Magnetic & Crystal structure studies with neutron powder diffraction

2016. 5.27

Seongsu Lee KAERI, Korea

Contents

- Introduce HANARO
- Introduction Neutron diffraction?
- Some examples

- Hexagonal Manganite
- Magnetic structure change under external magnetic field
- Incommensurate magnetic structure

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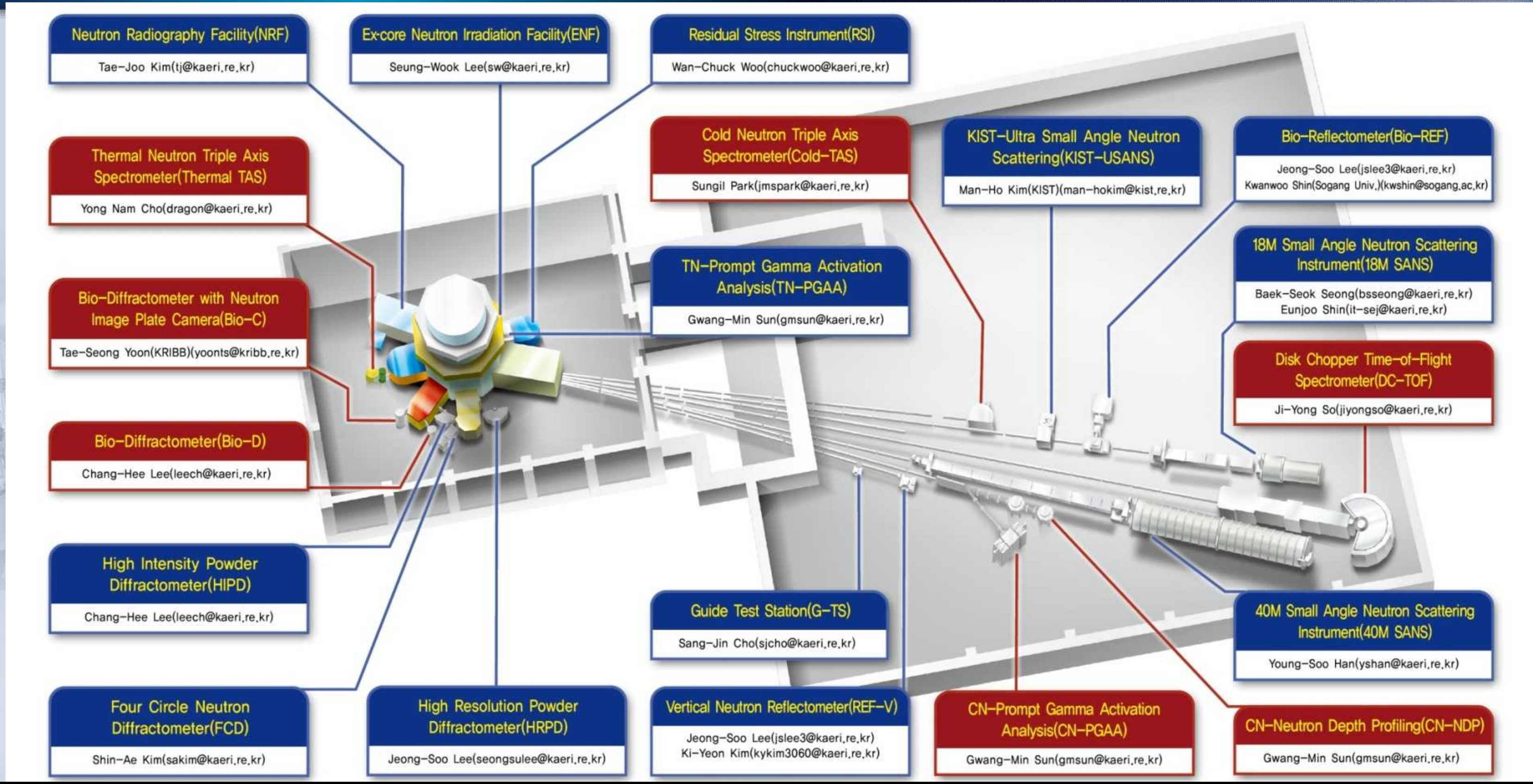
HANARO 30MW (High Flux Advanced Neutron Application Reactor)

Reactor Hall: thermal neutron

Location of HANARO

Cold neutron Guard Hall: cold neutron

HANARO neutron instruments



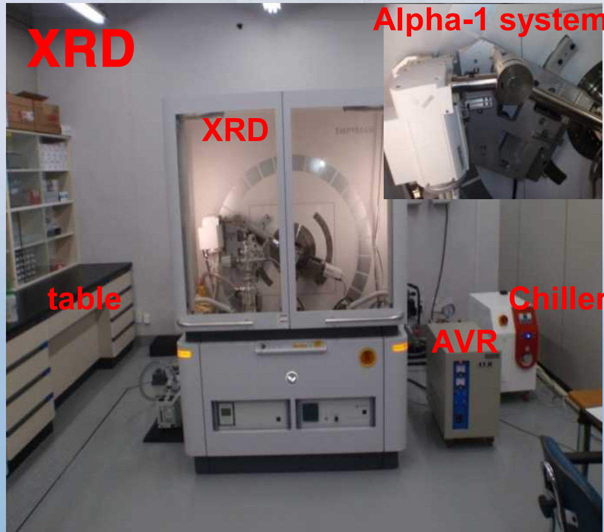
- 16 Neutron instruments + 4 PGAA modules operating in 2015
- 13 in operation
  (HRPD, FCD, RSI, NRF, Bio-D ENF, PGAA / 18M & 40M SANS, REF-V, G-TS, DC-ToF, Cold-TAS, KIST-USANS)
- 4 under commissioning
  (Th-TAS, Bio-REF, C-PGAA, C-NDP)
- Bio-C under installation
- Prompt Gamma Imaging, Cold Neutron Radiography in planning

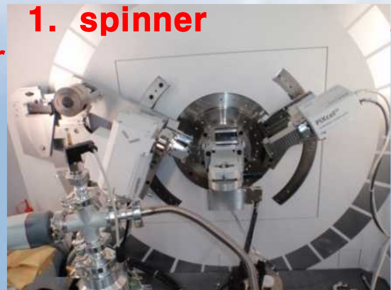
HRPD & XRD

seongsulee@kaeri.re.kr

Part	Characteristic
Monochromator Wavelength Resolution Neutron Flux at sample	Ge(331),Ge(335) 1.836 Å ⊿d/d > 2.0% ~ 3.5 x 10^6 n/cm^2/sec
Multi-detectors PSD (position sensitive detectors) Take off angle	32 He-3 proportional counters (tube: dia. 50mm) 1-D (100mm 200mm and 200mm 100mm), 2-D (200mm 200mm) 90°
Collimators	-In-pile RSC (rotating shutter collimator) : 20' , 30' , open(~50') -FCU (first collimator unit) : 6', 10', 20', open(~50') -Second collimator : 30' , open

-Auto sample changer for RT
-High Temp. vacuum chamber : up to 950 K
-Low Temp. CCR : RT to 4.5 K
-Magnetic Field : Max. 0.8 T, Electromagnet
Max. 500G, Helmholtz Coil
-Pressure cell (up to 10 kbar)
-Cryo-furance (20K to 800K)
-Dilution refrigerator & Super conducting magnet : coming soon

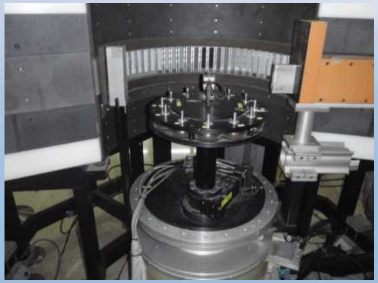




Sample environments of HRPD

NAME	Sample condition
Auto sample changer	Room temperature (12 samples)
High Temp. Furnace	Up to 1000 K, up to 2000 K
Low Temp. CCR	From 4 K to 300 K
Pressure cell	Up to 10 Kbar
Cryo-furnace	20 K to 800 K
Super conducting magnet	1.5 K & 10 tesla(1.5K+10Tesla+10kbar)
Dilution refrigerator	Down to 50 mK

Auto sample changer



4K CCR

SC magnet

Furnace

User Supports :proposal based system
:call for proposal two times/year

Call for proposals

Website: hanaro4u.kaeri.re.kr
E-mail: useroffice@kaeri.re.kr

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Why Neutron Diffraction ?

→ **Neutron diffraction issues inside story**

→ **Simultaneously understand Crystal & Magnetic Structure**

To see light element(s)

- Lithium Battery, Oxides, …

To distinguish neighbor element(s) or isotopes

- Substitution of TM or RE ions, H/D substitution …

To see bulk properties

- Inter-grain reactions in composite materials, …

To see spin (magnetic) structure

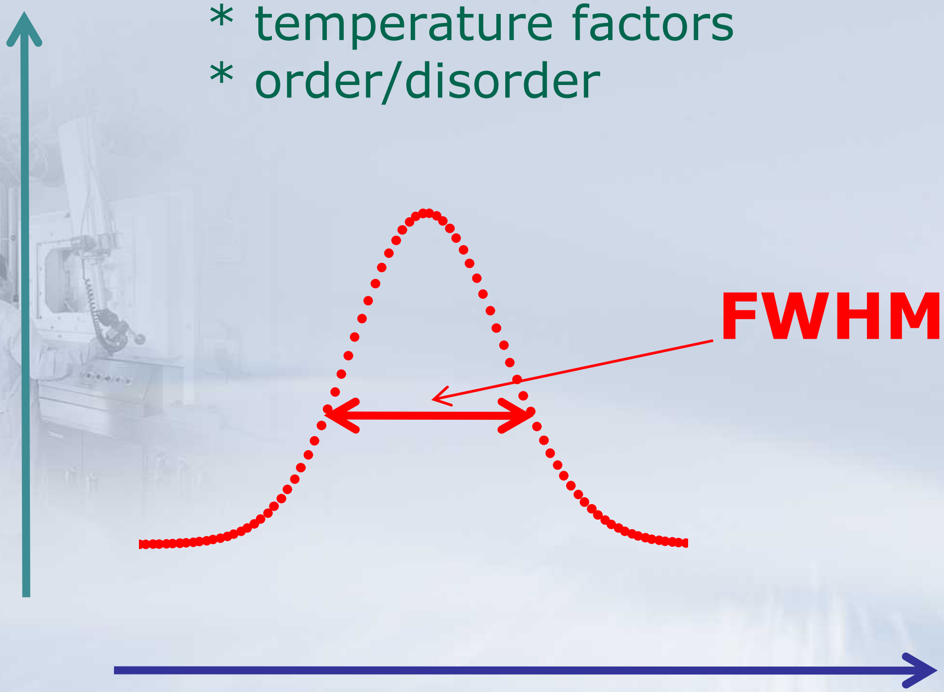
- FM, AFM, Magnetic Incomensurate Structure, …

To see sample in a container with thick wall

- various sample environments (low T, high T, pressure, magnetic field, …)

Simplified Powder Diffractogram

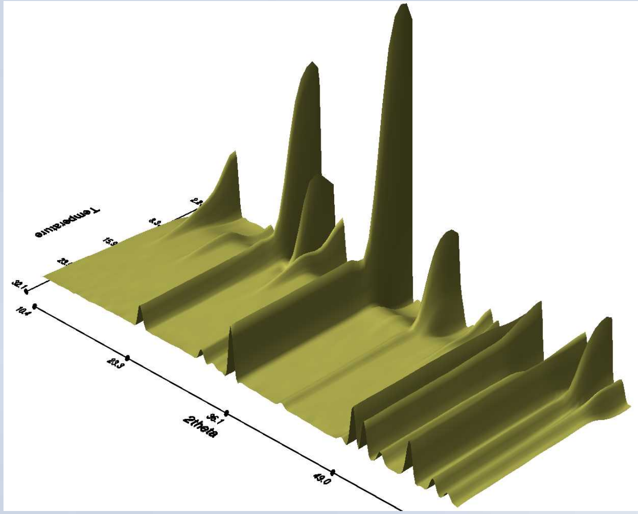
Intensity → * atomic/ionic positions
* temperature factors
* order/disorder



FWHM →
* domain sizes
* habit

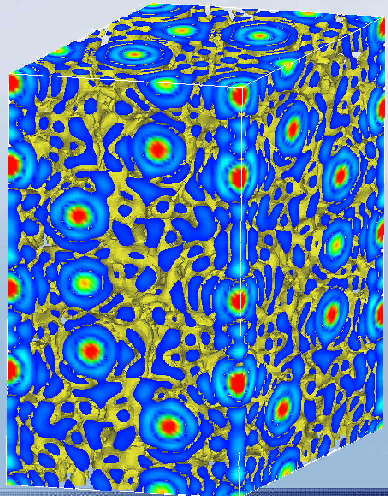
Position 2θ (˚) →
* crystal system
* unit cell dimensions
* space group

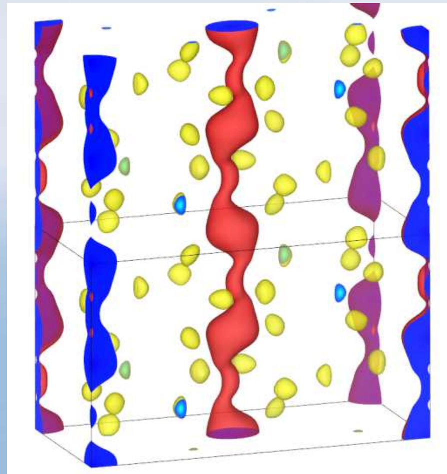
Crystal & Magnetic structure



Crystal structure

-Unit cell information
-atomic position
-bond length and angle
-bond valence sum
-thermal motion information
-hidden structure
-local structure





Magnetic structure

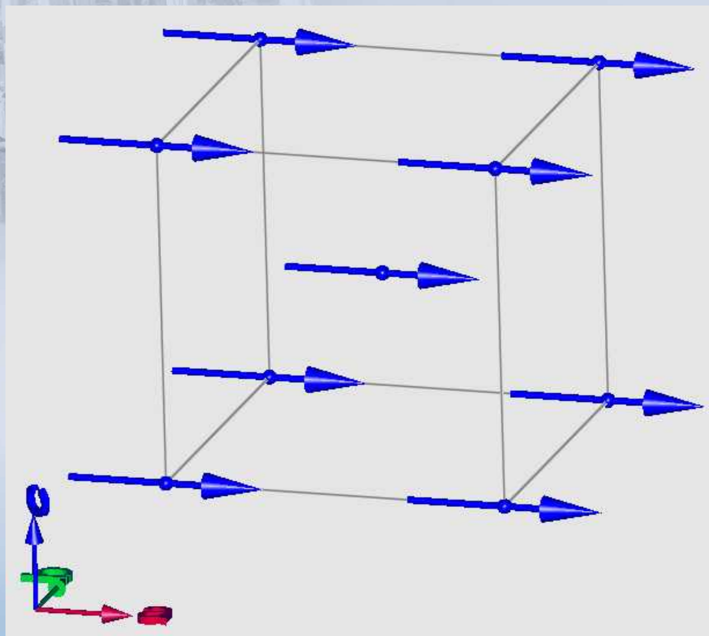
-spin configuration
-magnetic moment
-short range ordering
-order-disorder
-spin-lattice coupling

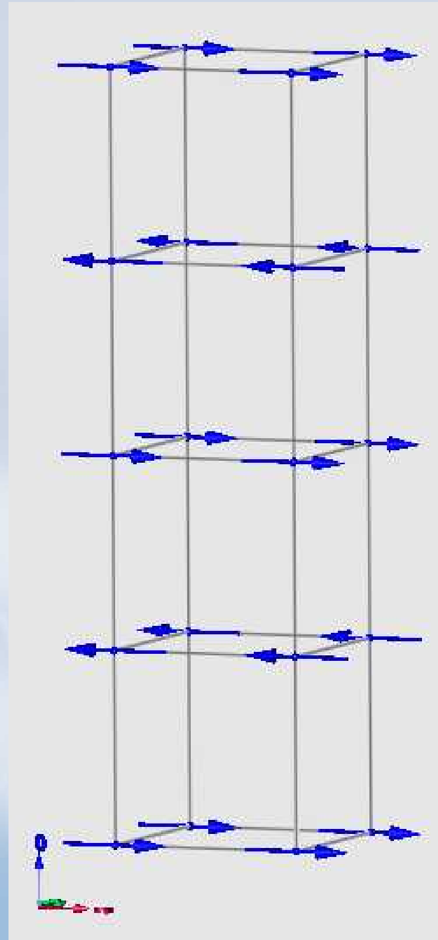
Magnetic structure

Collinear magnetic structure

Antiferromagnetic

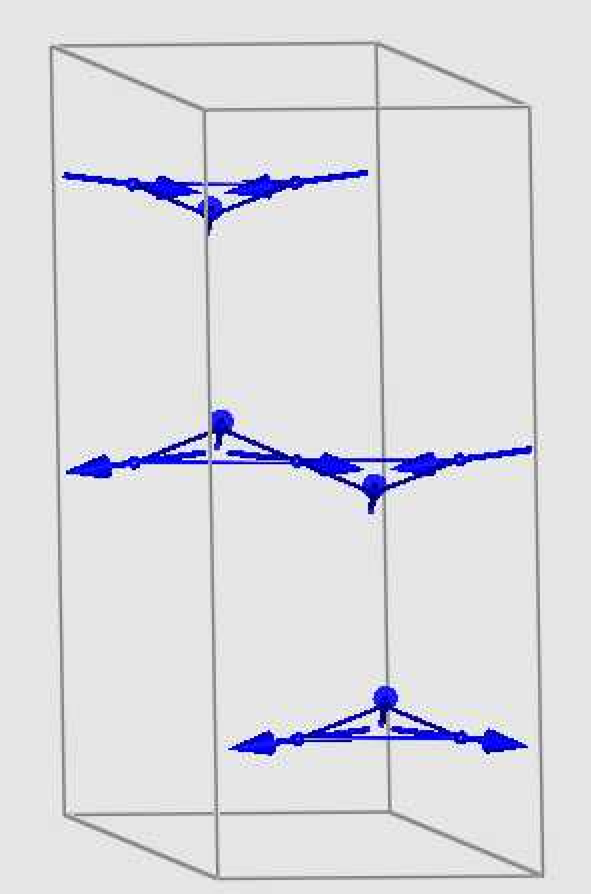
Ferromagnetic



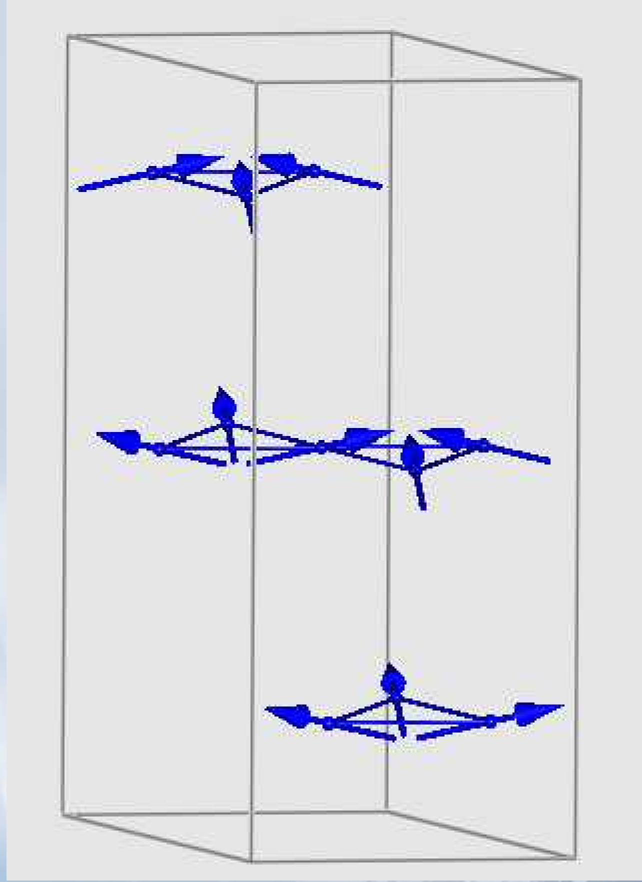


Noncollinear magnetic structure

Frustration: triangle

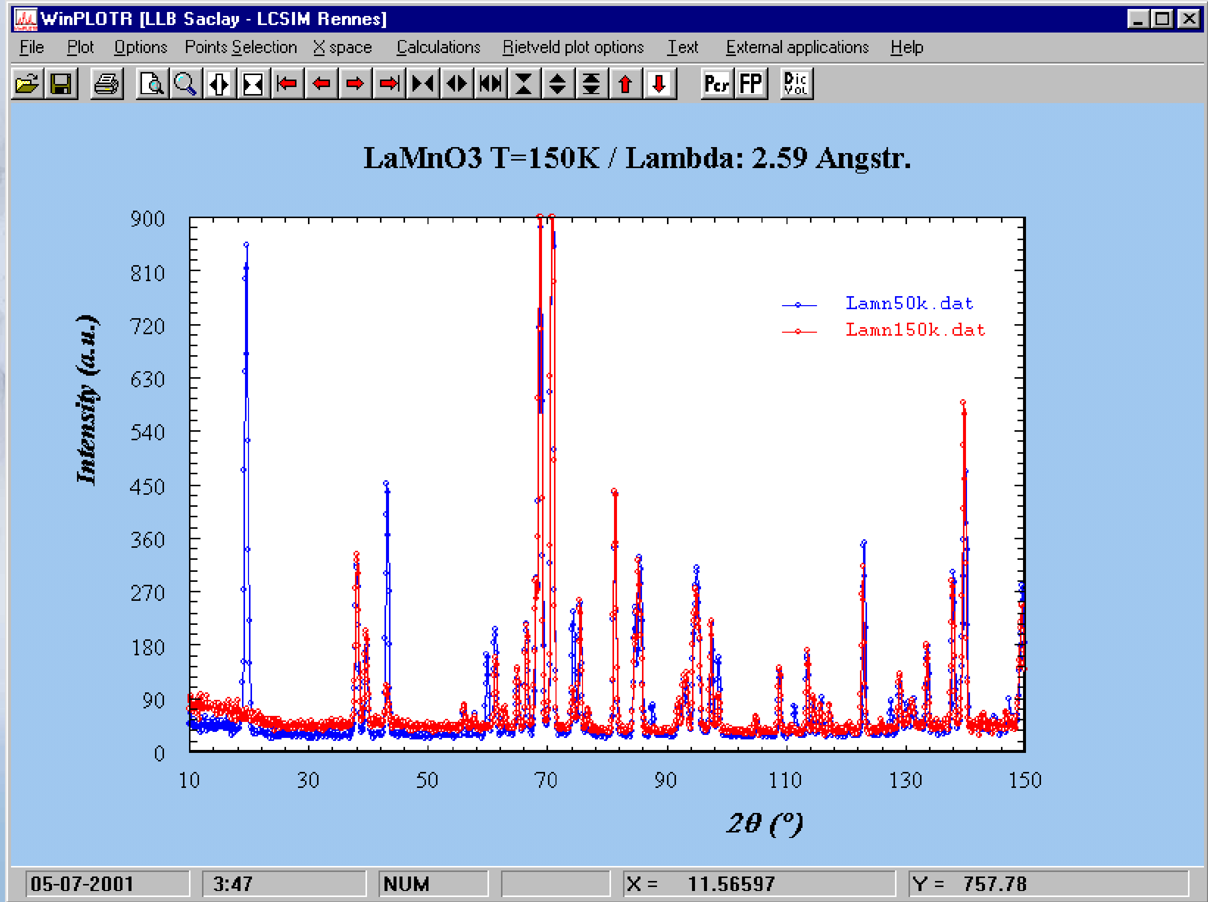


umbrella



Magnetic scattering in $LaMnO_3$

$LaMnO_3$: 50K and 150 K



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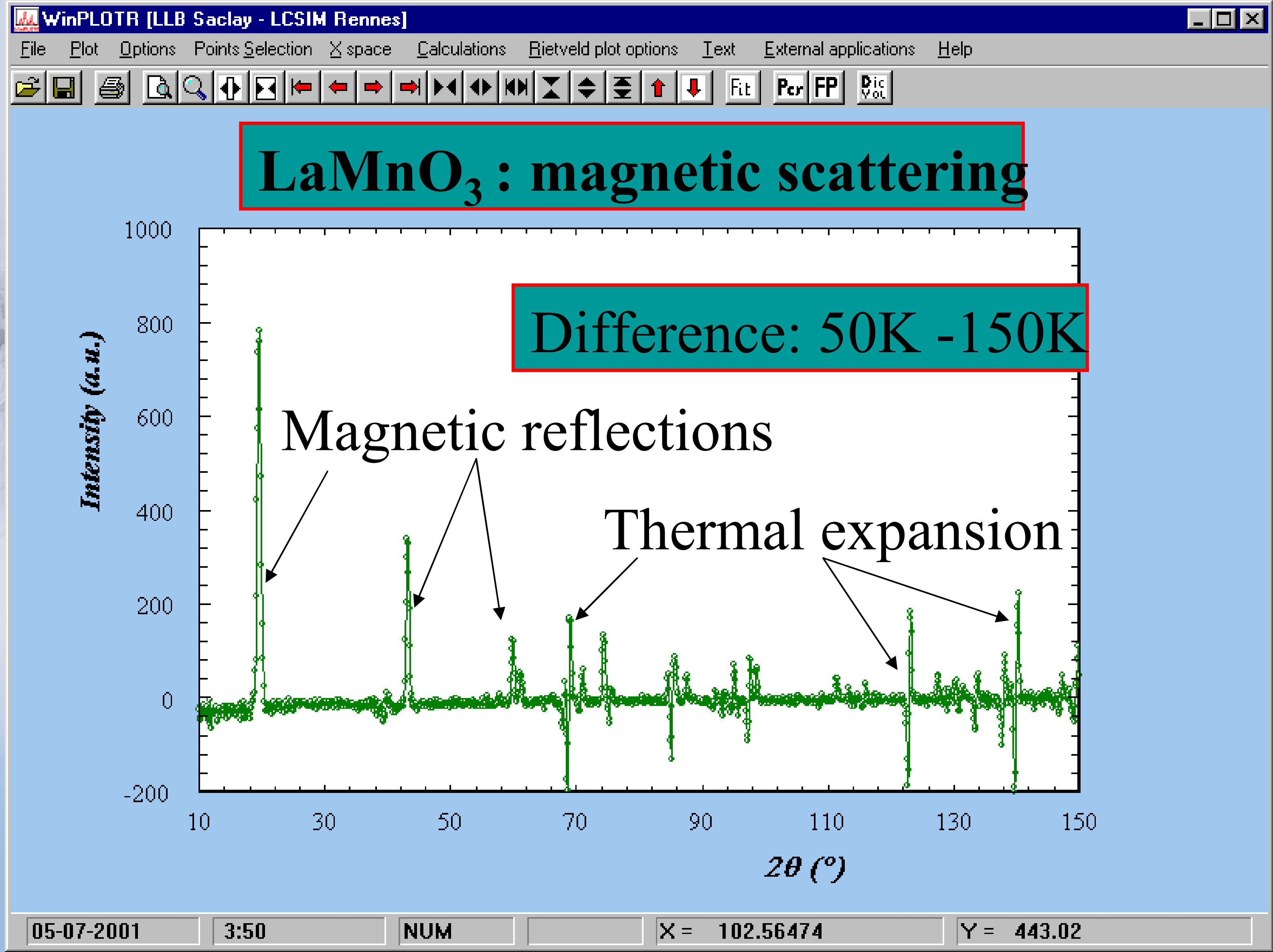
Magnetic scattering in $LaMnO_3$



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- For magnet materials(Neutron irradiation studies)
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1^{st} example for neutron powder diffraction

Long rang magnetic ordering
: coupling between magnetic order and
crystal order in hexagonal manganite

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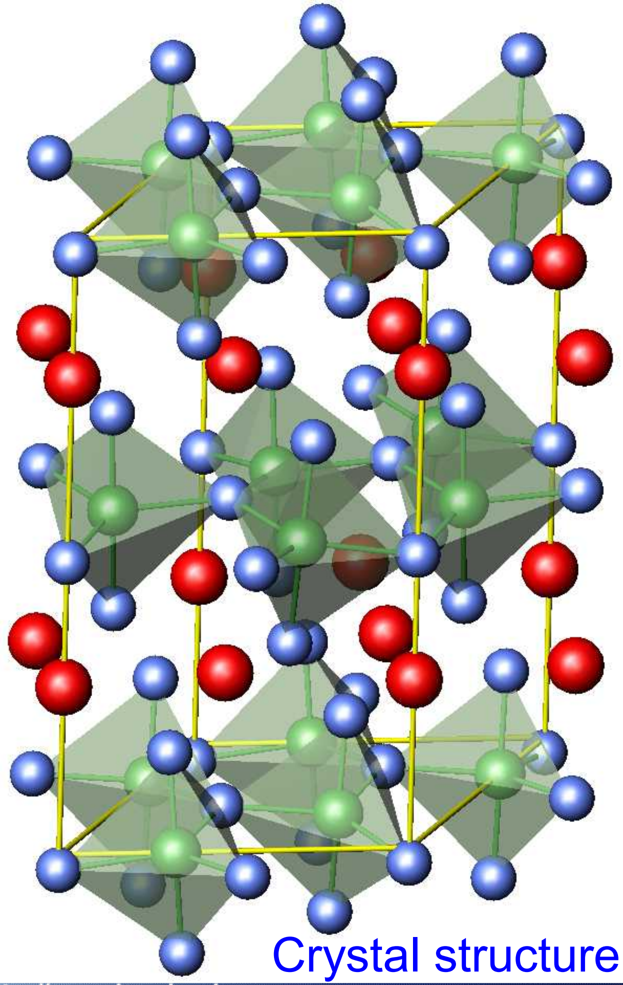
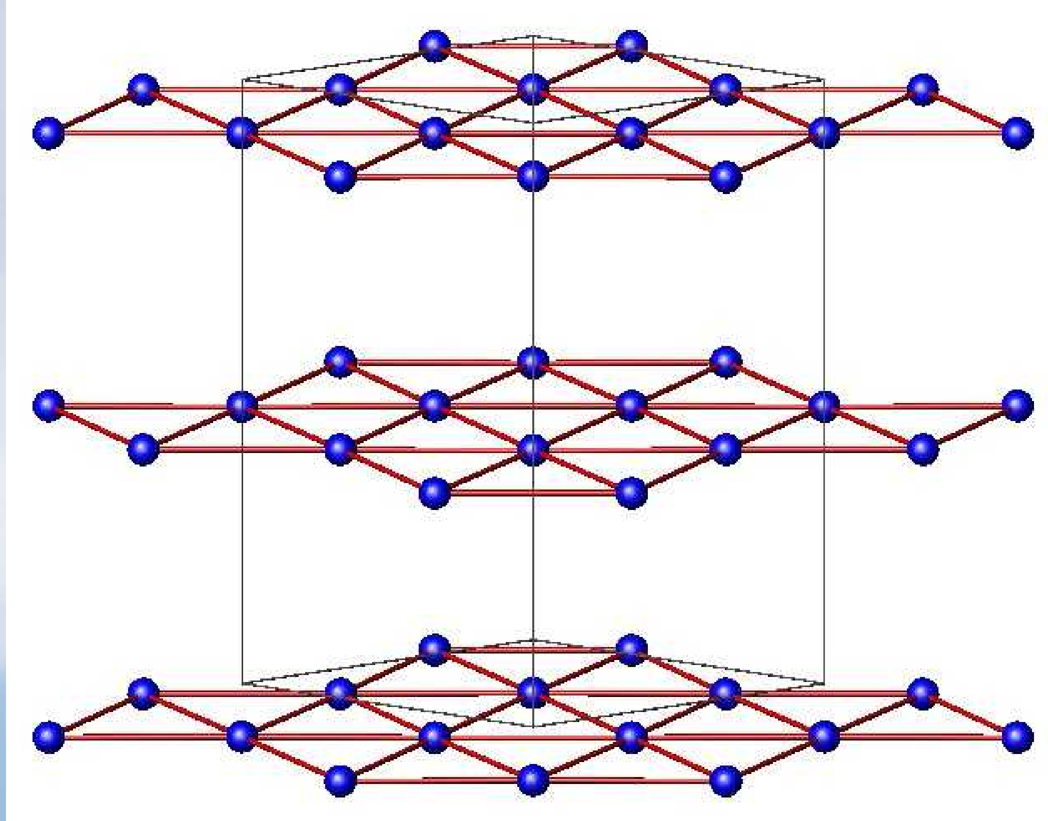
Why are hexagonal manganite interesting?

Triangular lattice of Mn moments:
geometrical frustration effects



Crystal structure



Triangular lattice

Mutiferroic system

Ferroelectric

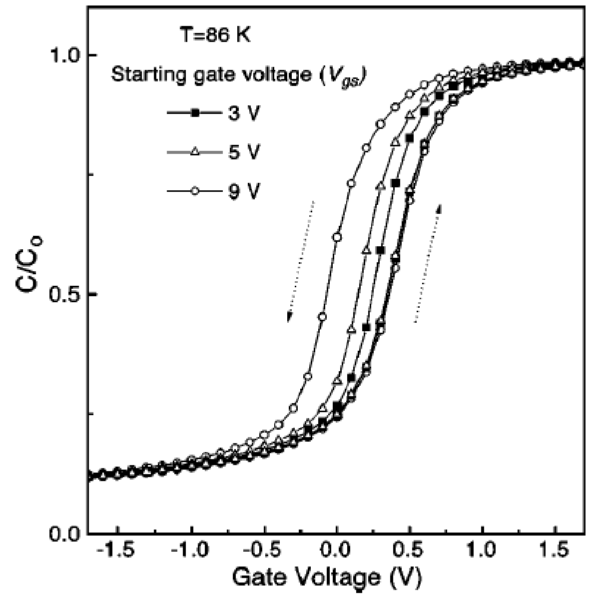
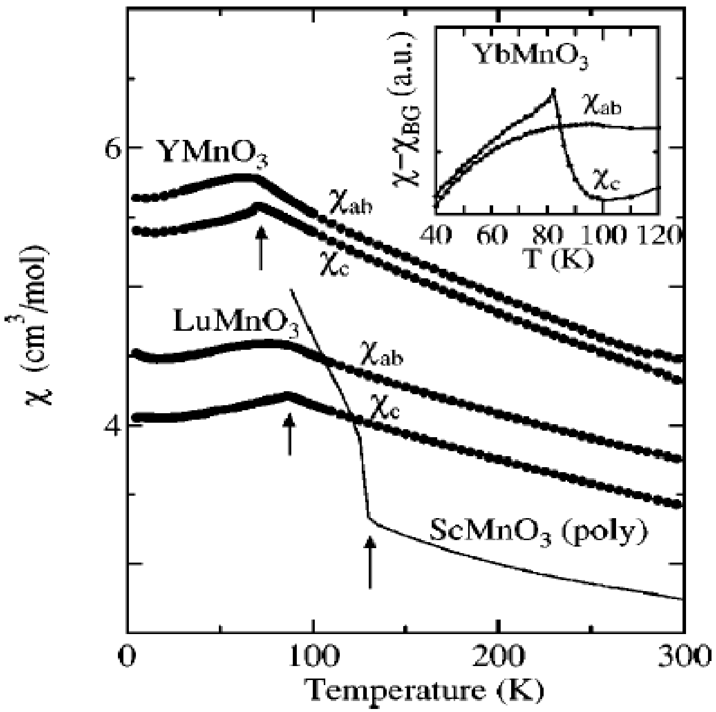


FIG. 4. Gate voltage dependences of the $C-V$ characteristics at 86 K (C_o = 54 nF/cm^2).

Antiferromagnetic



Wo-chul Yi et al.Appl. Phys. Lett., (1998)

T.Katsufuji et al., PRB (2001)

Rare-earth Manganites $RMnO_3$ Phase

Large ionic radius (R= La, Pr, Nd, Sm, Eu, Gd *etc.*) : Orthorhombic (Pbnm)
Small ionic radius (R= Ho, Eu, Tm, Yb, Lu, Sc, and Y): Hexagonal($P6_3cm$)

Ferroelectric and Antiferromagnetic transitions of hexagonal manganites

	antiferromagnetic ordering temperature (K)	ferroelectric ordering temperature (K)	a (Å)	c (Å)
$ScMnO_3$	129		5.833	11.17
$YMnO_3$	70	920	6.139	11.39
$HoMnO_3$	76	873	6.142	11.42
$ErMnO_3$	78	833	6.112	11.40
$TmMnO_3$	86	>573	6.092	11.37
$YbMnO_3$	87	993	6.062	11.36
$LuMnO_3$	95	>750	6.042	11.37

G.A. Smolenskii and I.E. Chupis, Sov. Phys. Usp. 25, 475 (1982)

Our samples

$YMnO_3$ Γ_1

$(YEr)MnO_3$ $\Gamma_1 + \Gamma_2$ $(YLu)MnO_3$

$ErMnO_3$ Γ_2 $LuMnO_3$

$Y(MnX)O_3$, $TmMnO_3$ $\Gamma_1 + \Gamma_2$

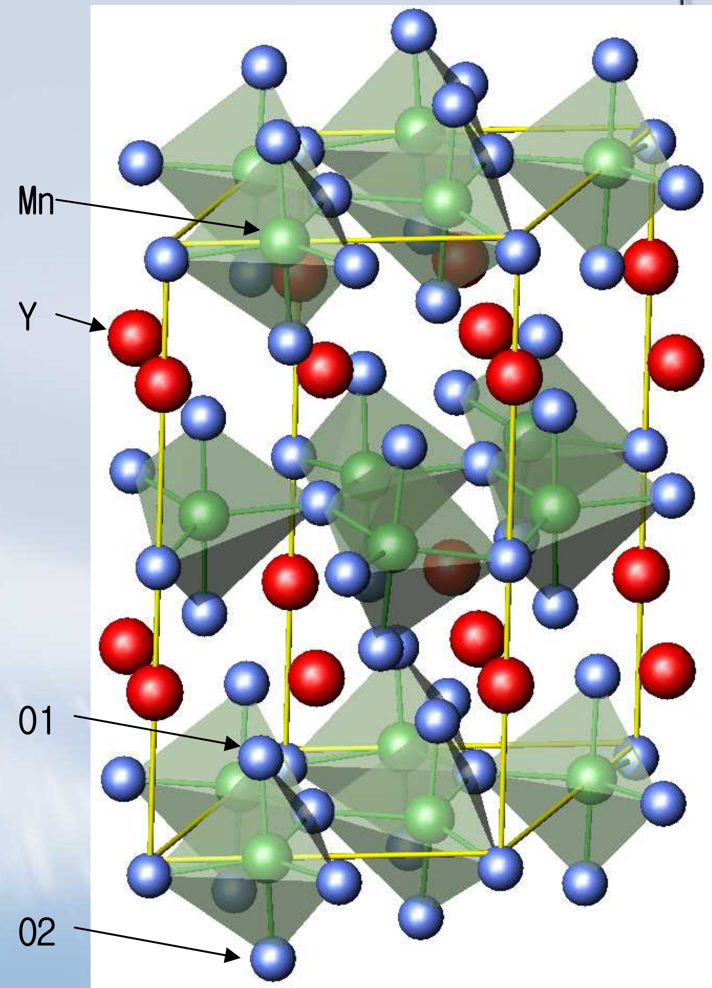
Pressure effect, Isotope effect

Possible magnetic structure to be obtained symmetry analysis

-Magnetic basis function studies using MODY and BasIreps program.

-Space group : $P6_3cm$(No.185)

-position of magnetic atom: Mn(x,0,0)
-wave vector k =(0,0,0)



Wyckoff Positions of Group 185 ($P6_3cm$)

	Multiplicity	Wyckoff letter	Site symmetry	Coordinates
	12	d	1	(x,y,z) (-y,x-y,z) (-x+y,-x,z) (-x,-y,z+1/2) (y,-x+y,z+1/2) (x-y,x,z+1/2) (-y,-x,z+1/2) (-x+y,y,z+1/2) (x,x-y,z+1/2) (y,x,z) (x-y,-y,z) (-x,-x+y,z)
Mn,O1,O2	6	c	..m	(x,0,z) (0,x,z) (-x,-x,z) (-x,0,z+1/2) (0,-x,z+1/2) (x,x,z+1/2)
Y2,O4	4	b	3..	(1/3,2/3,z) (2/3,1/3,z+1/2) (1/3,2/3,z+1/2) (2/3,1/3,z)
Y1,O3	2	a	3.m	(0,0,z) (0,0,z+1/2)

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Steps for magnetic structure determination using powder diffraction

Step		Input
Propagation vector(s) *SuperCell*	⇐	*Peak positions of magnetic reflections* *Cell parameters*
Symmetry Analysis *BasIreps, MODY, SARAh*	⇐	*Propagation vector* *Space Group* *Atom positions*
Magnetic structure solution (Sim. Ann.) *FullProf*	⇐	*Integrated intensities* *Atomic components of basis functions*

How we can get the basis function described the magnetic structure and the displacement?

Symmetry: space group

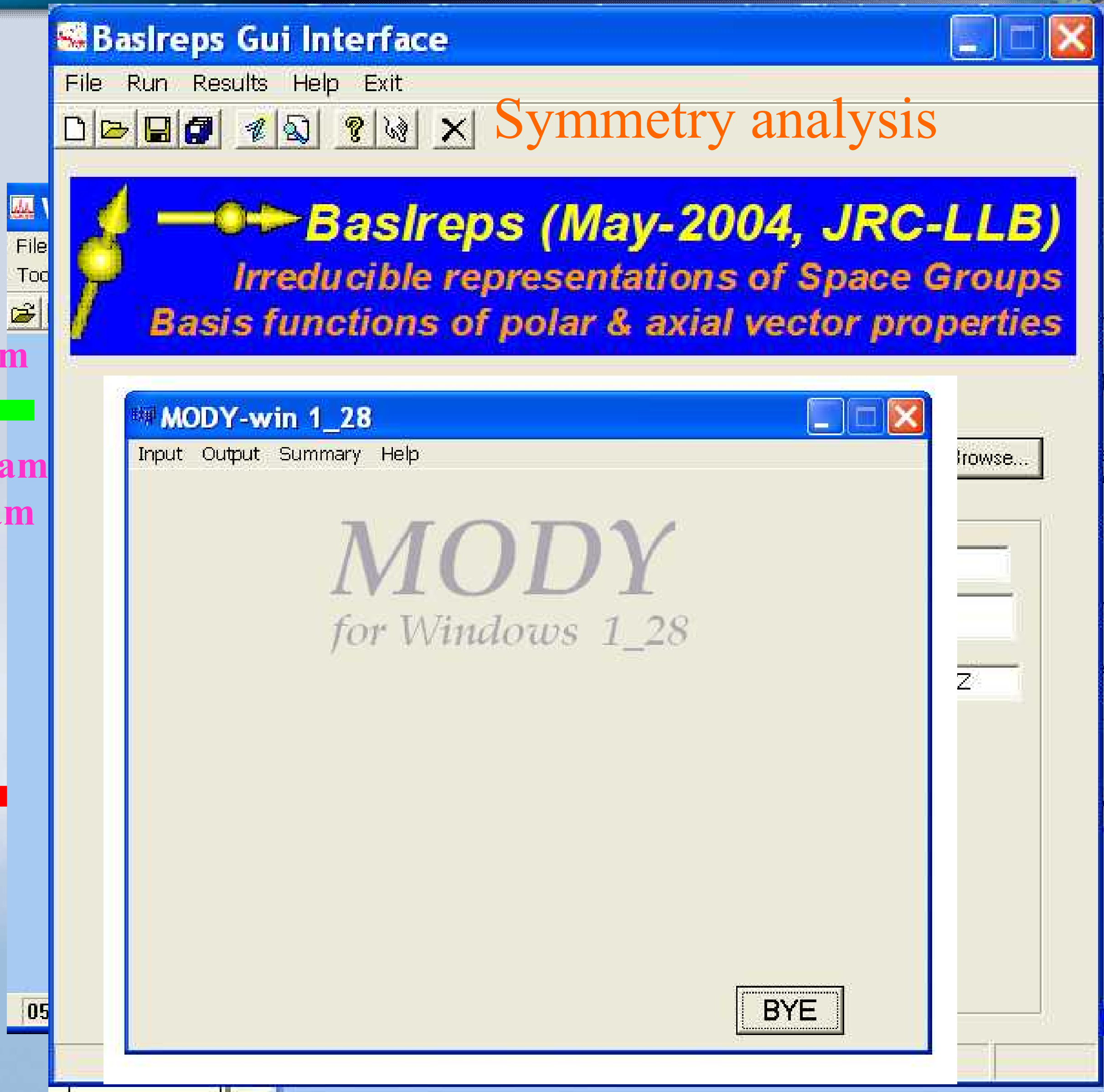
MODY program

Baslreps program
SARAh Program

Possible magnetic structure
:magnetic basis function
:displacement basis function

Magnetic structure
Displacement mode

Symmetry analysis



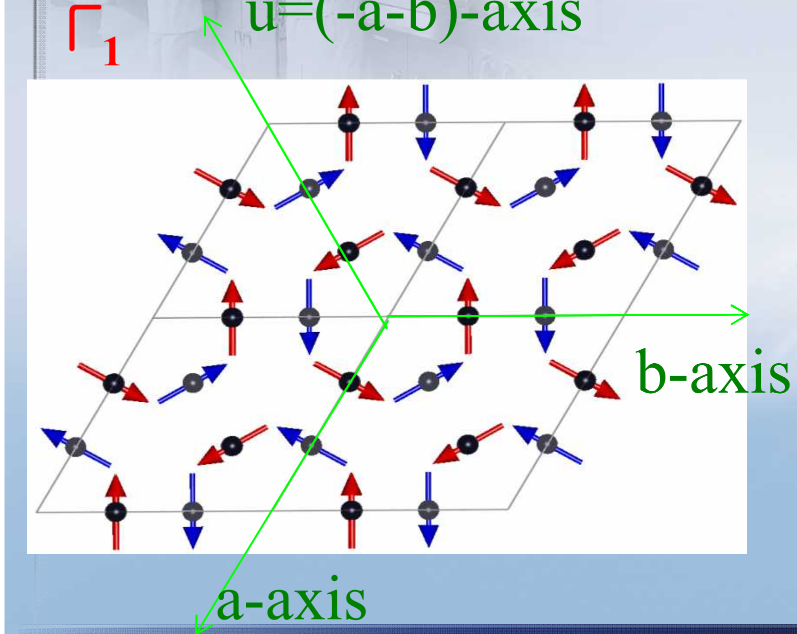
Possible magnetic structure of hexagonal manganites

decomposition of the six irreducible representation

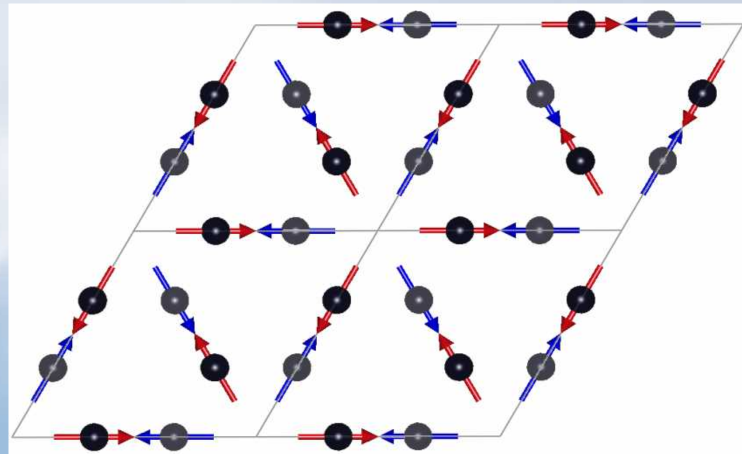
$$\Gamma = \Gamma_1 + 2\,\Gamma_2 + 2\,\Gamma_3 + \Gamma_4 + 3\,\Gamma_5 + 3\,\Gamma_6$$

Repr. irred.	Basis Vector	6c site					
		(x, 0, 0)	(-x+1, 0, 1/2)	(0, x, 0)	(0, -x+1, 1/2)	(-x+1, -x+1, 0)	(x, x, 1/2)
Γ_1	$V^2{}_1$	(1 2 0)	(−1 −2 0)	(−2 −1 0)	(2 1 0)	(1 −1 0)	(−1 1 0)
Γ_2	$V^1{}_1$	(1 0 0)	(−1 0 0)	(0 1 0)	(0 −1 0)	(−1 −1 0)	(1 1 0)
	$V^1{}_2$	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)
Γ_3	$V^4{}_1$	(1 0 0)	(1 0 0)	(0 1 0)	(0 1 0)	(−1 −1 0)	(−1 −1 0)
	$V^4{}_2$	(0 0 1)	(0 0 −1)	(0 0 1)	(0 0 −1)	(0 0 1)	(0 0 −1)
Γ_4	$V^3{}_1$	(1 2 0)	(1 2 0)	(−2 −1 0)	(−2 −1 0)	(1 −1 0)	(1 −1 0)

Γ_1



Γ_2

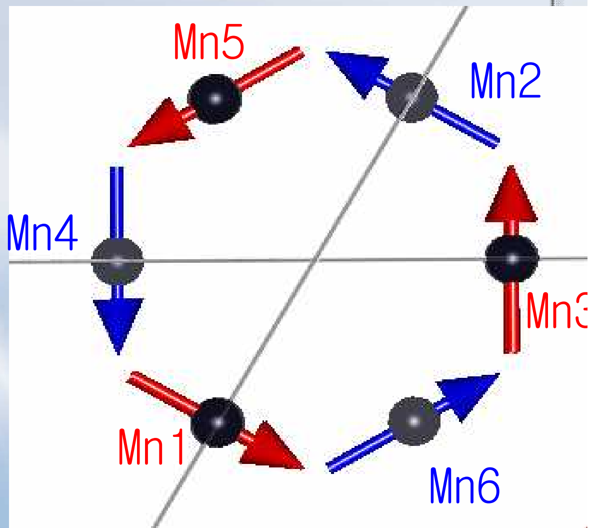


Repr. irred.	Basis Vector	6c site					
		(x, 0, 0)	(-x+1, 0, 1/2)	(0, x, 0)	(0, -x+1, 1/2)	(-x+1, -x+1, 0)	(x, x, 1/2)
Γ_1	V^2_1	(1 2 0)	(-1 -2 0)	(-2 -1 0)	(2 1 0)	(1 -1 0)	(-1 1 0)

Name	Mom(sMo)	Phi(sPhi)	Tet(sTet)	MPhas sMPhas
	Mx (sMx)	My(sMy)	Mz(sMz)	
Mn1	3.314(0.032)	90.000(0.000)	90.000(0.000)	0.0000(0)
	1.914(0.019)	3.827(0.037)	0.000(0.000)	
Mn2	3.314(0.032)	270.000(0.000)	90.000(0.000)	0.0000(0)
	-1.914(0.019)	-3.827(0.037)	0.000(0.000)	
Mn3	3.314(0.032)	210.000(0.000)	90.000(0.000)	0.0000(0)
	-3.827(0.037)	-1.914(0.019)	0.000(0.000)	
Mn4	3.314(0.032)	390.000(0.000)	90.000(0.000)	0.0000(0)
	3.827(0.037)	1.914(0.019)	0.000(0.000)	
Mn5	3.314(0.032)	330.000(0.000)	90.000(0.000)	0.0000(0)
	1.914(0.019)	-1.914(0.019)	0.000(0.000)	
Mn6	3.314(0.032)	510.000(0.000)	90.000(0.000)	0.0000(0)
	-1.914(0.019)	1.914(0.019)	0.000(0.000)	

Z=0;Mn1,Mn3,Mn5
Z=1/2;Mn2,Mn4,Mn6

120o, trangle
:Mn1,Mn3,Mn5
:Mn2,Mn4,Mn6



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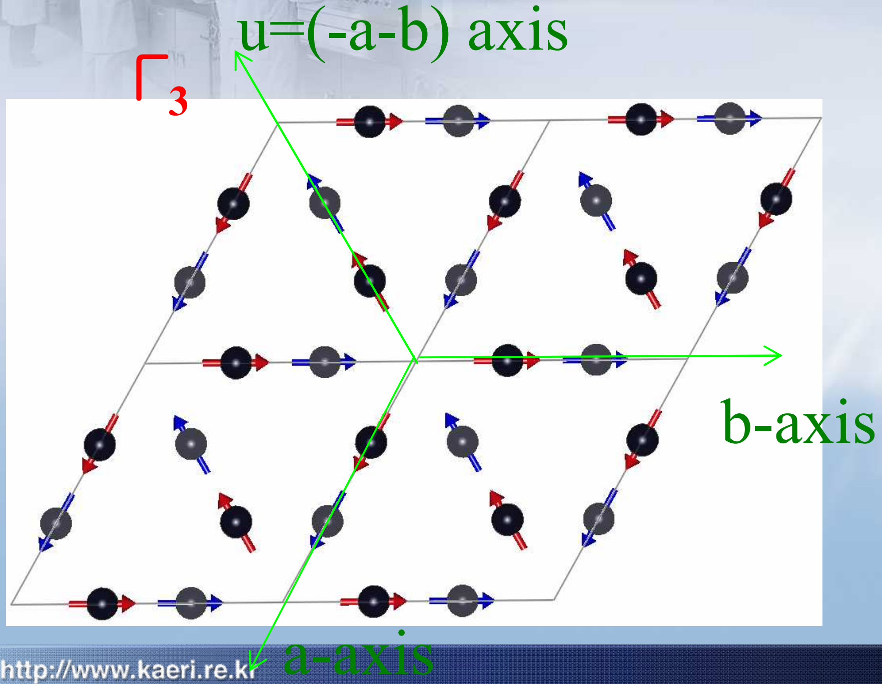
Possible magnetic structure of hexagonal manganites

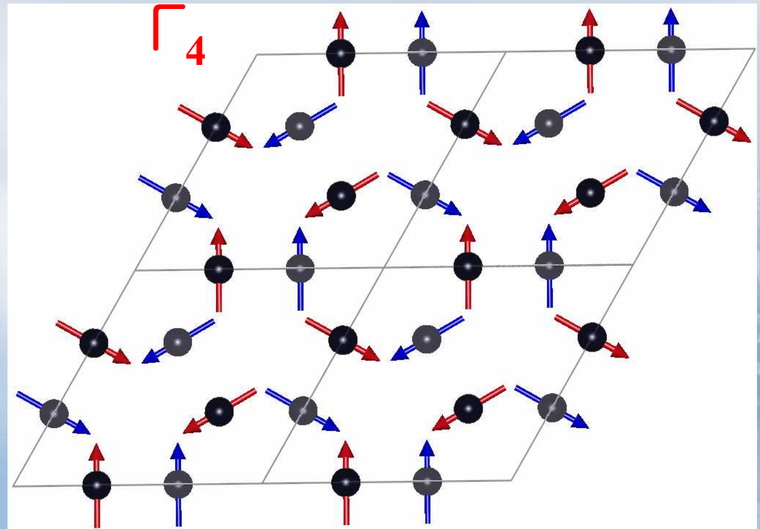
$\Gamma = \Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + \Gamma_4 + 3\Gamma_5 + 3\Gamma_6$

Repr. irred.	Basis Vector	6c site					
		(x, 0, 0)	(-x+1, 0, 1/2)	(0, x, 0)	(0, -x+1, 1/2)	(-x+1, -x+1, 0)	(x, x, 1/2)
Γ_1	V^2_1	(1 2 0)	(-1 -2 0)	(-2 -1 0)	(2 1 0)	(1 -1 0)	(-1 1 0)
Γ_2	V^1_1	(1 0 0)	(-1 0 0)	(0 1 0)	(0 -1 0)	(-1 -1 0)	(1 1 0)
	V^1_2	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)
Γ_3	V^4_1	(1 0 0)	(1 0 0)	(0 1 0)	(0 1 0)	(-1 -1 0)	(-1 -1 0)
	V^4_2	(0 0 1)	(0 0 -1)	(0 0 1)	(0 0 -1)	(0 0 1)	(0 0 -1)
Γ_4	V^3_1	(1 2 0)	(1 2 0)	(-2 -1 0)	(-2 -1 0)	(1 -1 0)	(1 -1 0)

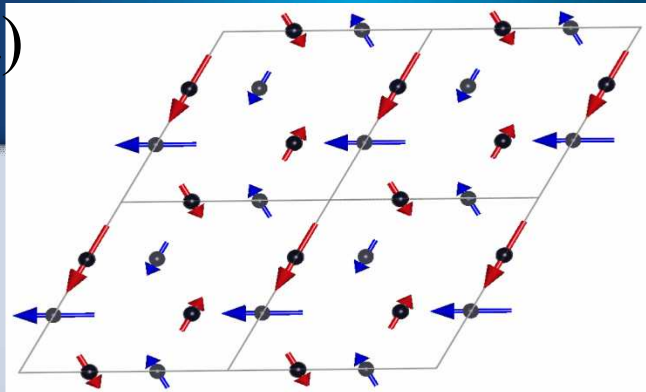
Γ_3



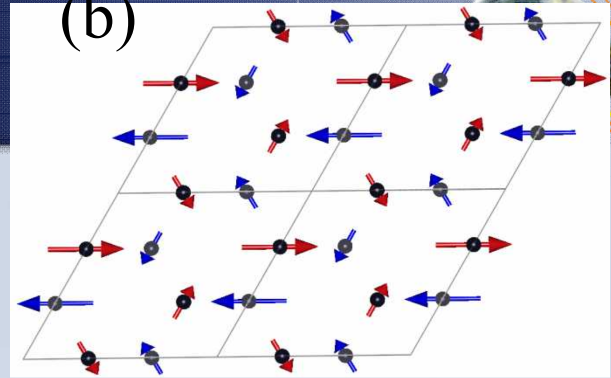
Γ_4



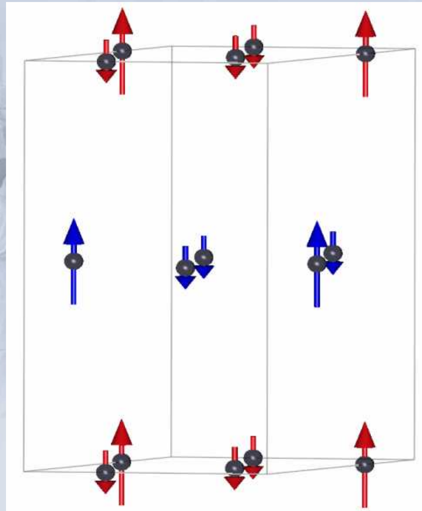
(a)



(b)

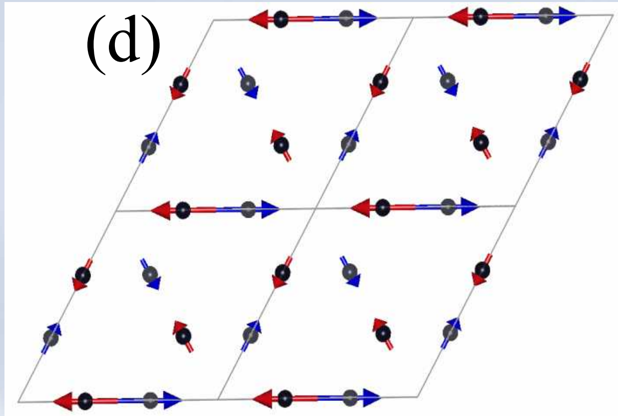


(c)

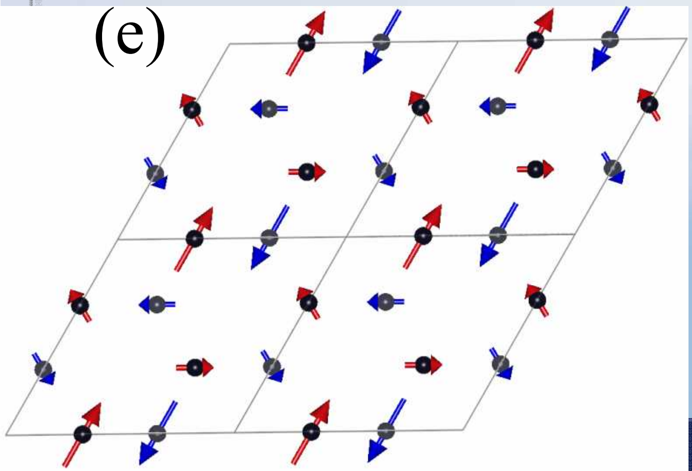


Γ_5 magnetic structure
2D

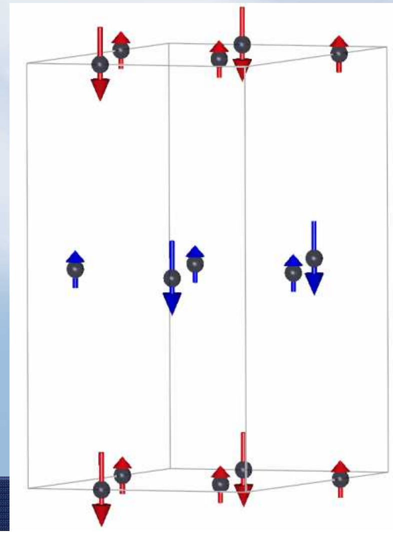
(d)



(e)

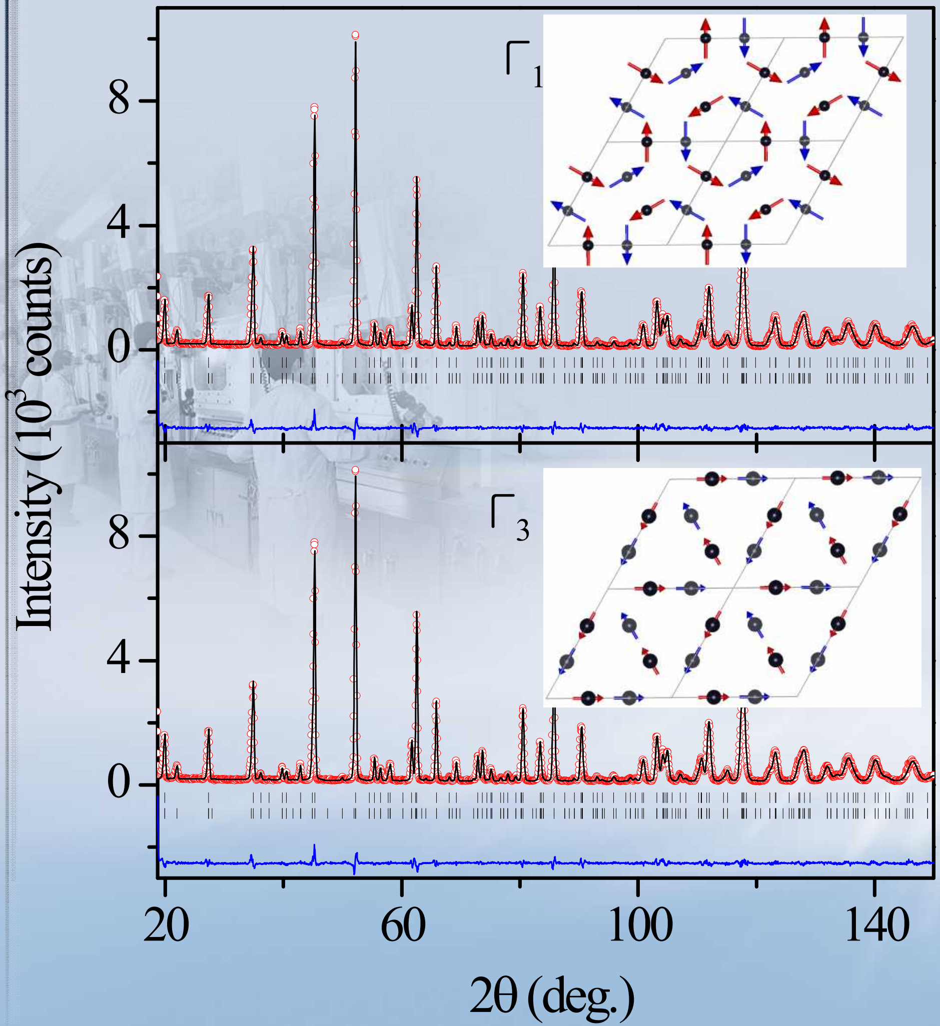


(f)



Refinement results of $YMnO_3$

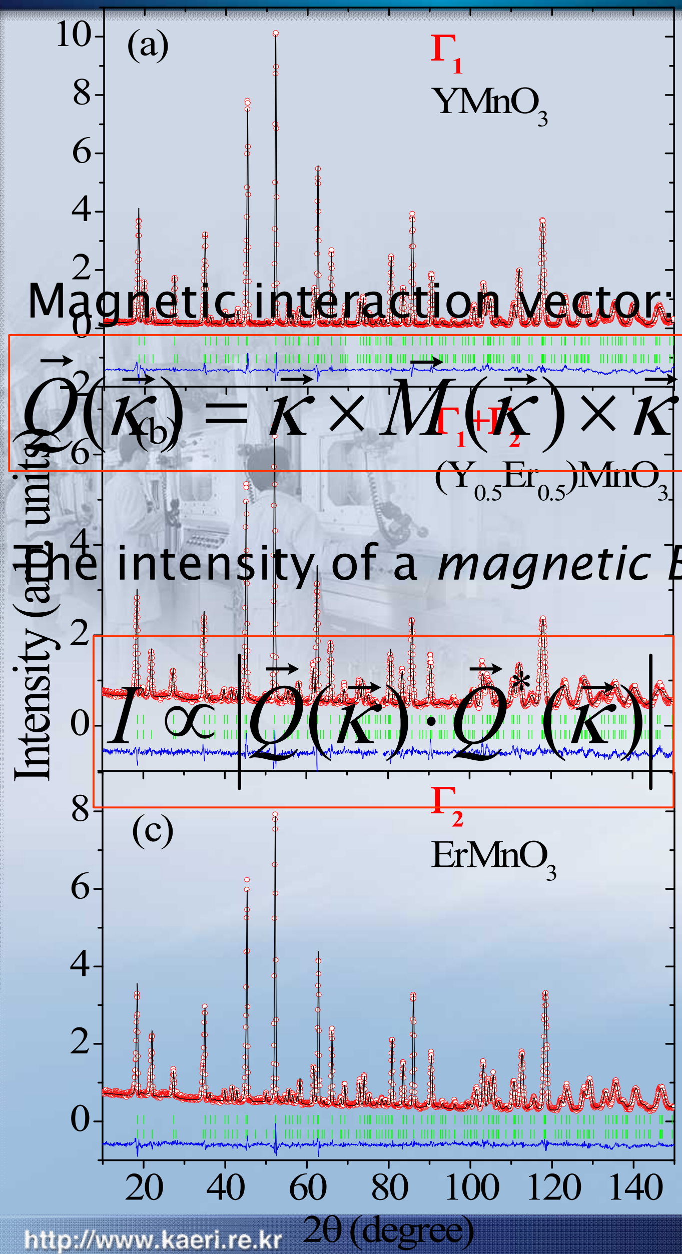
Junghwan Park, JGP et al.,
Applied Physics A (2002)



Γ_1	Γ_3
a (Å) = 6.1208(1) b (Å) = 11.4015(2) V (Å^3) = 369.91(1)	a (Å) = 6.1208(1) b (Å) = 11.4015(2) V (Å^3) = 369.91(1)
Magnetic Moment (μ_B) 3.30(2)	Magnetic Moment (μ_B) 3.25(2)
Reliability factors R_p = 5.79 % R_{wp} = 7.93 % R_{mag} = 7.88 % χ^2 = 2.70	Reliability factors R_p = 5.83 % R_{wp} = 7.98 % R_{mag} = 7.35 % χ^2 = 2.74

Magnetic structure of $ErMnO_3$
: Γ_2 or Γ_4

Commensurate Magnetic structure of (YEr)MnO_3

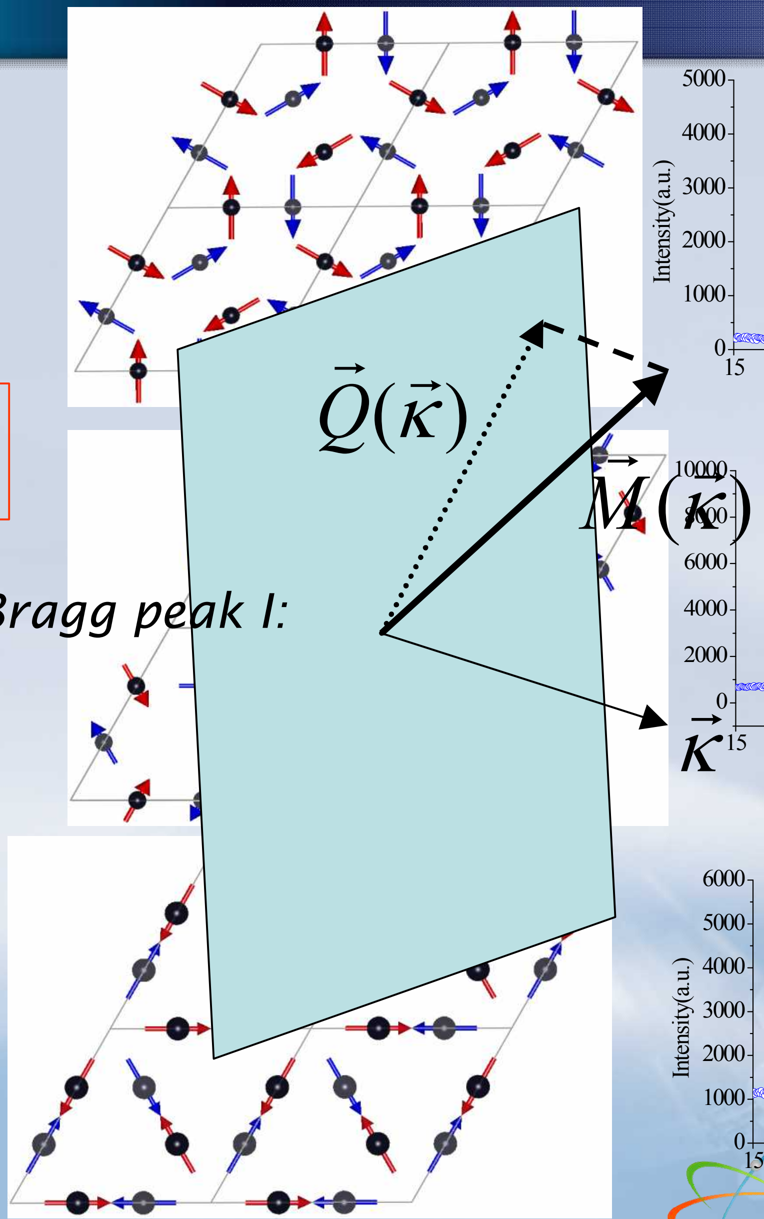


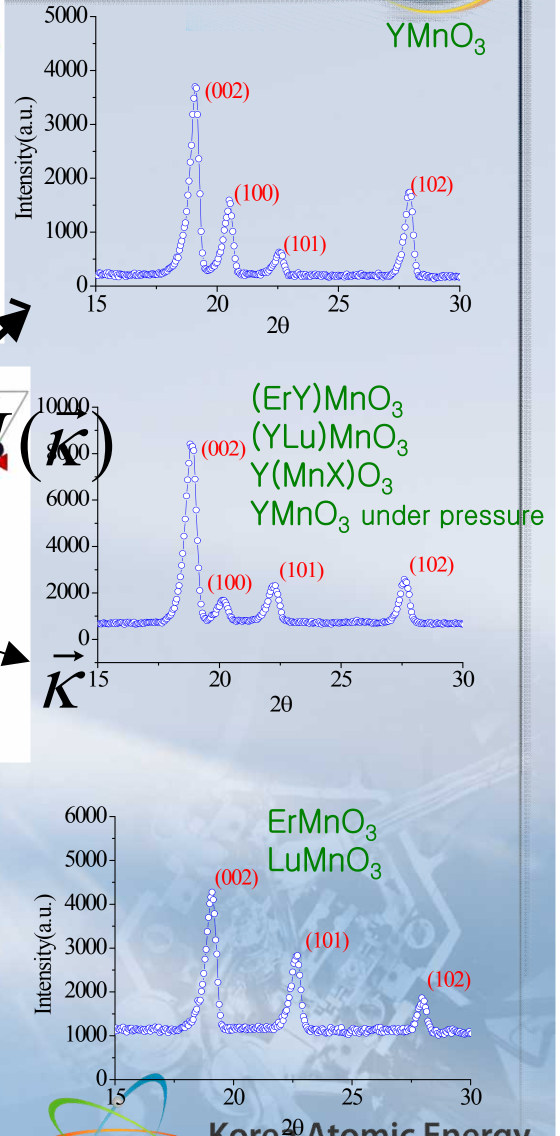
Magnetic interaction vector:

$$\vec{Q}(\vec{\kappa}) = \vec{\kappa}\times\vec{M}(\vec{\kappa})\times\vec{\kappa}$$

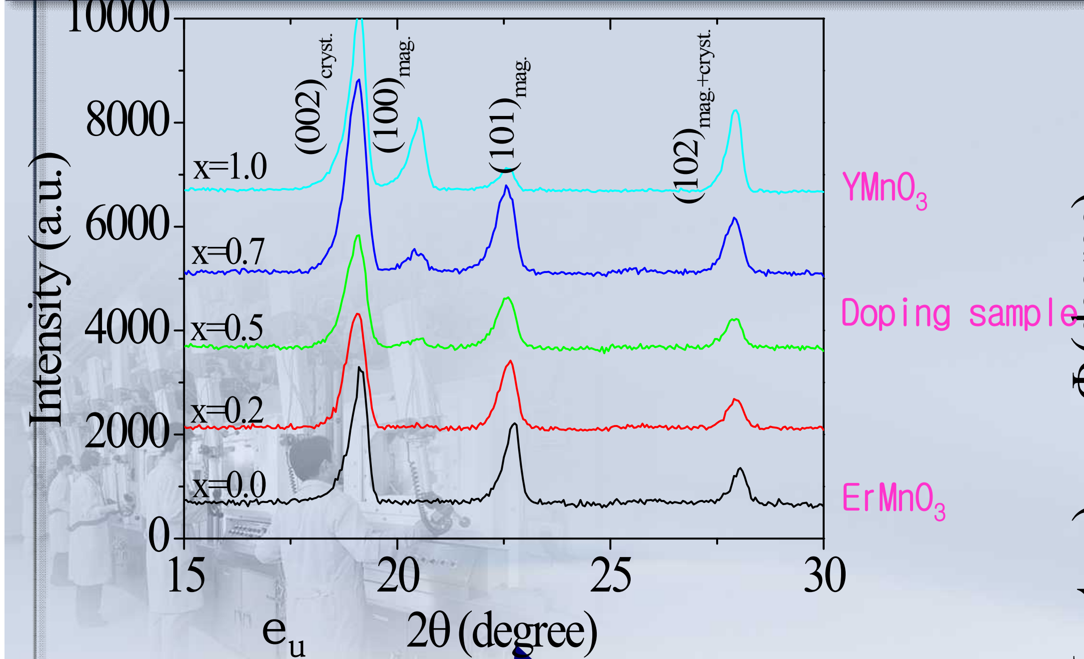
The intensity of a *magnetic Bragg peak I:*

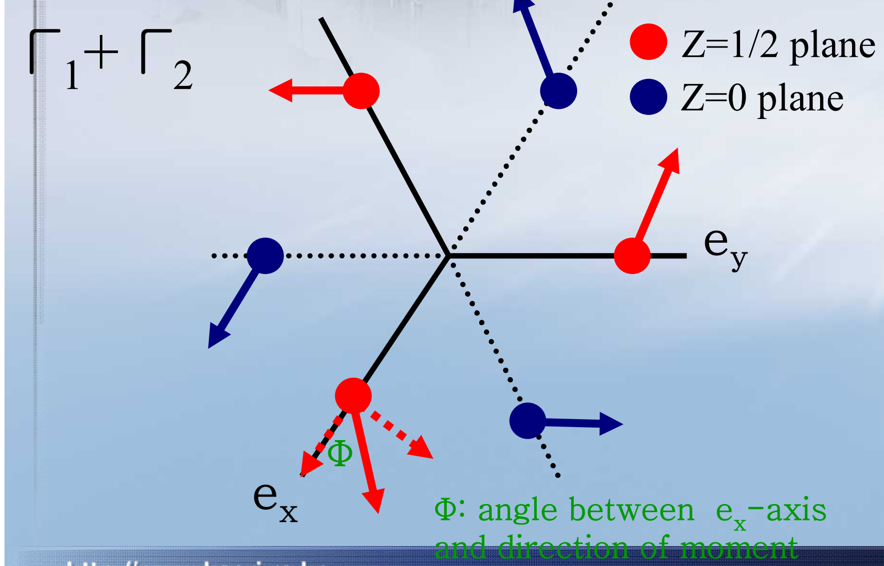
$$I \propto \left|\vec{Q}(\vec{\kappa})\cdot\vec{Q}^{*}(\vec{\kappa})\right|$$

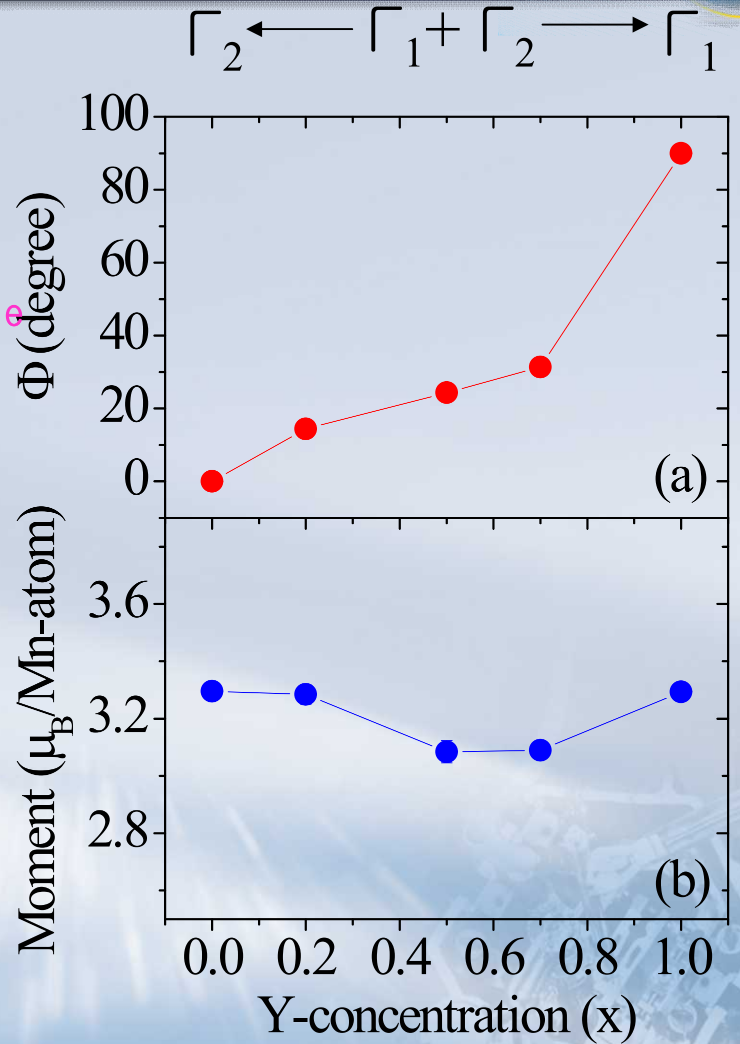




Doping effects of Magnetic structure







Summary : Magnetic Structure of Hexagonal Manganites

	Γ_1 or Γ_3	Γ_2 or Γ_4	$\Gamma_1 + \Gamma_2$
$YMnO_3$	O		
$ErMnO_3$		O	
$LuMnO_3$		O	
$(YEr)MnO_3$			O
$(YLu)MnO_3$			O
$YMnO_3$ under pressure			O
$Y(XMn)O_3$			O

Amorphous–crystalline state transformation induced by annealing in R2Fe14B (R = Nd, Er) compounds

Nd2Fe14B compound possess record values of maximal magnetic energy product

Annealing effects

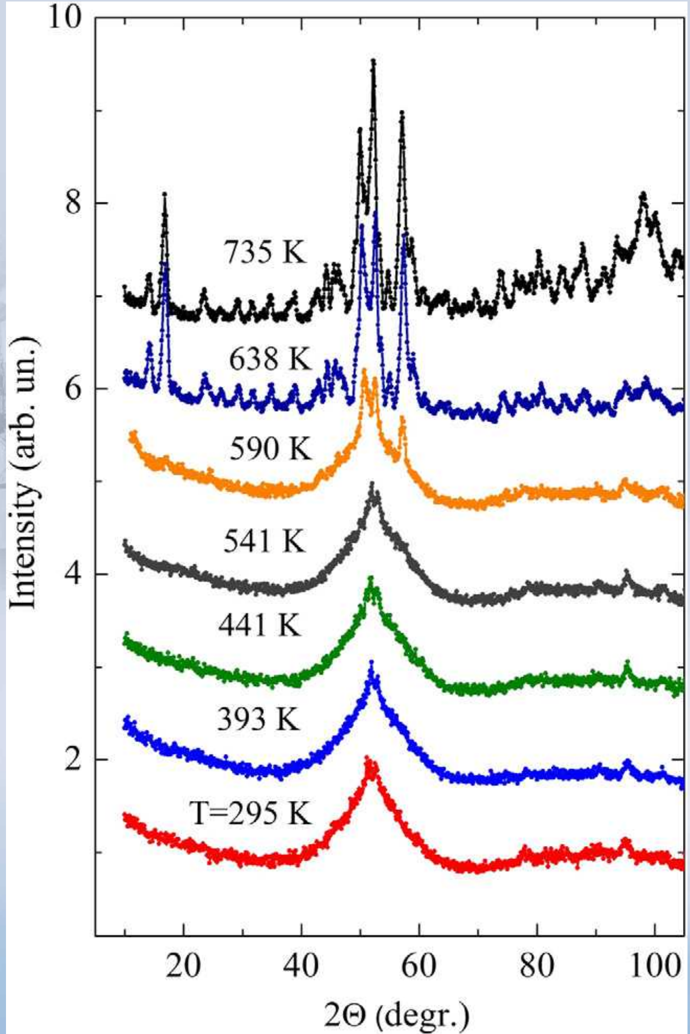


Fig. 1. Evolution of observed neutron powder diffraction patterns of the Er2Fe14B alloy with annealing temperature.

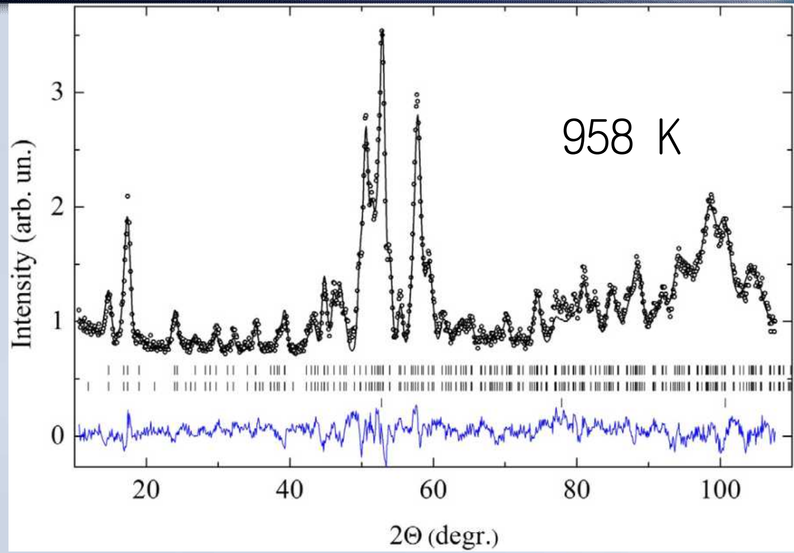


Table 1
Lattice constants *a*, *b*, *c* and unit cell volume *V*, coordinates of positions (space group $P4_2/mnm$), the average Er- and Fe-ion magnetic moments μ_x^{Er} and μ_x^{Fe}, magnetization per formula unit *M*, contents of the $Nd_2Fe_{14}B$-type and α-Fe phases, agreement factor of magnetic structure R^m_{Bragg} and χ^2 for the crystalline and annealed $Er_2Fe_{14}B$ samples at room temperature.

Structural parameter	Sample	
	Initial crystalline	Annealed at T_{an} = 993 K
a,b (nm)	0.8744(1)	0.8725(1)
c (nm)	1.1968(2)	1.1973(2)
V (nm^3)	0.9143(5)	0.9116(5)
Er, 4*f*: *x*	0.273(1)	0.265(1)
Er, 4*g*: *x*	0.147(1)	0.141(1)
Fe, 4*e*: *z*	0.112(1)	0.116(1)
Fe, $8j_1$: *x*	0.097(1)	0.097(1)
z	0.201(1)	0.203(1)
Fe, $8j_2$: *x*	0.318(1)	0.316(1)
z	0.249(1)	0.247(1)
Fe, $16k_1$: *x*	0.222(1)	0.224(1)
y	0.567(1)	0.566(1)
z	0.127(1)	0.128(1)
Fe, $16k_2$: *x*	0.036(1)	0.035(1)
y	0.360(1)	0.358(1)
z	0.170(1)	0.171(1)
B, 4*g*: *x*	0.636(2)	0.630(2)
μ_x^{Er} (μ_B)	−4.1(1)	−3.6(2)
μ_x^{Fe} (μ_B)	1.9(1)	1.8(1)
M (μ_B)	18.4(3)	17.8(4)
$Nd_2Fe_{14}B$-phase, weight%	98.0	84.0
α-Fe, weight%	2.0	16
R^m_{Bragg} (%)	5.5	7.9
χ^2	4.46	4.03

Annealing effects

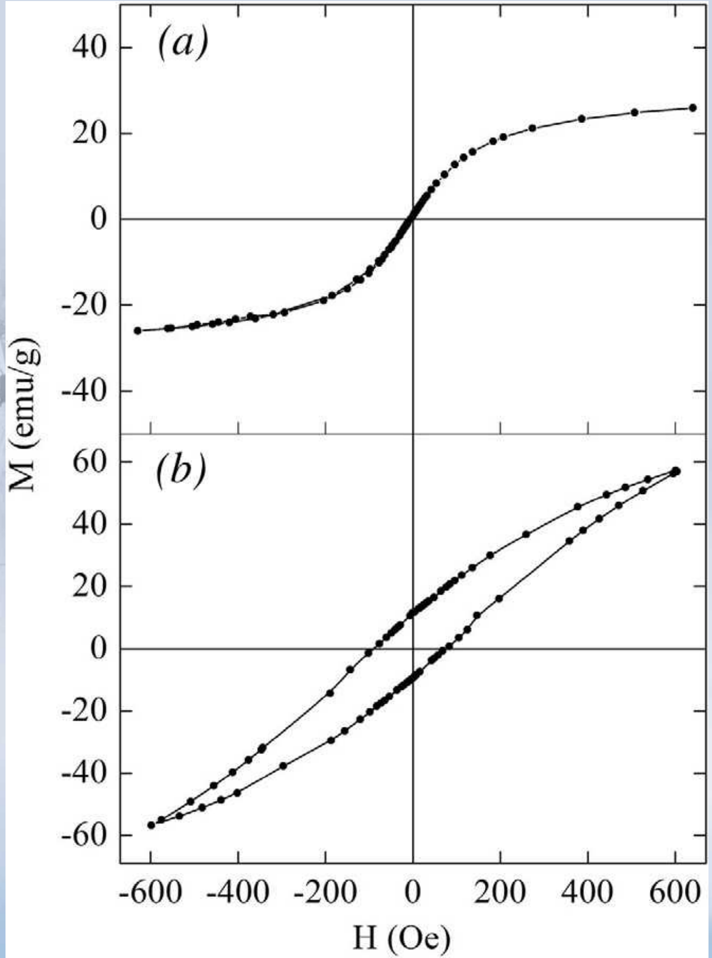


Fig. 3. Hysteresis loops for Er2Fe14B at (a) 393 K and (b) 958 K.

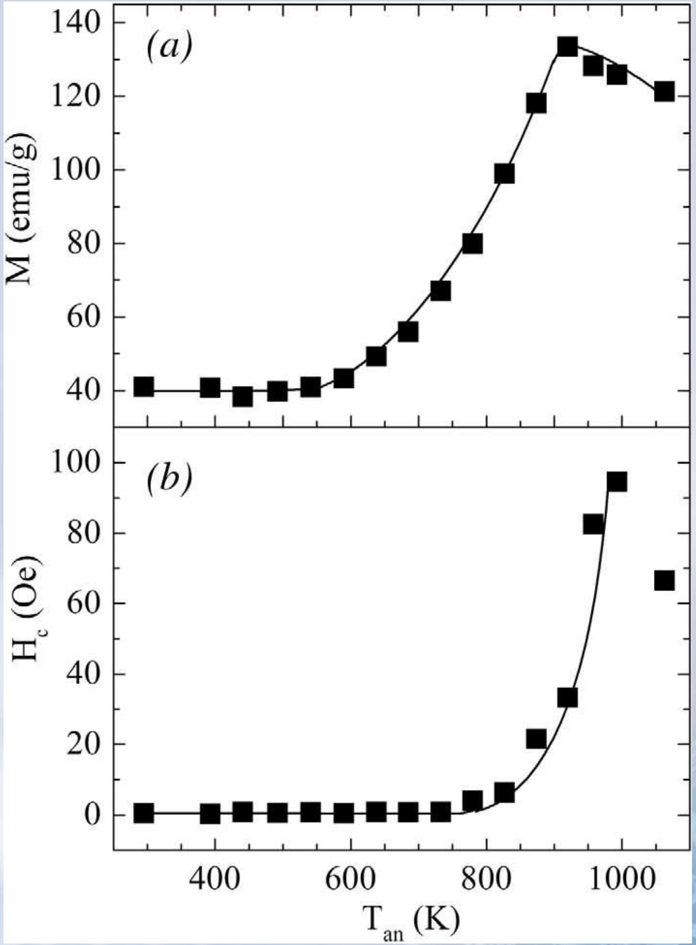


Fig. 4. Dependencies of (a) magnetization and (b) coercive field of the Er2Fe14B on annealing temperature.

Annealing effects

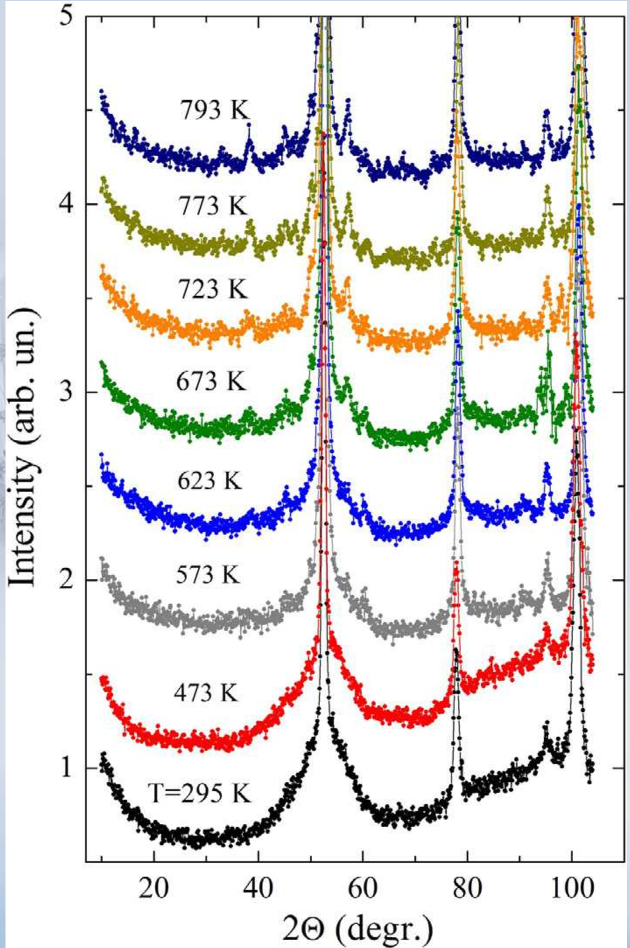


Fig. 5. Evolution of observed neutron powder diffraction patterns of the Nd2Fe14B alloy with annealing temperature

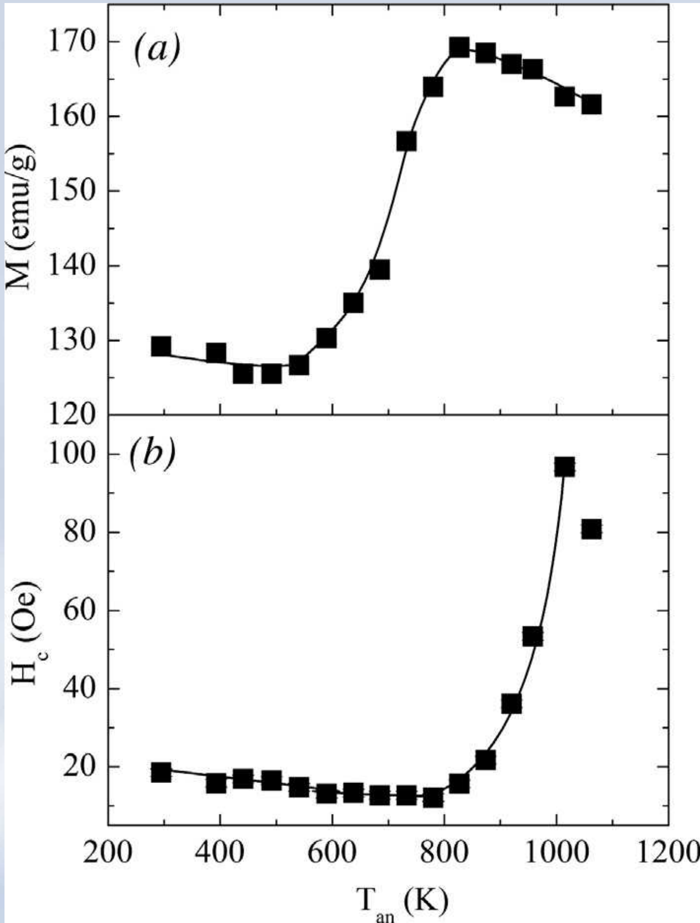


Fig. 6. Dependencies of (a) magnetization and (b) coercive field of the Nd2Fe14B on annealing temperature.

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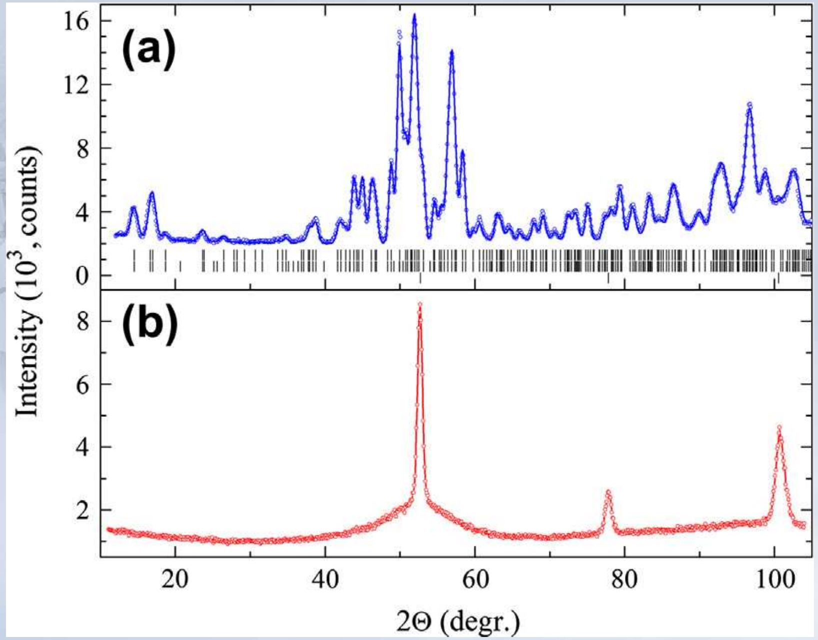
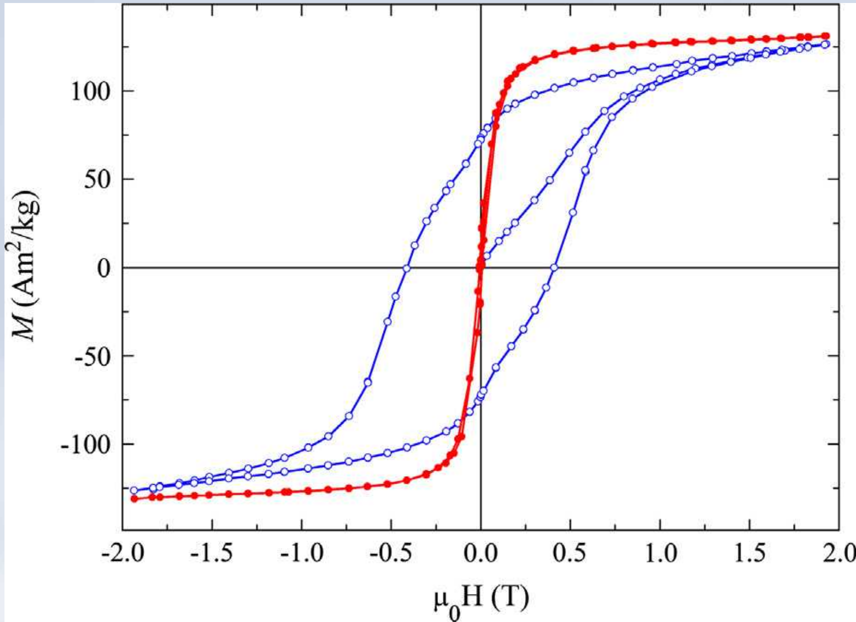
Neutron irradiation



Neutron diffraction patterns of the Nd12Fe82B6 sample at room temperature before (a) and after (b) neutron irradiation.



Magnetization curves of the Nd12Fe82B6 sample at room temperature before (open circles) and after (filled circles) neutron irradiation.

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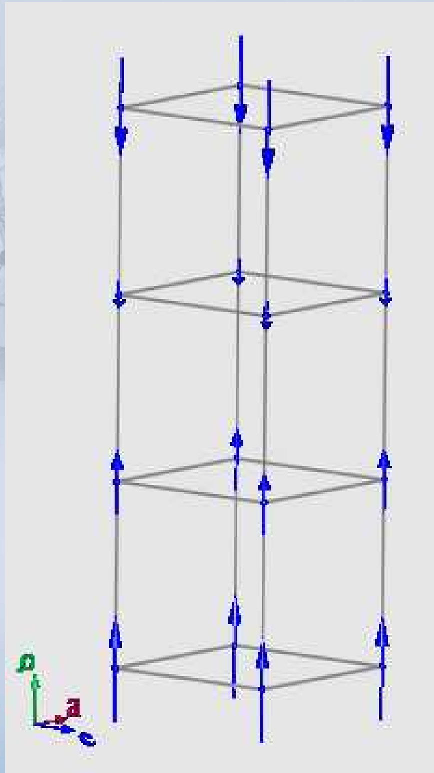
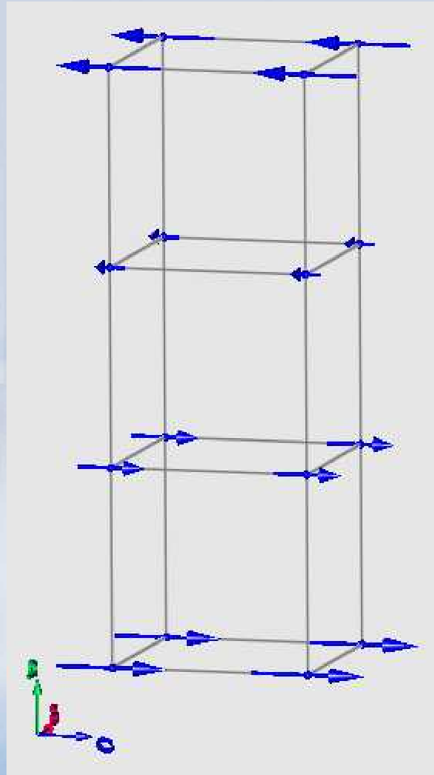
3rd example for neutron powder diffraction

Incommensurate magnetic structure

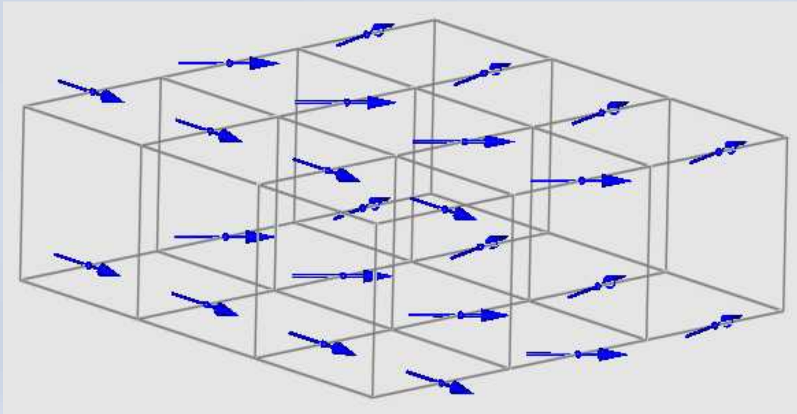
longitudinal SDW



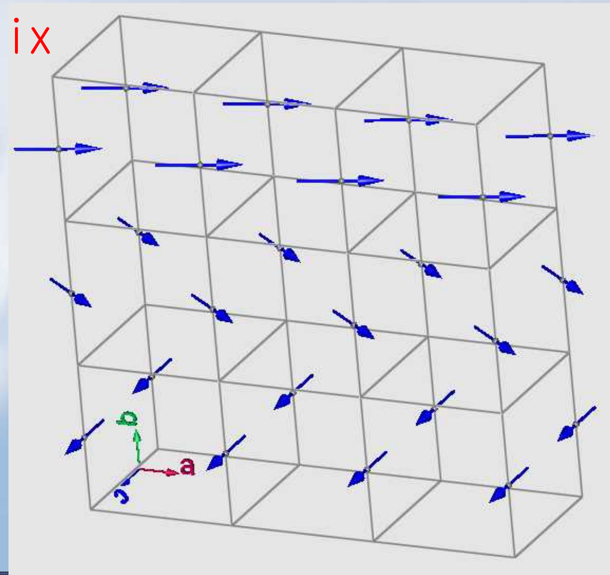
transverse SDW



cycloid



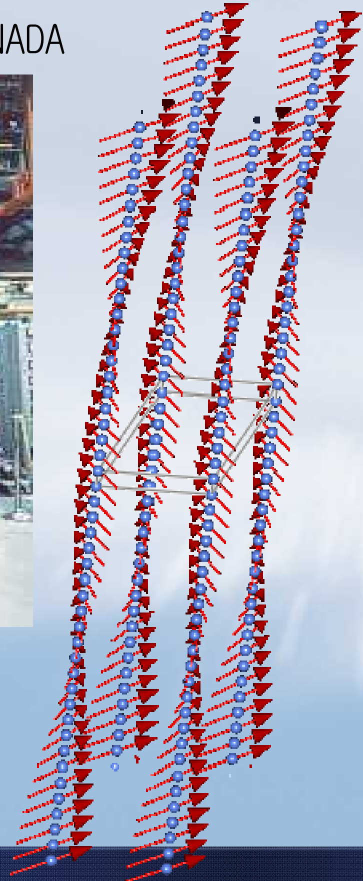
helix



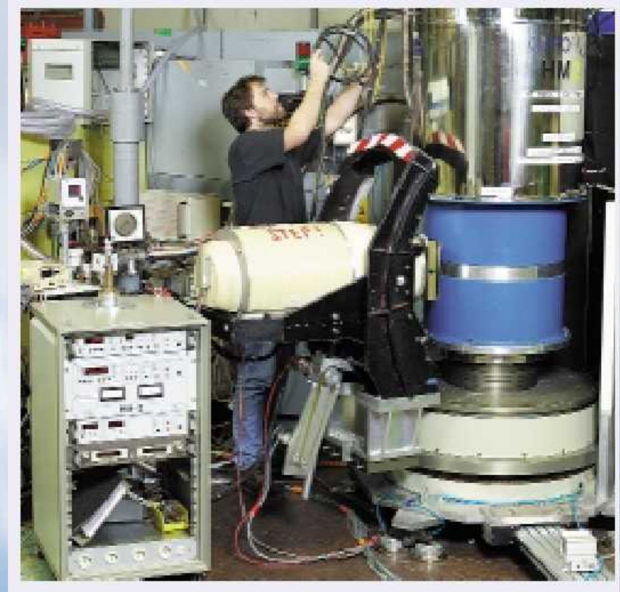
Magnetic phase transition in $TbNi_5$: bulk properties and neutron diffraction studies

Seongsulee *et al.* JETP Letters, Vol. **82**, (2005)
A.P. Vokhmyanin *et al.* JMMM accepted (2005)
Seongsulee *et al.* Europhys. Lett., **62**, 350 (2003)

Powder neutron diffraction
The C2 Spectrometer : NRC-CNRC CANADA



Single crystal neutron diffraction
the double-axis E-4 diffractometer
at the BENSC, Hahn-Meitner Institute Germa



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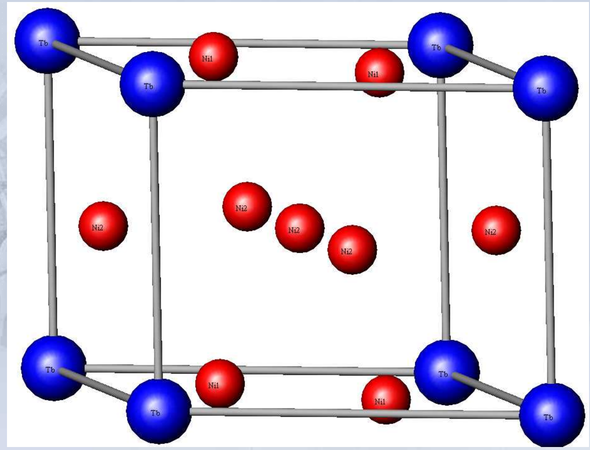
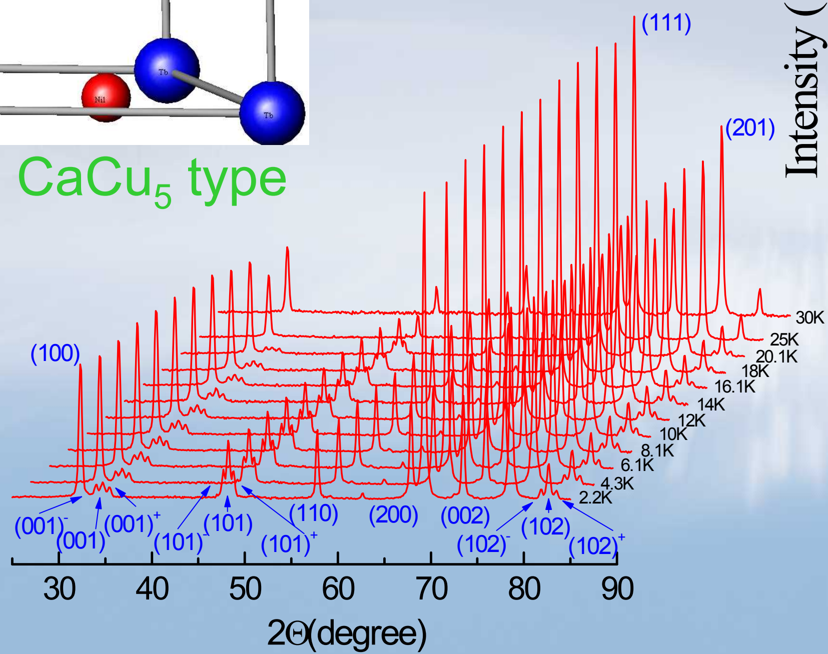
Neutron diffraction

Space group : hexagonal P6/mmm
a=4.8998Å c=3.9599Å
Neutron wave length=2.37Å

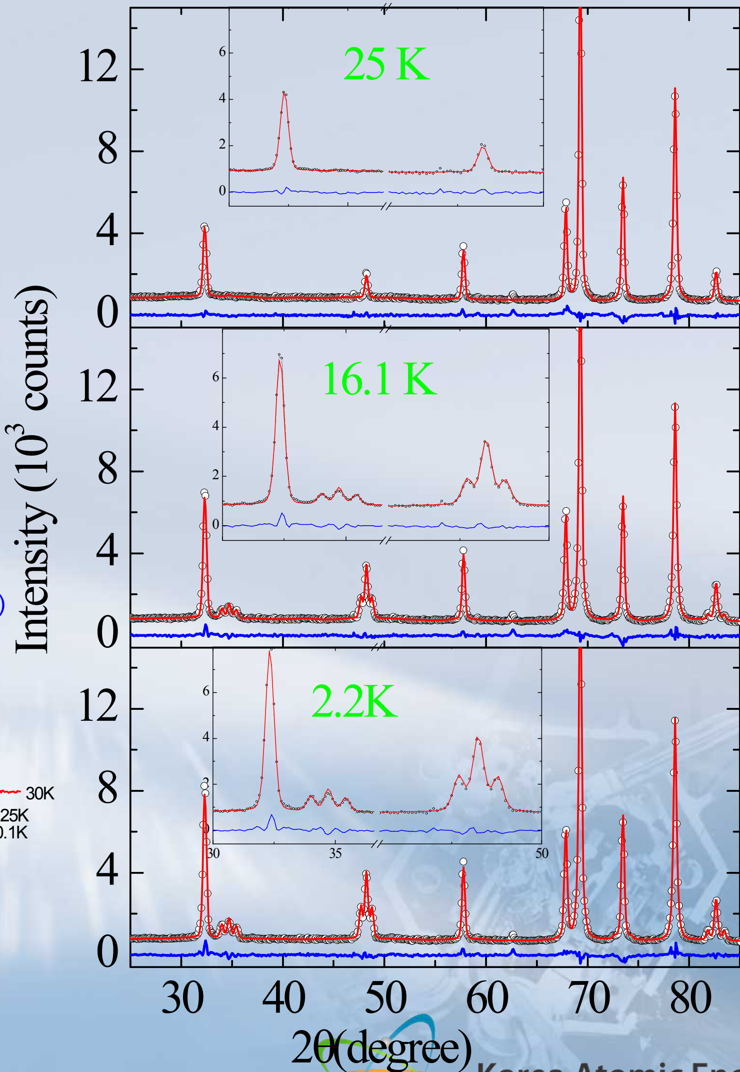


Hexagonal $CaCu_5$ type



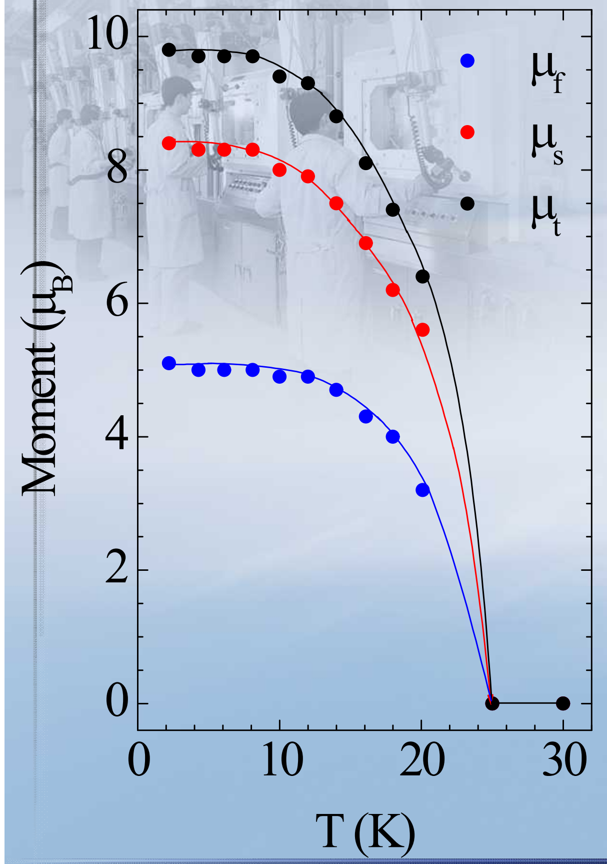
Neutron diffraction pattern

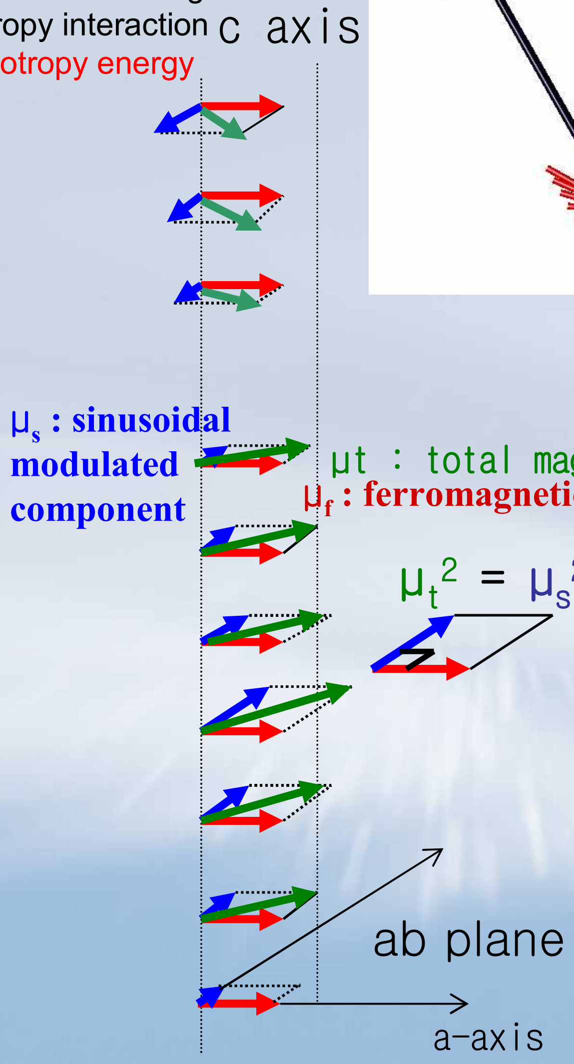
Refinement results

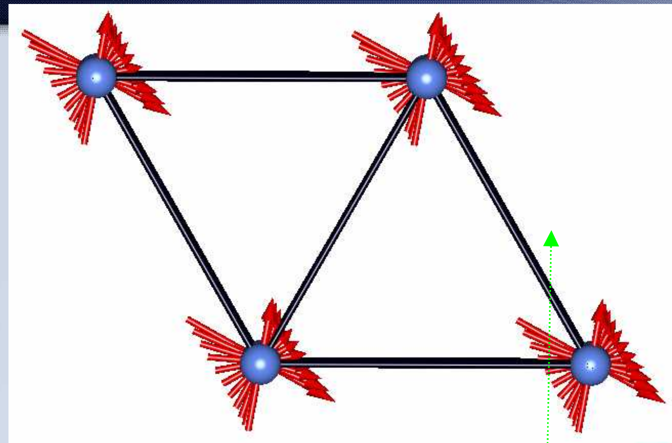


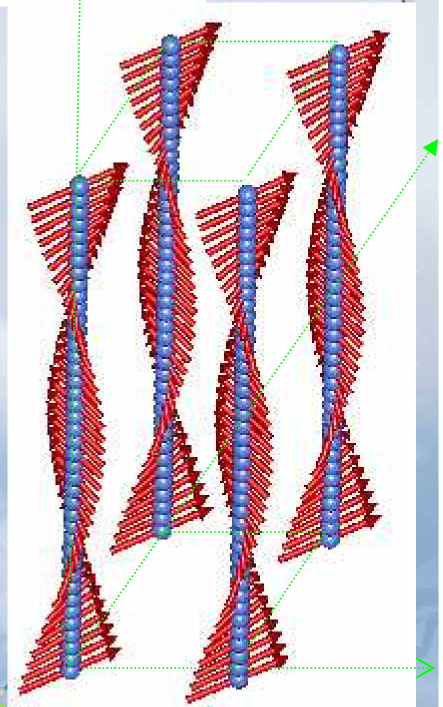
FAN-like magnetic structure

Modulated magnetic structure
: Ex. competition between the non-local RKKY exchange interaction and the local magnetic anisotropy interaction
$TbNi_5$ completion between magnetic anisotropy energy and exchange energy









FAN-like magnetic structure

$$\vec{S}_{nj} = \vec{S}_{0j} \bullet \exp(i\vec{k} \bullet \vec{t}_n)$$

$$\tau = \frac{2\pi}{c}(0, 0, 0.018)$$

$$phase(\text{between 1st and 2nd atom}) = 2\pi\tau \approx 7^\circ$$

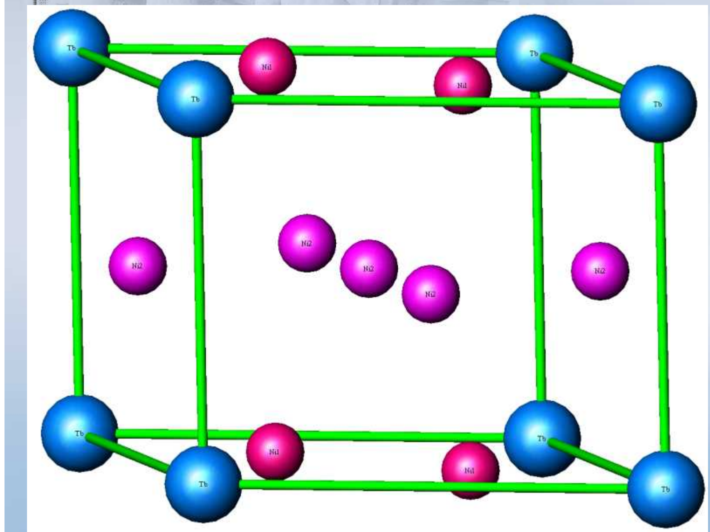
$$\text{magnetic unit cell along c} = 200\,\mathring{A}$$

Reason of large magnetic unit cell

1st: magnetic anisotropy energy >> exchange energy

2nd: smaller magnetic anisotropy energy in the basal plane

Crystal unitcell

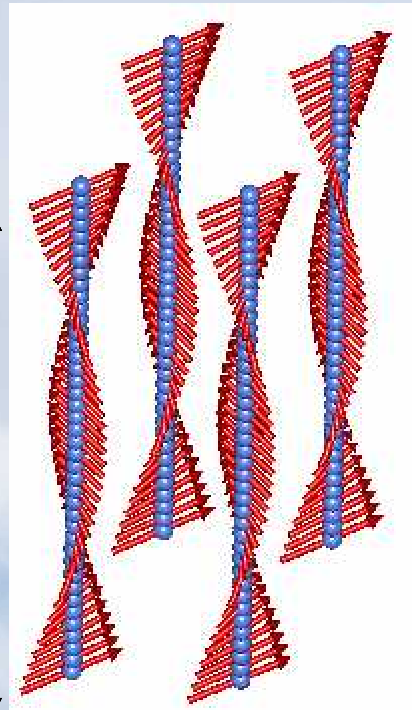


c ~4Å

~50*c

~200Å

Magnetic unitcell



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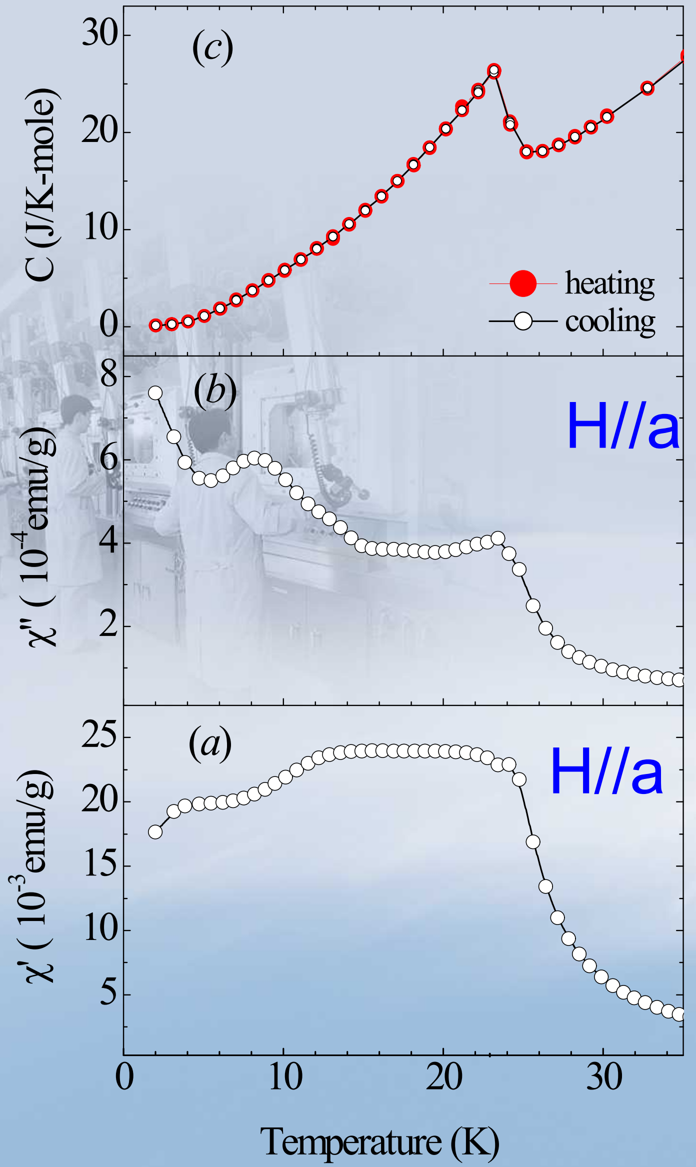
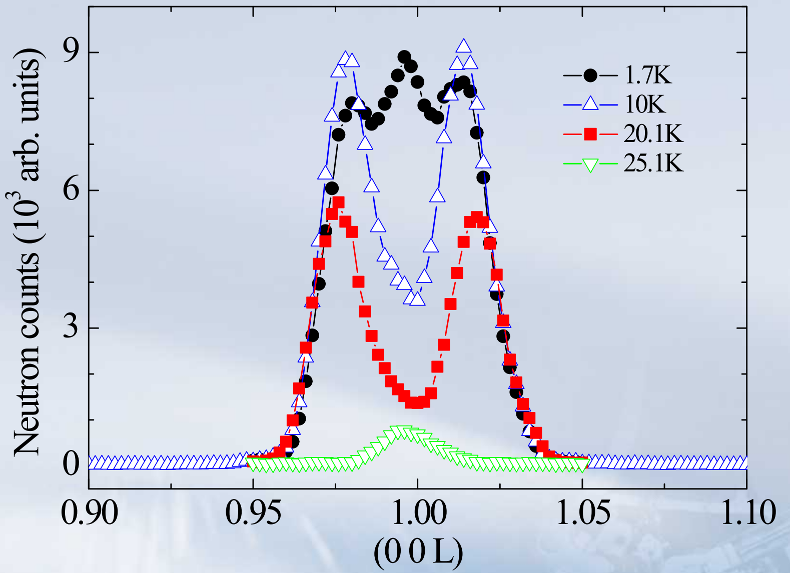
Bulk properties: single crystal: magnetic structure



Neutron diffraction

(001) reflection temperature dependence



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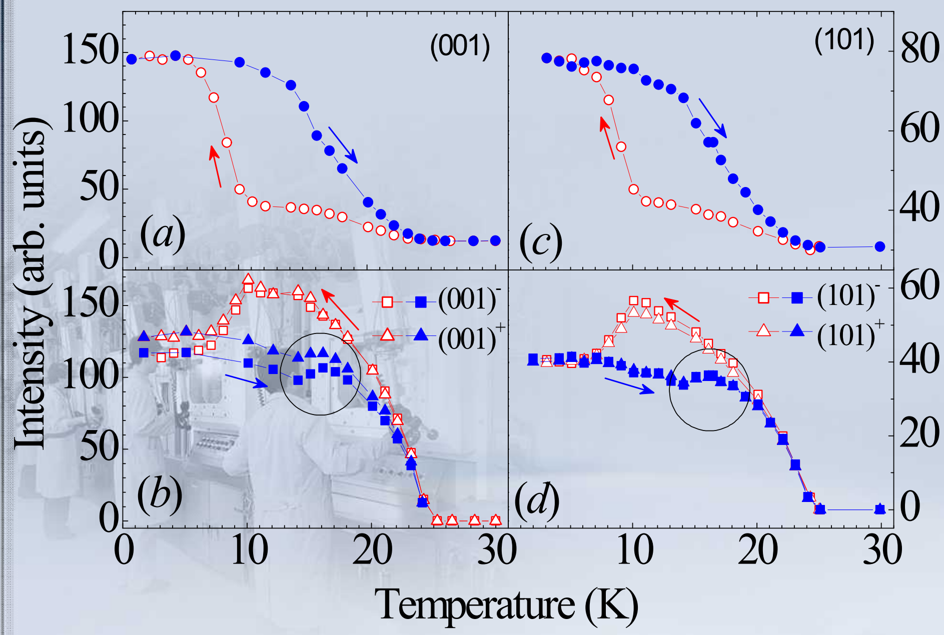
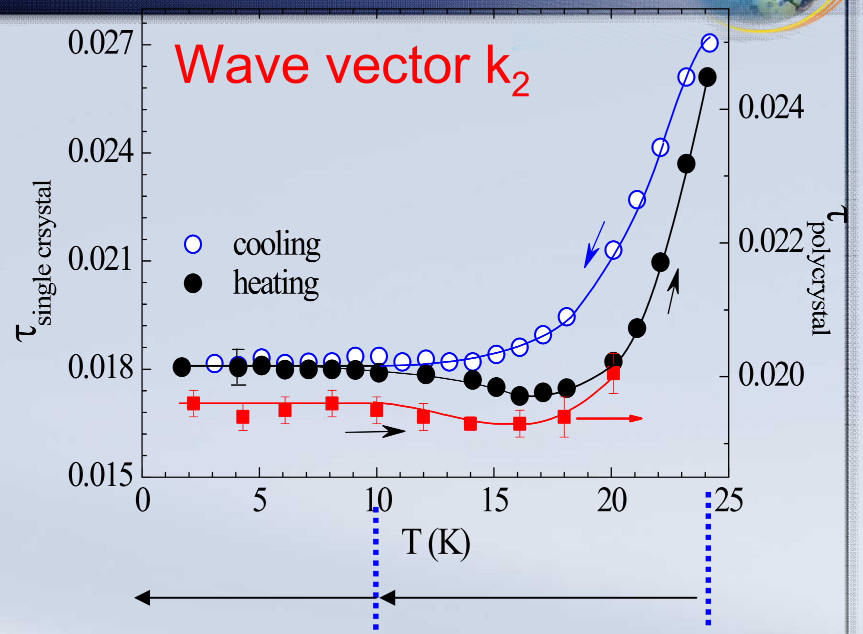
Bulk properties: single crystal: magnetic structure

Integrated peak intensity



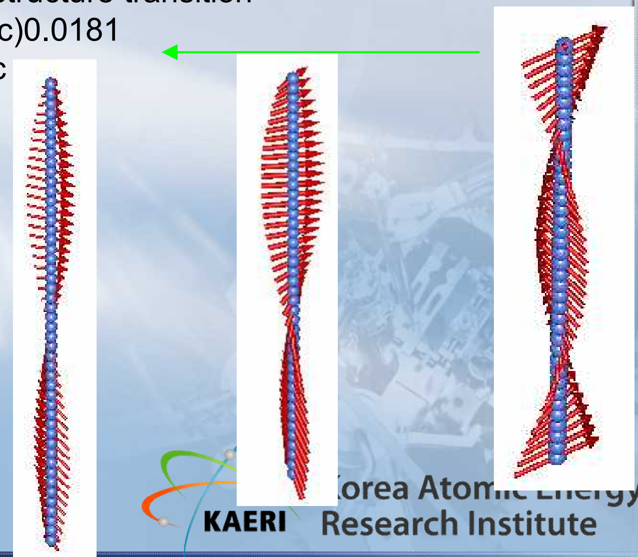


Lock-in structure transition

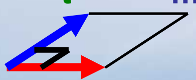
k_2~(2π/c)0.0181

~55*c

Order-disorder transitic



$\mu_t^2 = \mu_m^2 + \mu_f^2$



Below 10K, Increase magnetic anisotropy energy

->Increase component of easy axis (a-axis)

->decrease modulated magnetic moment

Summary

Neutron diffraction is very powerful and unique experiment tool for crystal and magnetic structure studies.

The reasonable neutron diffraction data and good refinement results should give us the clue of finding interesting physics of our system!

Thank you for your attention.

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