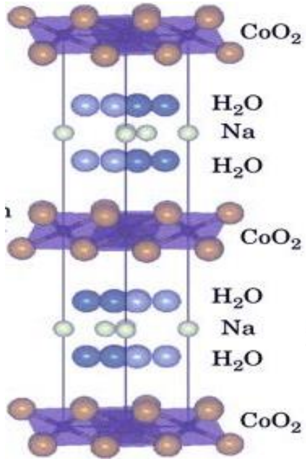


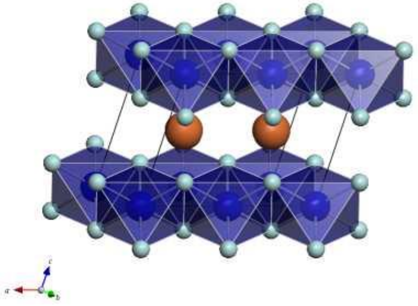
Cryptomelane

- ✓ Mn oxides: mixed valency: Mn can exist in more than one oxidation state
- ✓ MnO, Mn_2O_3 – antiferromagnetism – superexchange interaction
- ✓ Mn^{+3}, Mn^{+4} – ferromagnetism – double exchange interaction
- ✓ H_2O, Na, K: (electrical charge compensation)
- ✓ Crystalline defects
- ✓ Distinctive physicochemical properties
- ✓ High modification capacity
- ✓ Many applications (particle size and structure): primary batteries, recharge batteries, supercapacitors, sensors, spintronics

Lamellar Co oxides







Synthesis of compounds (samples)

Synthesis: soft chemical		
Compound	**Co/Mn molar ratio**	**Description - lamellar**
OL-Mg	0.000	Manganese oxide synthesized with magnesium salt
OL	0.000	Manganese oxide synthesized without magnesium salt
OL-1	0.014	Manganese oxide synthesized with cobalt salt
OL-2	0.037	Manganese oxide synthesized with cobalt salt
OL-3	0.057	Manganese oxide synthesized with cobalt salt
OL-4	0.074	Manganese oxide synthesized with cobalt salt
OL-5	0.096	Manganese oxide synthesized with cobalt salt

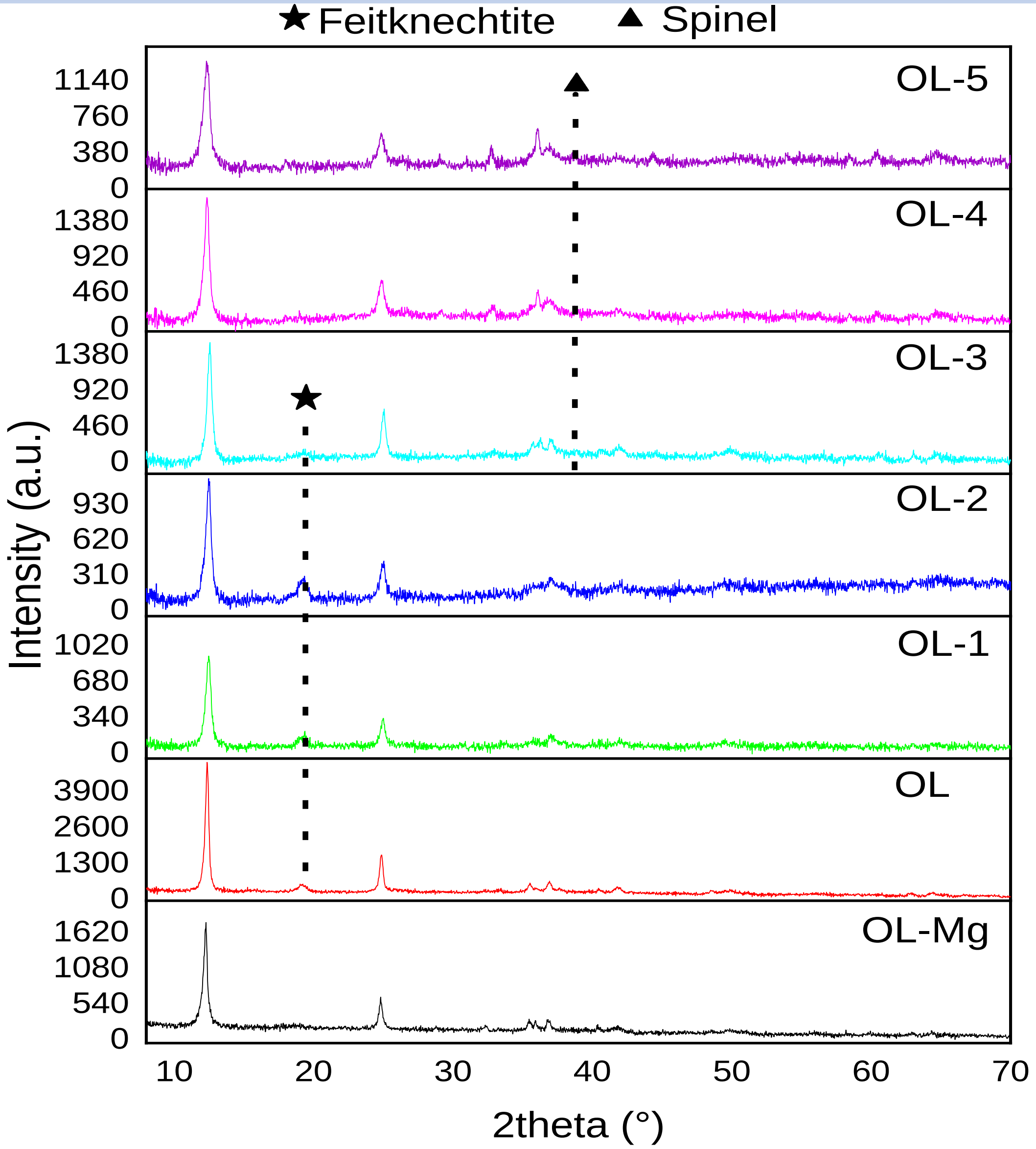
XRD - estructural characterization – main structure: birnessite

Synthesis: soft chemical				
Compound	**Peak**	**Interlamellar distance (Å)**	**FWHM**	**Crystal size (nm)**
OL-Mg	12.229	7.232	0.339	24.635
OL	12.345	7.164	0.282	29.618
OL-1	12.445	7.107	0.439	19.027
OL-2	12.269	7.208	0.463	18.038
OL-3	12.535	7.056	0.393	21.256
OL-4	12.337	7.169	0.424	19.698
OL-5	12.313	7.182	0.587	14.228

Note:
Main peak at 2theta ≅ 12 (°): main phase – birnessite phase

Secondary peaks at:
2theta ≅ 20 (°): feitknechtite phase (compounds: OL, OL-1, OL-2)
2theta ≅ 39 (°): spinel phase (compound OL-5)

Compound OL-Mg (stable compound): absence of peak at 2theta ≅ 20 (°) implies absence of the feitknechtite phase (β – MnOOH), this phase tends to degrade the thermal stability of the compound.



Chemical and thermal analysis - AAS, potentiometric titration, TGA experiments

AAS: Atomic Absorption Spectroscopy

Compound	Metal content (% weight)					Molar ratio Mg/Mn	Molar ratio Na/(Mn+Co)	Molar ratio K/(Mn+Co)	Molar ratio Co/Mn	AOS Mn
	Mn	Mg	Na	K	Co					
OL-Mg	49.1	1.3	1.8	0.0	0.0	0.058	0.087	0.001	0.000	3.73
OL	55.6	0.0	1.9	0.0	0.0	0.000	0.083	0.000	0.000	3.71
OL-1	48.6	0.0	1.4	0.1	0.7	0.000	0.069	0.002	0.014	3.71
OL-2	47.6	0.0	1.4	0.1	1.9	0.000	0.066	0.002	0.037	3.70
OL-3	42.6	0.0	1.3	0.0	2.6	0.000	0.067	0.001	0.057	3.69
OL-4	41.4	0.0	1.3	0.1	3.3	0.000	0.067	0.001	0.074	3.68
OL-5	40.9	0.0	1.4	0.0	4.2	0.000	0.063	0.001	0.096	3.65

Chemical and magnetic analysis

Compound	Structural formula	T_i(K)	θ_f(K)	C (emu·K/g)	C/χ_0 (K)	μ_{eff}/μ_B Exp	μ_{eff}/μ_B Teo
OL-Mg	$Na_{0.087}Mg_{0.058}Mn^{4+}_{0.73}Mn^{3+}_{0.27}O_2\cdot0.31H_2O$	34.25	34.10	0.02545	-53.11	4.16	4.17
OL	$Na_{0.083}Mn^{4+}_{0.71}Mn^{3+}_{0.29}O_2\cdot0.25H_2O$	34.22	34.19	0.02069	-60.19	3.75	3.60
OL-1	$Na_{0.069}(Co_{0.014}Mn^{4+}_{0.700}Mn^{3+}_{0.286})O_2\cdot0.31H_2O$	65.20	61.63	0.02489	-77.15	4.03	3.61
OL-2	$Na_{0.066}(Co_{0.037}\ (Mn^{4+}_{0.674}Mn^{3+}_{0.289})O_2\cdot0.25H_2O$	80.22	54.95	0.02522	-70.70	3.48	3.65
OL-3	$Na_{0.067}(Co_{0.057}\ Mn^{4+}_{0.651}Mn^{3+}_{0.292})O_2\cdot0.28H_2O$	72.77	70.22	0.03032	-56.39	3.77	3.67
OL-4	$Na_{0.067}(Co_{0.074}\ Mn^{4+}_{0.630}Mn^{3+}_{0.296})O_2\cdot0.46H_2O$	76.74	66.97	0.05458	-45.78	3.49	3.69
OL-5	$Na_{0.063}(Co_{0.096}\ Mn^{4+}_{0.588}Mn^{3+}_{0.316})O_2\cdot0.15H_2O$	70.20	66.03	0.04922	-37.95	3.23	3.63

AAS, TGA, and potentiometric titration experiments

For sample OL (undoped) AOS = 3.71 indicates:

The presence of both Mn^{3+} and Mn^{4+} ions, with concentration of Mn^{4+} ion > Mn^{3+} ion. An excess of Mn^{4+} ions in the MnO_6 octahedral sites. Ferrimagnetic structure with two sublattices. Main structural state: Feitknechtite

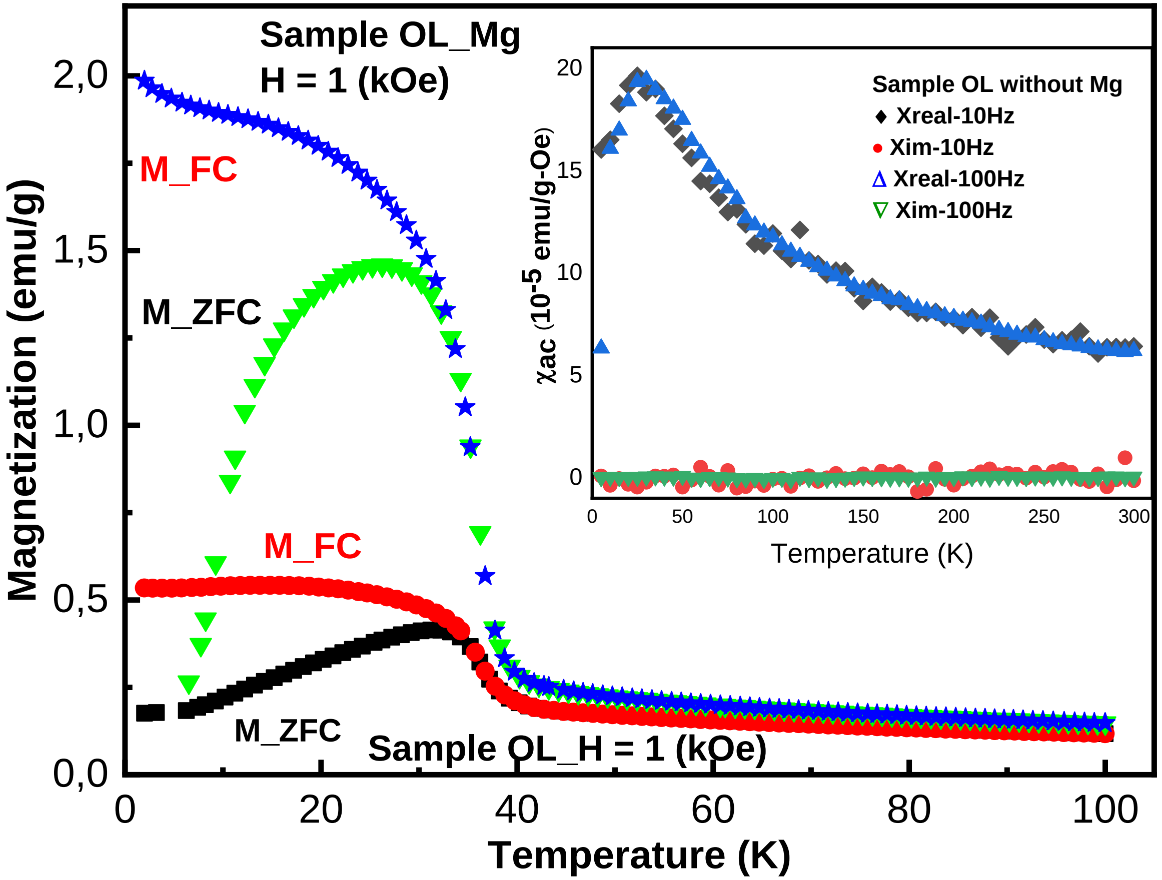
For samples doped (introduction of Co): both the AOS of the Mn ion and (Mn^{4+}/Mn^{3+}) molar ratio decrease slightly with increasing Co content, with concentration of Mn^{4+} ion ≥ (≅) concentration of Mn^{4+} ion. Mn^{3+} {[Ar]3d^{4} : S = 4]}; Mn4^{+} {[Ar]3d^{3} : S = 3]; Co^{3+} {[Ar]3d^{6} : S = 4}.

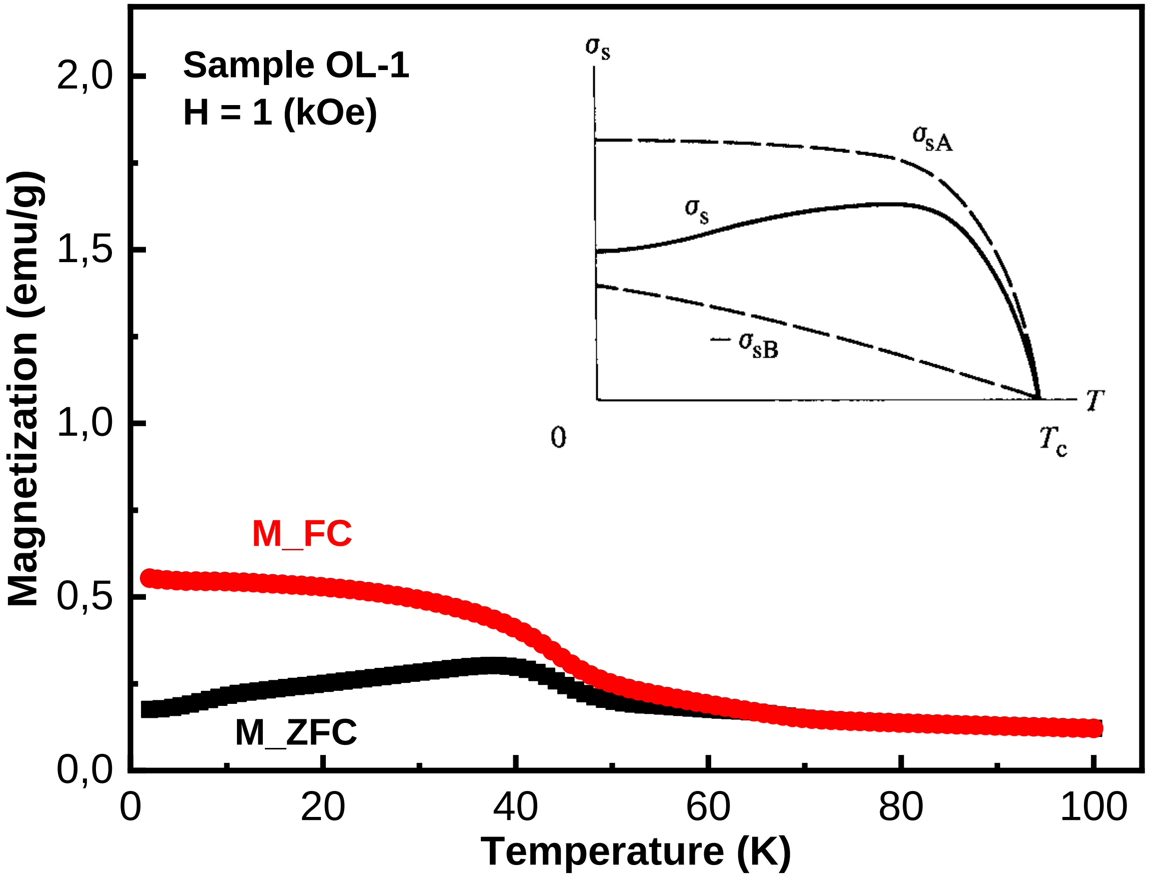
The interlayer Na ion concentration is higher in the OL sample than in the samples doped with Co.
No correlation was observed between increasing the Co and Na content, while the Mn ion concentration decreases as the Co ion concentration increases.

For sample OL-1: These results suggest that a fraction *x* of Mn^{4+} ion is initially replaced by a corresponding fraction *x* of Co^{3+} ion due to the initial excess of Mn^{4+} ion, with Co likely existing as a trivalent ion. This substitution is feasible since the coordination radius of low-spin Co^{3+} ion (0.61 Å) is very close to that of Mn^{4+} ion (0.62 Å), and the crystal field stabilization energy for Co^{3+} in octahedral coordination is higher than that of Mn^{4+} in the same coordination environment, which implies that low-spin Co^{3+} is more stable in an octahedral environment [13]–[14].

The introduction of the Co ion enhances the FM double exchange interaction, that together with the AF superexchange interaction, can to introduce frustration into the system opening possibilities that drastic changes in the magnetic behavior of the system occurs.

Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co





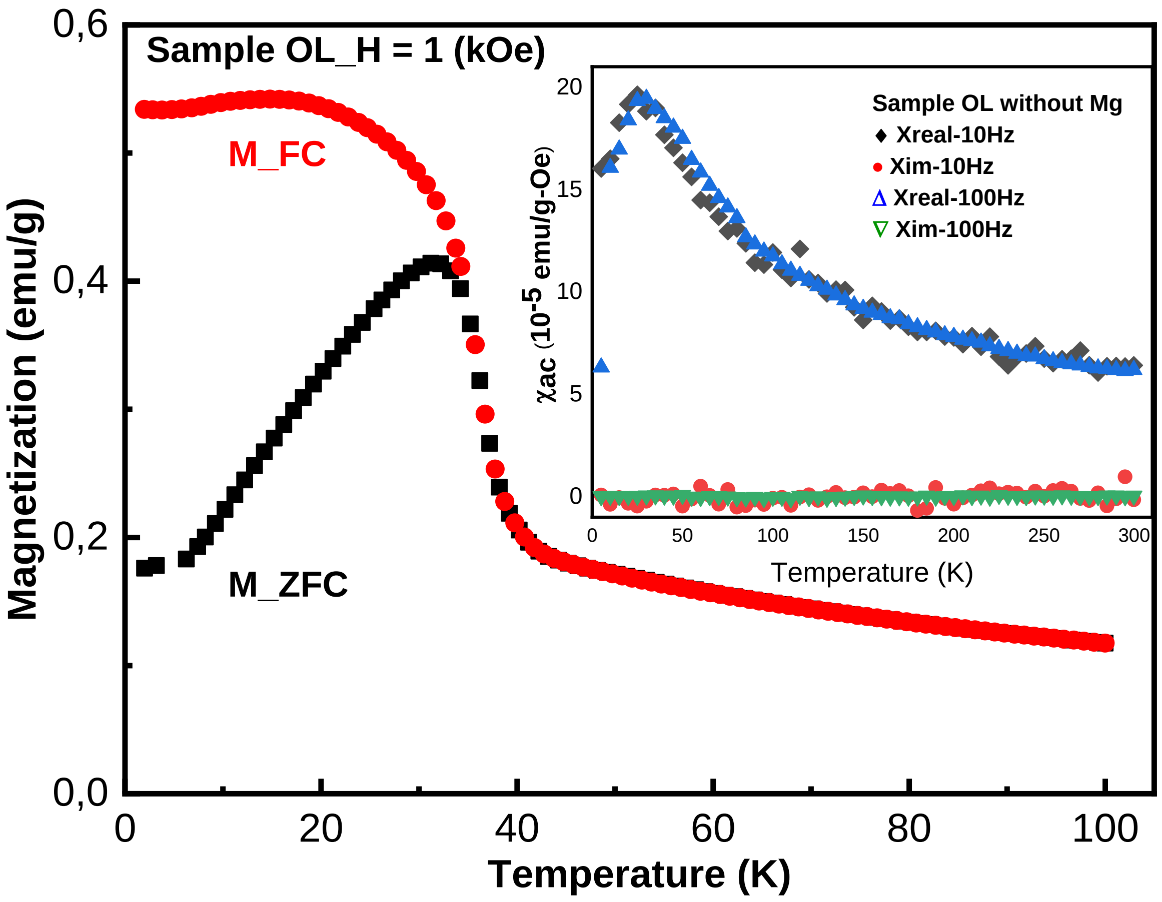
Sample OL

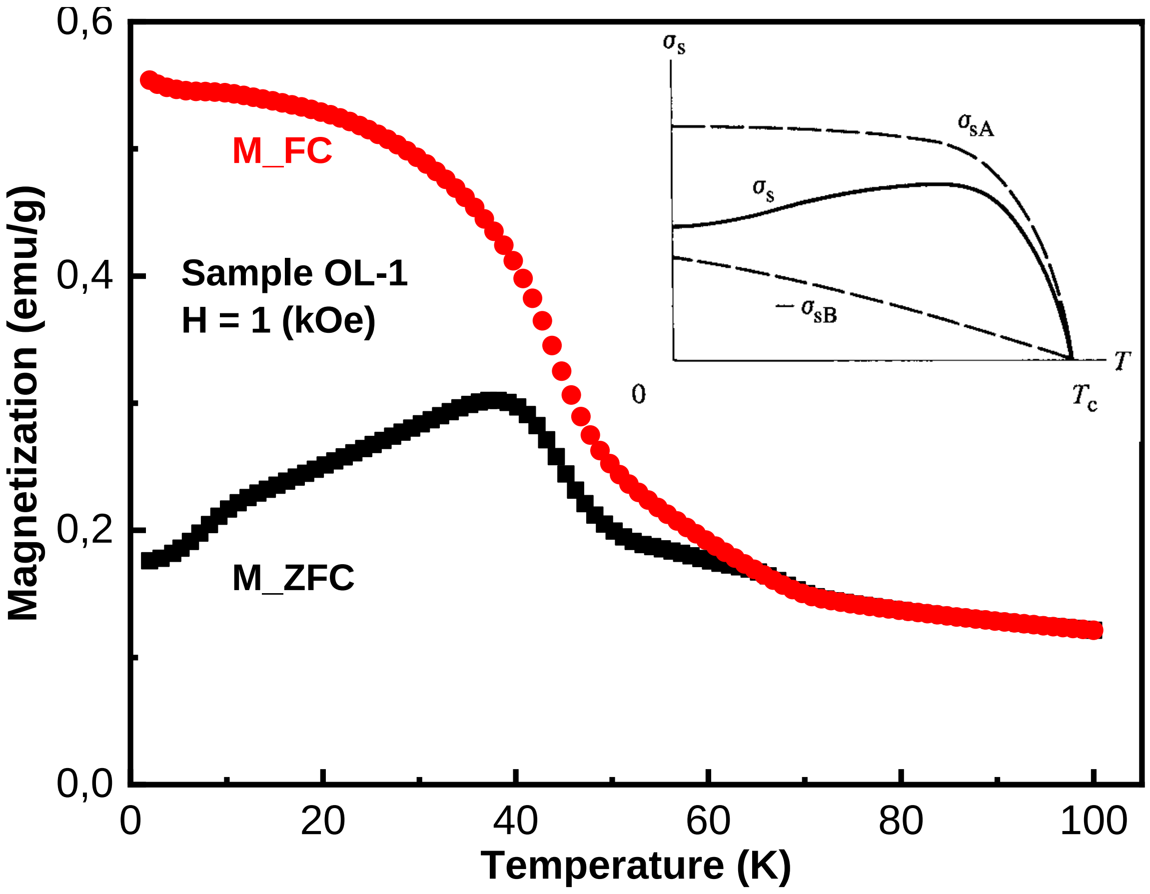
T_C (H = 0) = 30 ± 0.5 K

T_p (H = 1 kOe) = 29.84 ± 0.5 K

Insert adapted from Cullity

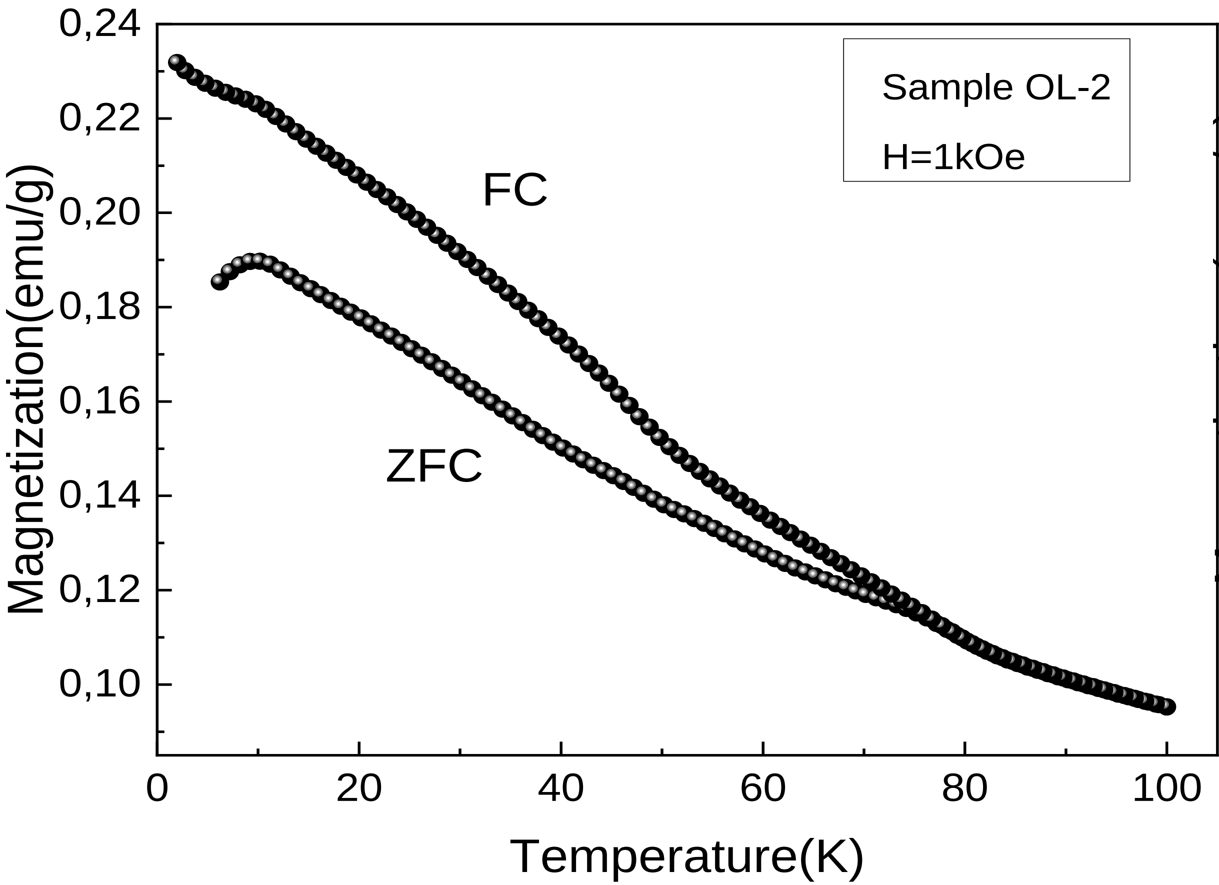
Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co

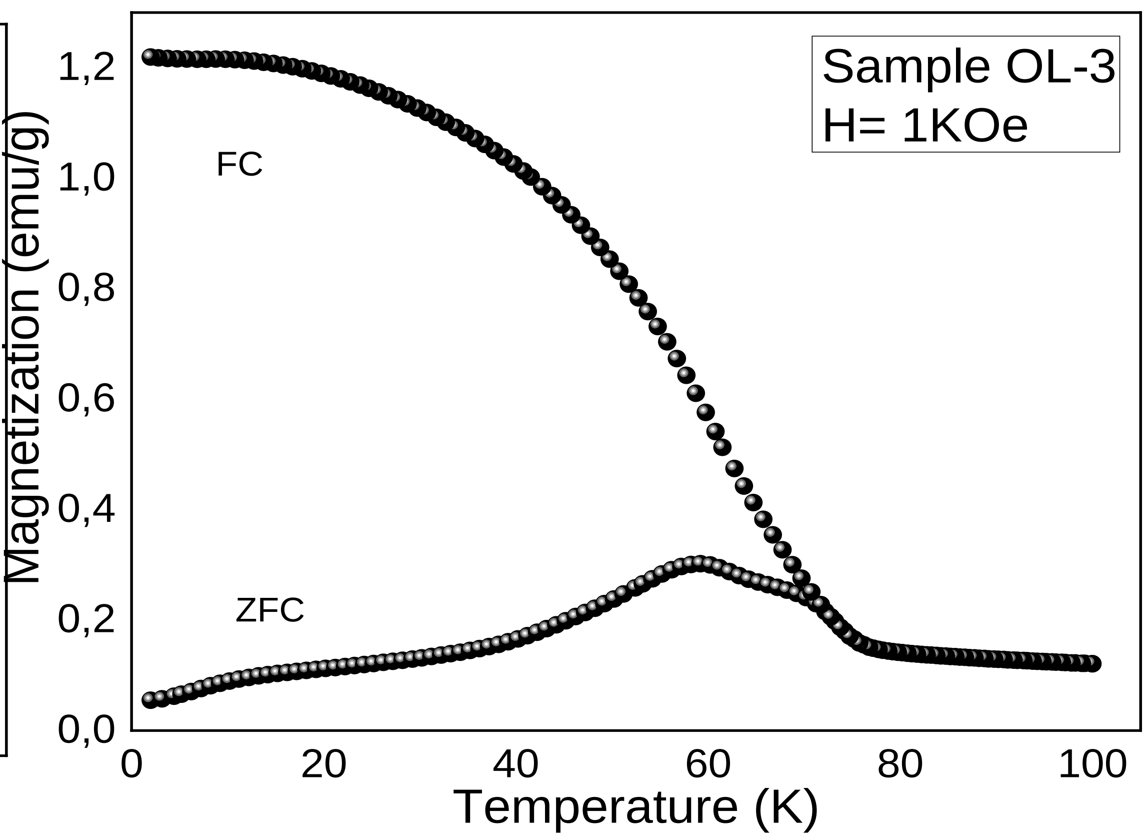




Sample OL
T_C (H = 0) = 30 ± 0.5 K
θ_p (H = 1 kOe) = 29.84 ± 0.5 K, this value for θ_p agree quite well with the value obtained independently from zero field ac susceptibility measurement for f = $2\pi/\omega$ = 10 and100 Hz of T_C(H = 0) = 30 ± 0.5 K.

Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co





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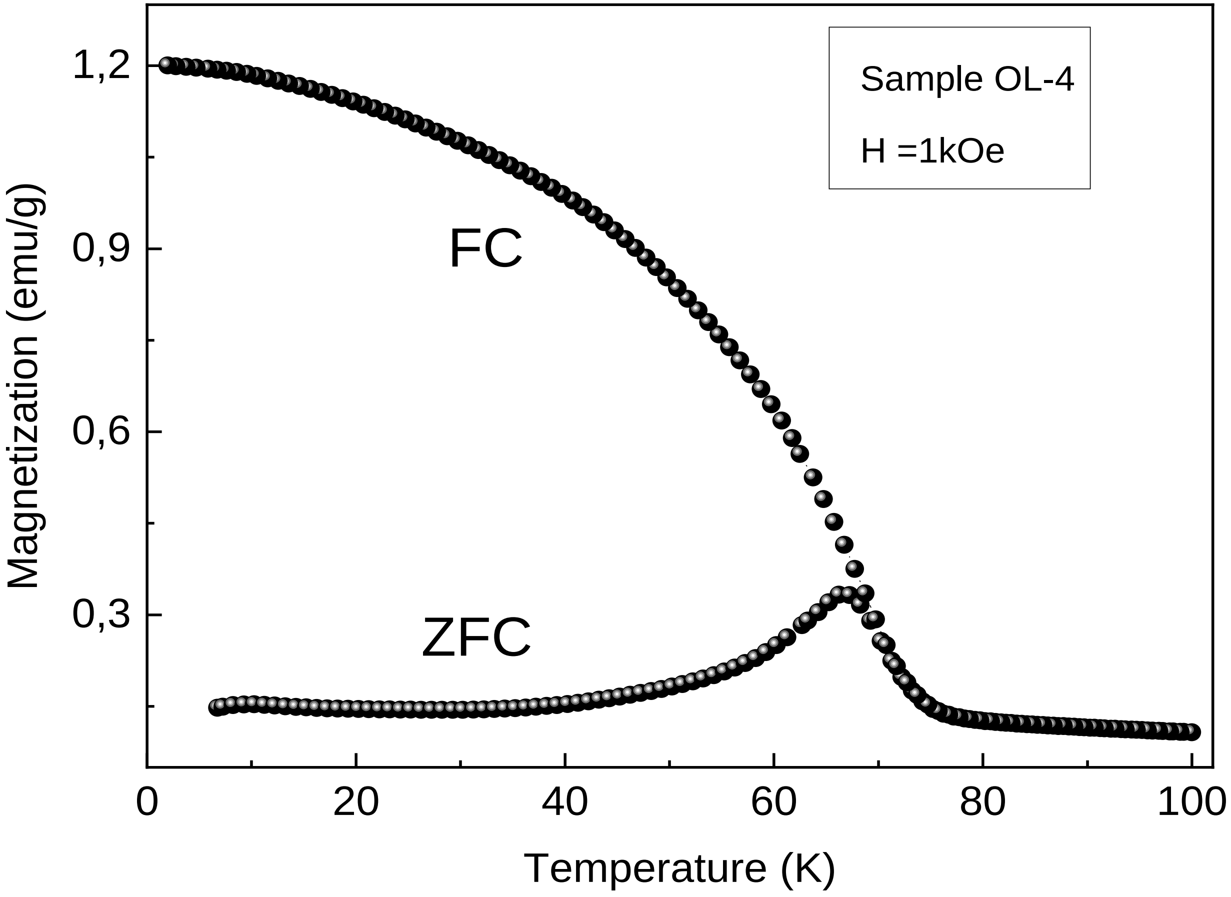
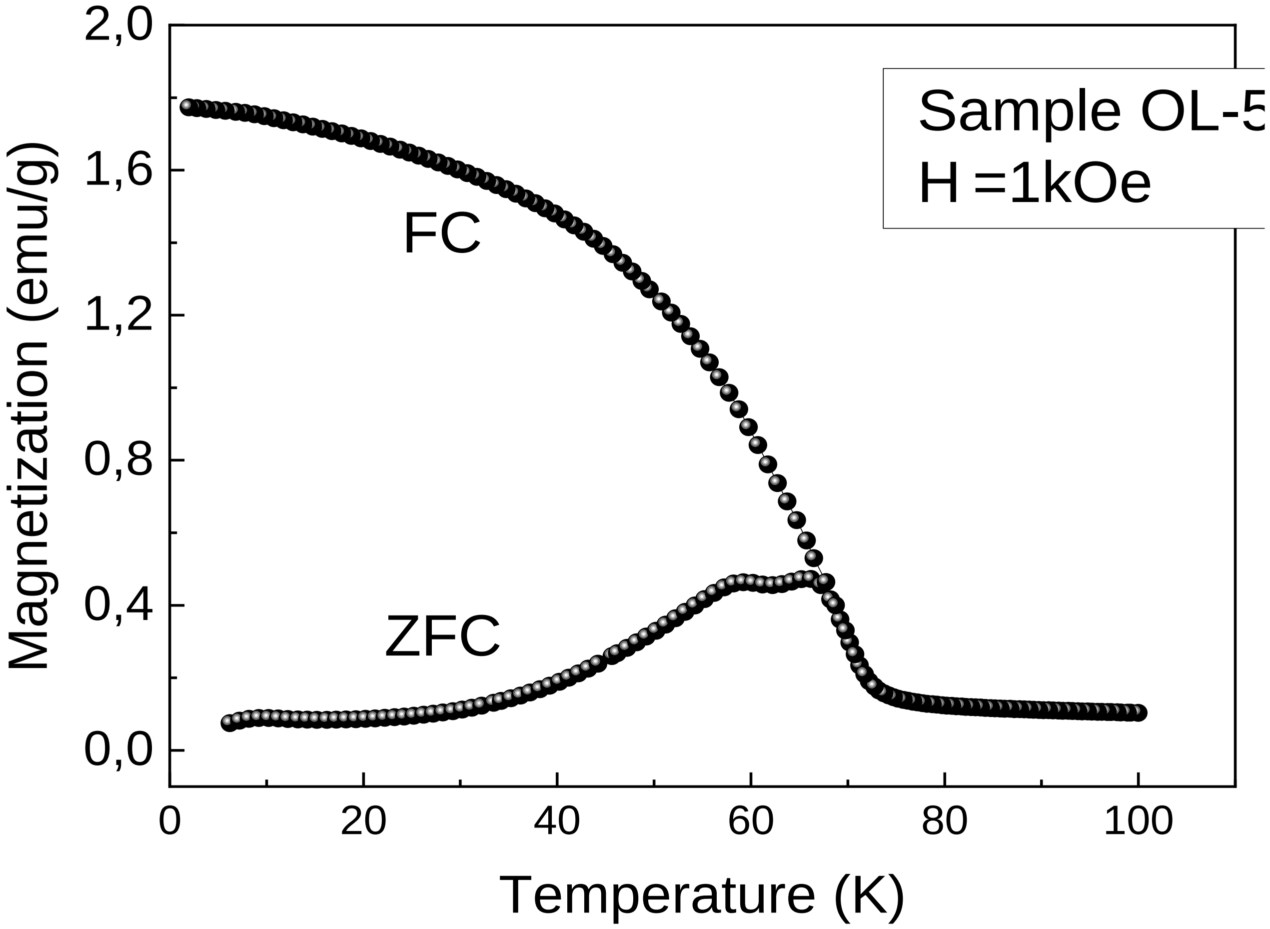
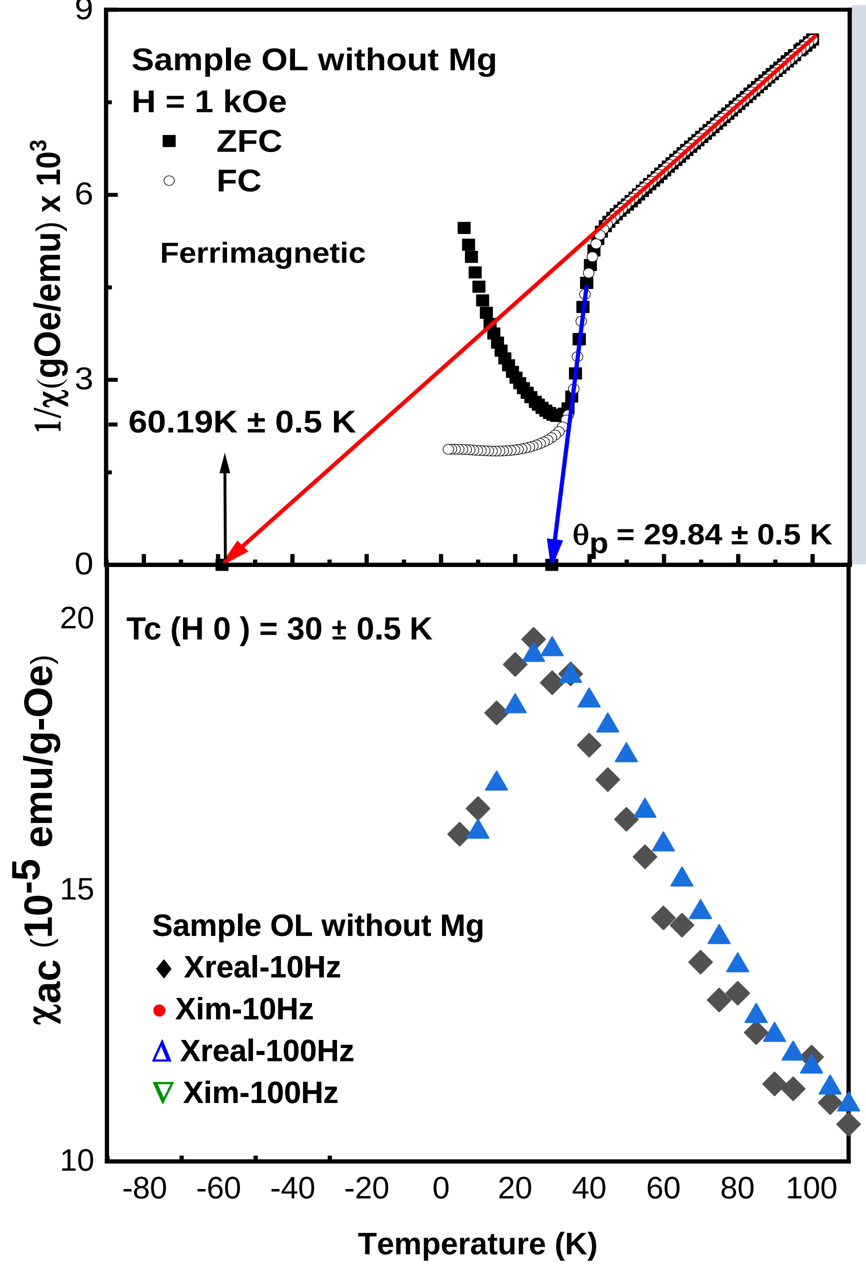


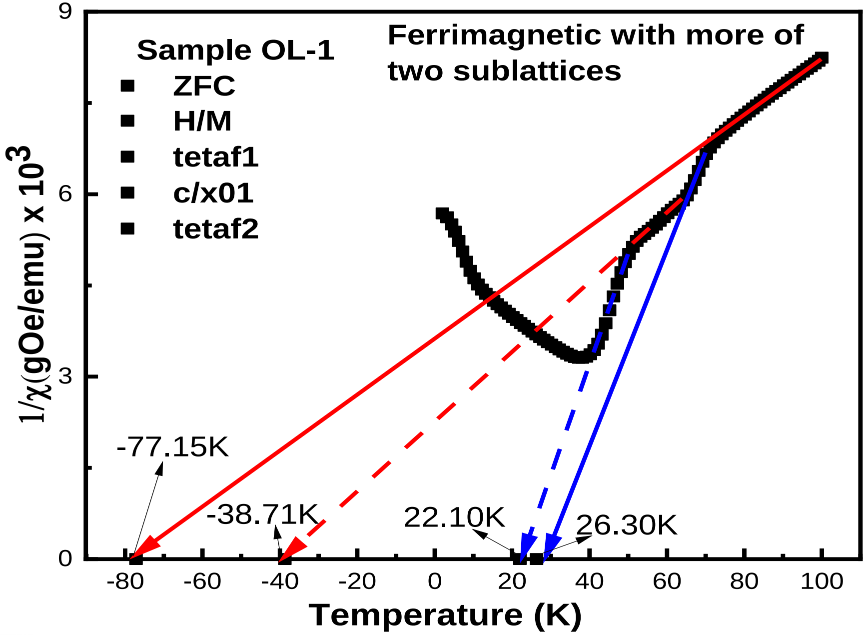


Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co



$$\frac{1}{\chi} = \frac{T + \left(\frac{C}{\chi_0}\right)}{C} - \frac{b}{T - \theta_f}$$

$\frac{1}{\chi}$ vs. T curve of sample OL fits well to Néel Eq., for ferrimagnetics



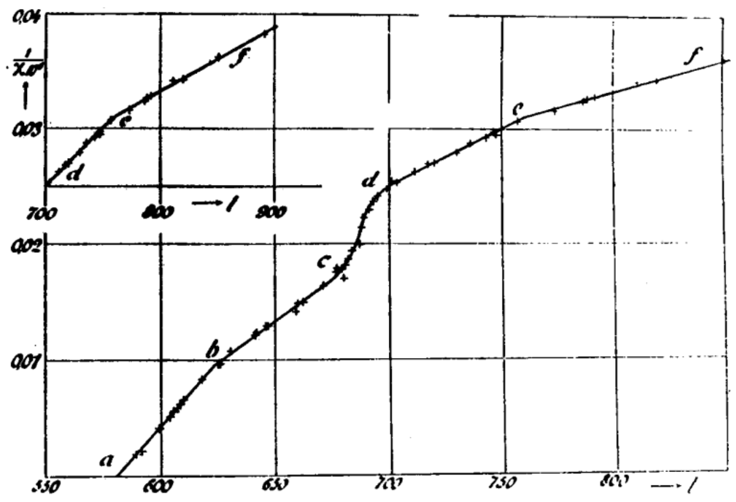
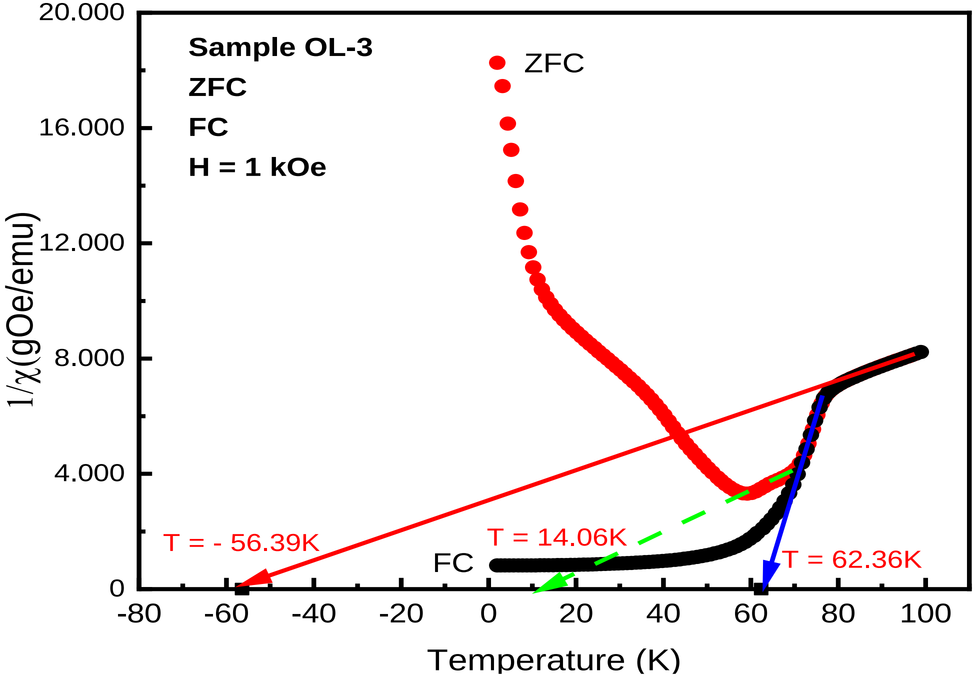
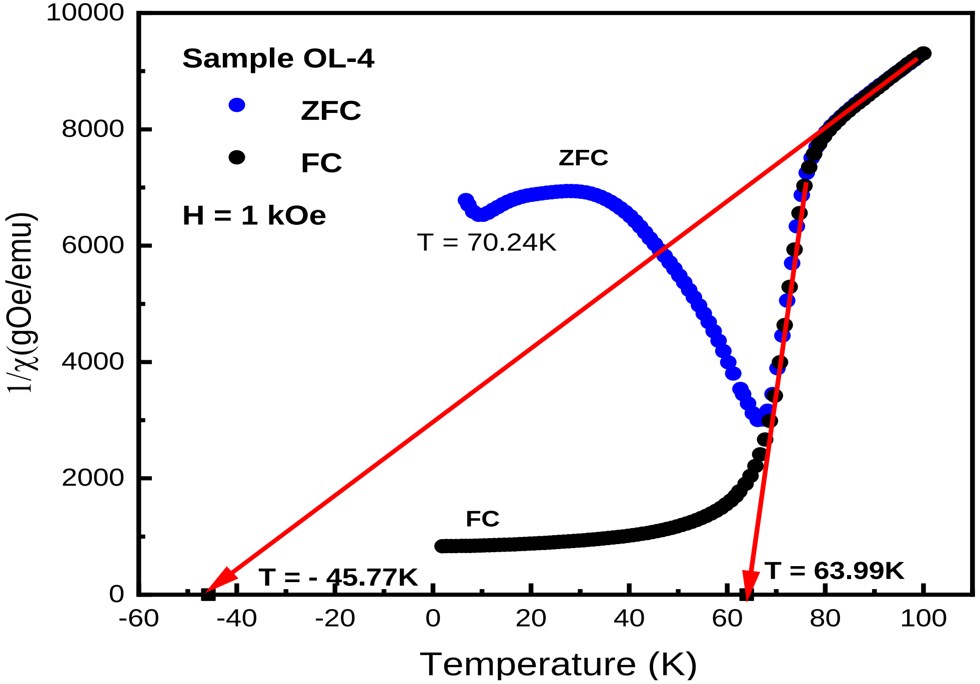


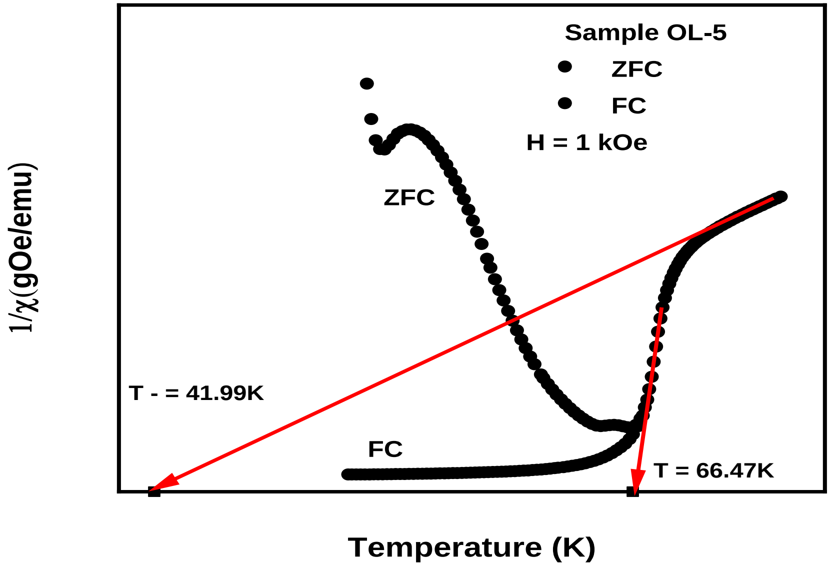
FIG. 1 Curve of inverse magnetic susceptibility versus temperature for magnetite. The apparent fact that this curve could be divided into separate straight line segments was taken as evidence for a fundamental unit, the Weiss magneton. Weiss (ref. 2), 80.

Weiss' Magneton: The Sin of Pride or a Venial Mistake?
Author(s): Pierre Quédec. Source: Historical Studies in the Physical and Biological Sciences, Vol. 18, No. 2 (1988), pp. 349-375. Published by: University of California Press. Stable URL: http://www.jstor.org/stable/27757606
Accessed: 21/06/2014 04:20

Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co







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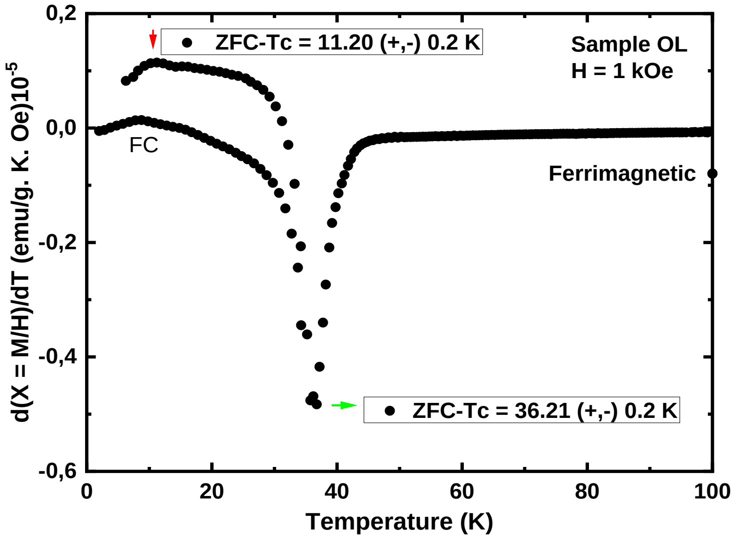
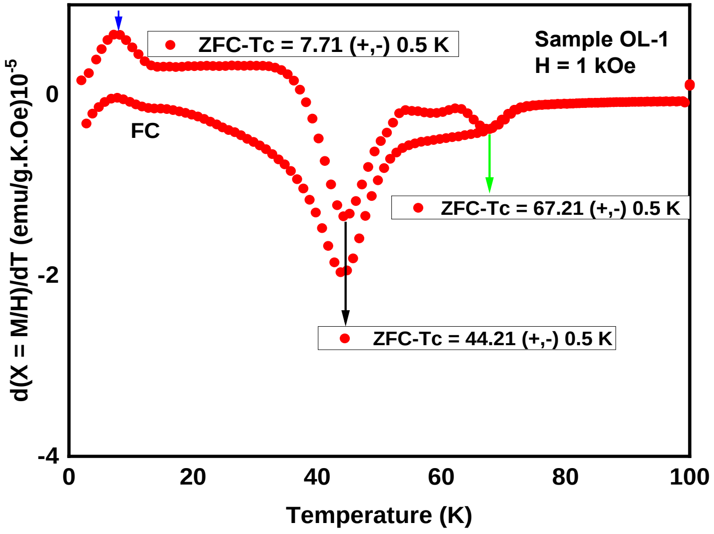
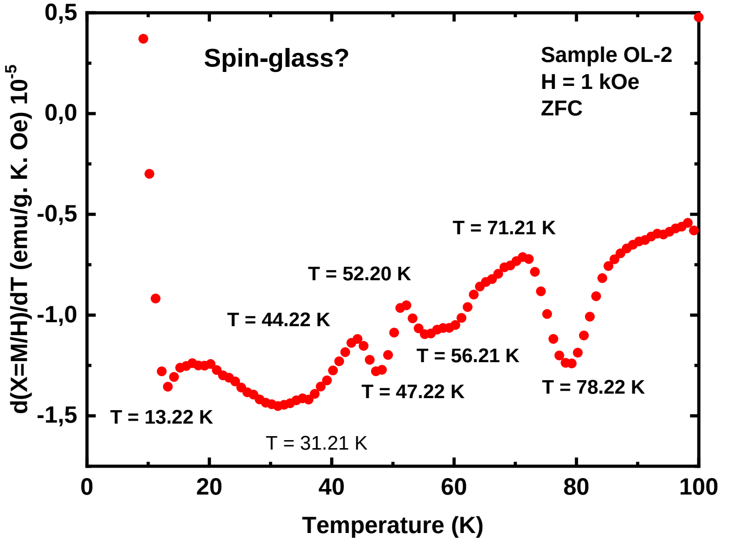
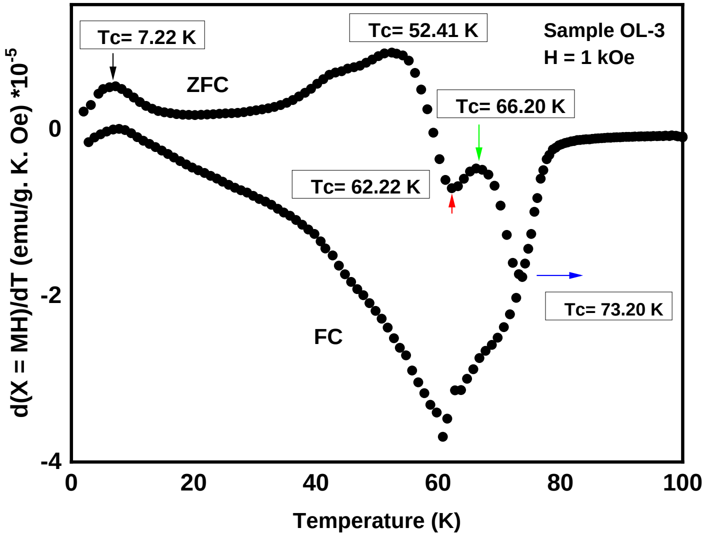
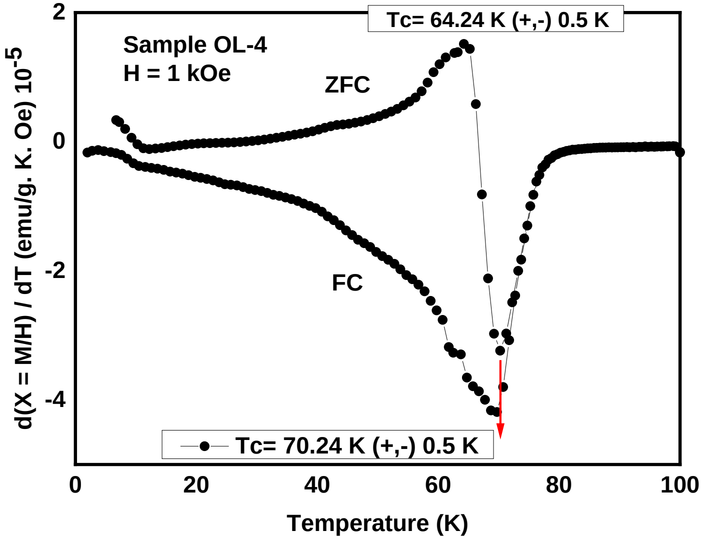
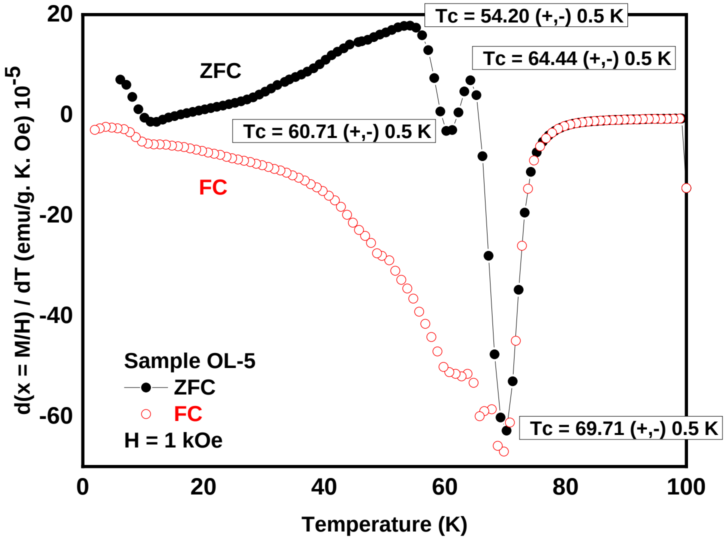




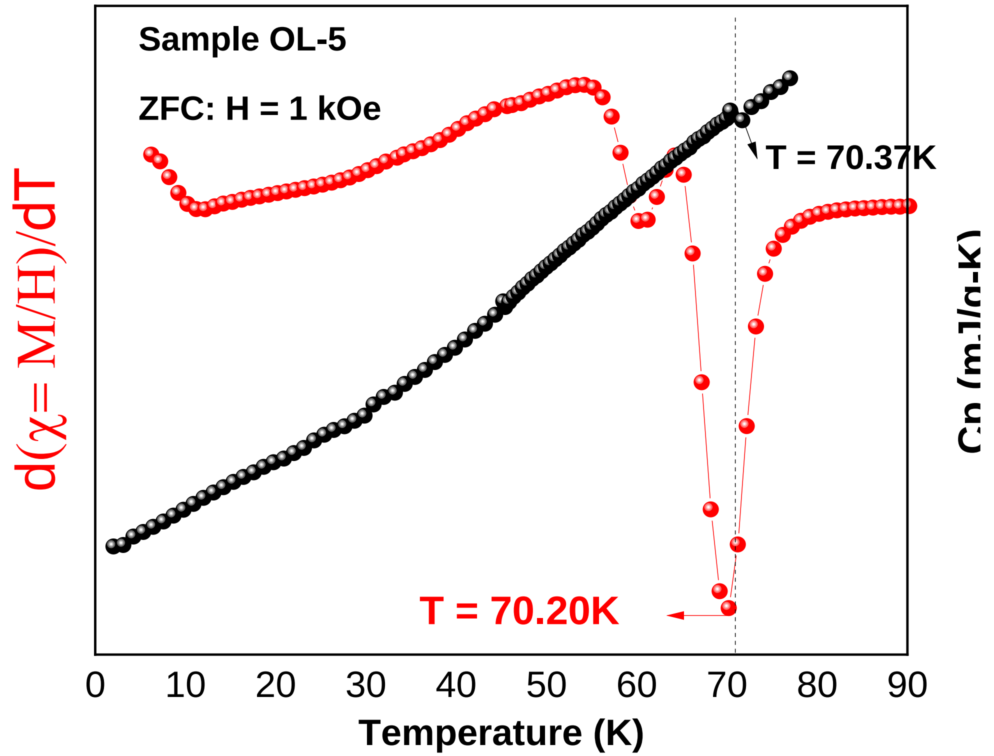








Evolution of the magnetic behavior of lamellar Mn-oxides undoped and doped with Co



$$C_H = \frac{< E^2 > - < E >^2}{k_B T^2}$$

$$\chi = \frac{< M^2 > - < M >^2}{V k_B T}$$

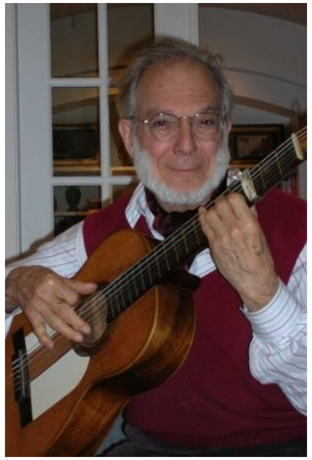
Energy includes the term - ***M*. *H***

Interpretation - how can we go about understanding the results? a possible road:

$$\left(\frac{d\chi}{dT}\right)_H \propto C_M(T)$$

M. Fisher, *Philos. Mag. A J. Theor. Exp. Appl. Phys.*, (3) **vol. 7, pp. 1731–1743, 1962.**

$$\chi_T = \frac{1}{N}\left(\frac{\partial\langle M\rangle}{\partial\beta H}\right)_H = \mu^2 \sum\nolimits_{ij} \Gamma_{ij} \qquad (4)$$



Michael Fisher

$$\chi_T = \frac{\left[\left(\frac{\partial M}{\partial T}\right)_H\right]^2}{C_H - C_M} \qquad (5)$$

[(*d*χ/*dT*) and *C*$_M$] : magnetization and energy fluctuations.

↓

Correlation between the (*d*χ/*dT*) and energy landscapes.

$\chi = Magnetic\ susceptibility$: $\frac{<M^2> - <M>^2}{V k_B T}$ $\qquad C_H = \frac{<E^2> - <E>^2}{k_B T^2}$

$M = Magnetization$

$T = Temperature$

$\Gamma = Correlation\ function$

$C = Heat\ capacity$

Interpretation - POSSIBLE PICTURE

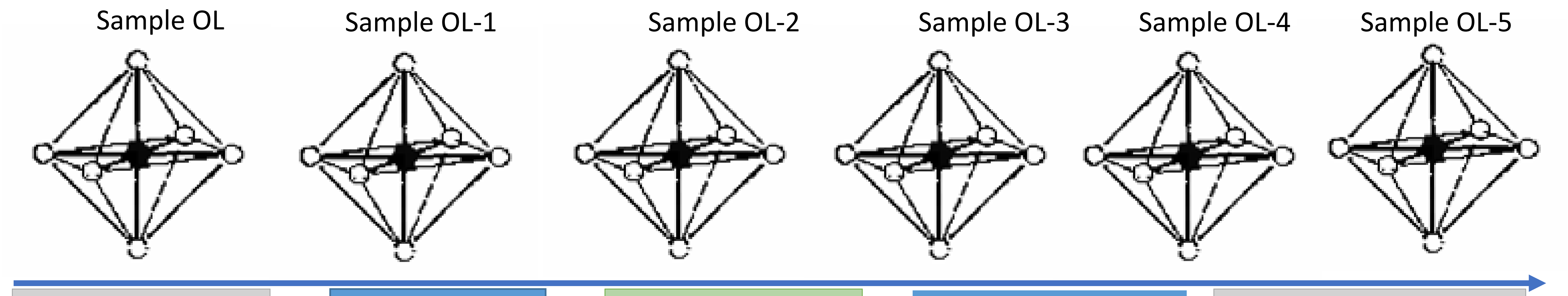
AOS = 3.71 indicates: presence of Mn^{3+} and Mn^{4+} ions, with concentration of Mn^{4+} ion > Mn^{3+} ion. An excess of Mn^{4+} ions in the MnO_6 octahedral sites. Ferrimagnetic structure with two sublattices.

Sample	AOS for Mn ion	(Co/Mn) ratio molar	(Mn^{4+}/Mn^{3+}) ratio molar	Magnetic Structure	Structural State (Main)	Frustration (Qualitative comment)	Interactions
OL (undoped)	**3.71**	**0.000**		**Ferrimagnetic with two sublattices**	**Birnessite**	**No**	**AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})**
OL-1 (doped)	**3.71**	**0.014**		**Ferrimagnetic with more of two sublattices**	**Birnessite**	**Yes-weak (presumably)**	**AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})**

Sample	AOS for Mn ion	(Co/Mn) ratio molar	(Mn^{4+}/Mn^{3+}) ratio molar	Magnetic Structure	Structural State (Main)	Frustration (Qualitative comment)	Interactions
OL-2 (doped)	**3.70**	**0.037**		**Spin-glass type**	**Birnessite**	**Yes-strong (presumably)**	**AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})**
OL-3 (doped)	**3.69**	**0.057**		**Ferrimagnetic (main)**	**Birnessite**	**Yes-weak (presumably)**	**AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})**

Sample	AOS for Mn ion	(Co/Mn) ratio molar	(Mn^{4+}/Mn^{3+}) ratio molar	Magnetic Structure	Structural State (Main)	Frustration (Qualitative comment)	Interactions
OL-4 (doped)	3.68	0.074		Ferrimagnetic with spin-cluster (short-to-medium range-ordered)	Birnessite	Yes-weak (presumably)	AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})
OL-5 (doped)	3.65	0.096		Ferrimagnetic with spin-cluster (short-to-medium range-ordered)	Birnessite + Spinel (Co-oxide)	Yes-weak (presumably)	AF super exchange (MnO, Mn_2O_3) + FM double exchange (Mn^{4+} and Mn^{3+})

Summary, Comments, NO Conclusions, Perspectives



Undoped
Sample OL
Mn/Co = 0
Concentration:
Mn^{4+} ion > Mn^{3+} ion
Excess of Mn^{4+} ion in the MnO$_6$ octahedral sites
Ferrimagnetic with two sublattices

Doped with Co
Sample OL1
Ferrimagnetic with more of two sublattices
fraction *x* of Mn^{4+} ion is initially replaced by a corresponding fraction *x* of Co^{3+} ion due to the initial excess of Mn^{4+} ion: (Mn^{4+} ion - Co^{3+} ion)

Further increasing of Co
Sample OL2
Spin-glass type
Frustration
Competent interactions
AF super exchange
+ FM double exchange
(Mn^{4+} and Mn^{3+})

Further increasing of Co
Samples OL3, OL4, OL5
(Mn^{4+} ion - Co^{3+} ion) tends to saturate (decreases)
(Mn3^{+} ion - Co^{3+} ion) tends to be predominant
Competent interactions tend to be compensated

Further increasing of Co
Sample OL5
Ferrimagnetic
with two sublattices +
Spin-clusters (short-to-medium range-ordered)
(Mn^{4+} ion - Co^{3+} ion) saturates and
(Mn3^{+} ion - Co^{3+} becomes predominant)
Birnessite +
Spinel (Co-oxide)

The present system goes from ferrimagnetic with two sub-lattices to ferromagnetic with of two sublattices to spin-glass and back to ferrimagnetic with two sublattices behavior.

Summary, Comments, NO Conclusions, Perspectives

Possible reconciliation

Inverse Susceptibility Curve -Weiss´ Magneton – The inverse susceptibility vs. T curves observed by Weiss occur, but their interpretation is not correct

L. Néel: To study the possibility of frustrate ferrimagnetism of more of two sub-lattices?

Acknowledgements

Prof.: Fernando L. A. Machado, Universidade Federal de Pernambuco, Recife, Brasil (AC susceptibility)

Profs.; Gabriel Téllez, UniAndes, Bogotá, Colombia

Alejandro Pérez y José Daniel Muñoz, Universidad Nacional de Colombia, Sede Bogotá, Colombia

FCEN – [(2006-2026) 20 years old], Unversidad Nacional de Colombia, Sede Manizales

THANKS FOR YOUR ATTENTION

Magnetism and Statistical Physisc – Upcoming Event
2026-2027
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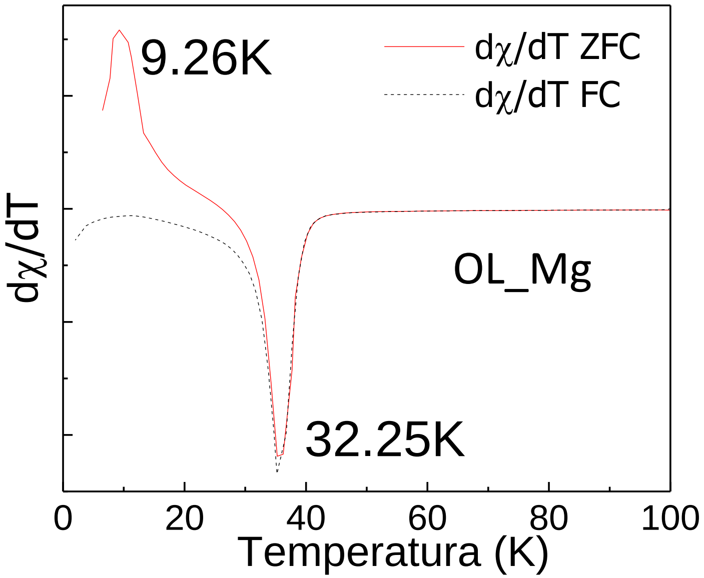
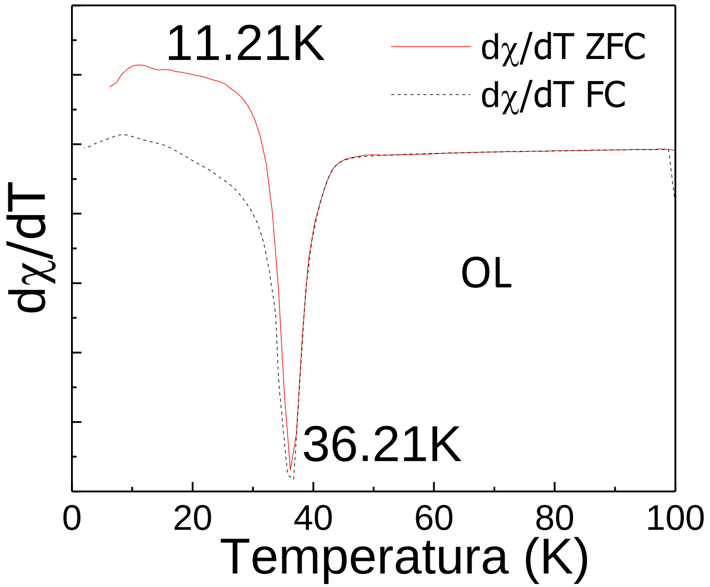
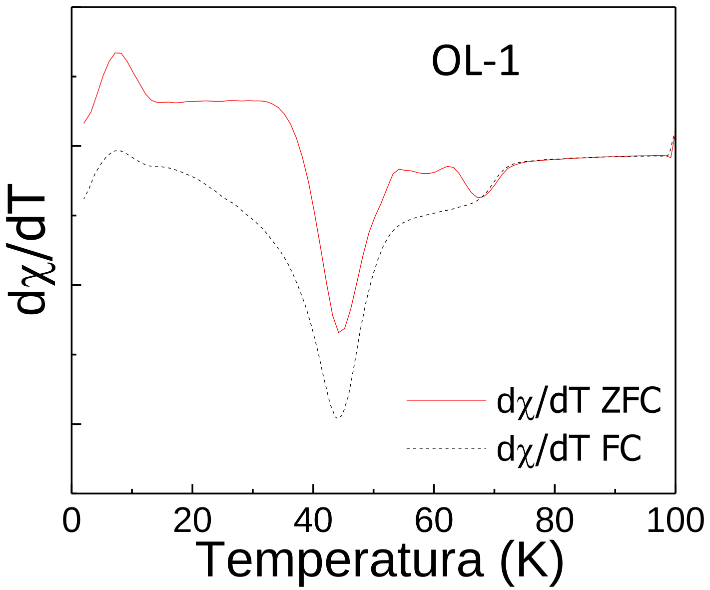
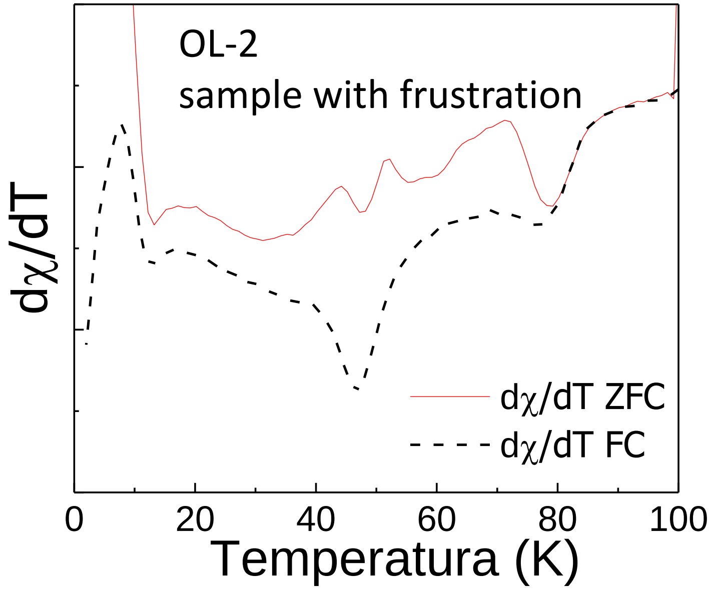
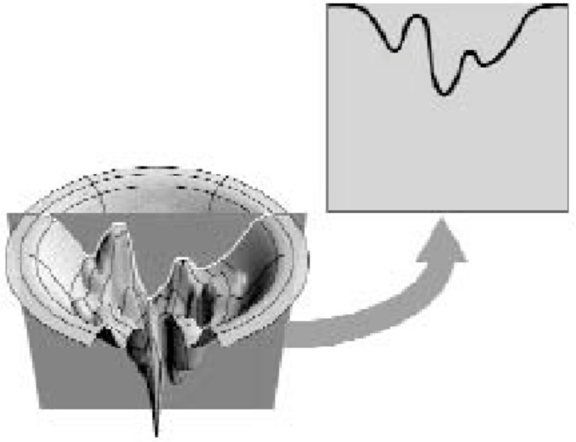


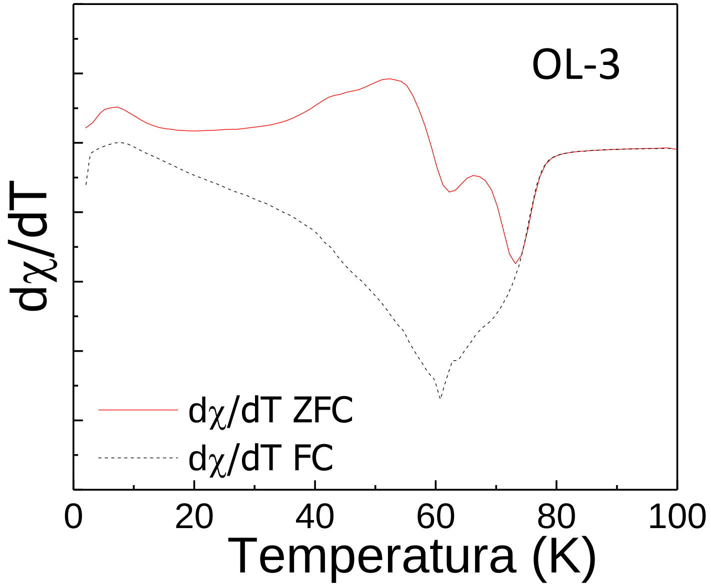








Energy Landscape for protein, (dx/dT) for sample OL-2, protein, and system with frustration



Determination of $(\mu_{eff})_{calc} = a\,(\mu)_{Mn^{4+}} + b\,(\mu)_{Mn^{3+}} + c\,(\mu)_{Co^{3+}}$ (2)