Magnetic structure and excitations in vanadates, $BaV_{10}O_{15}$ and CoV_2O_4

Sachith Dissanayake
(University of Virginia)

4th year research seminar

Outline

- **Introduction**

- Frustrated magnetism, , spin and orbital degrees of freedom
- neutron scattering basics

- **$BaV_{10}O_{15}$**

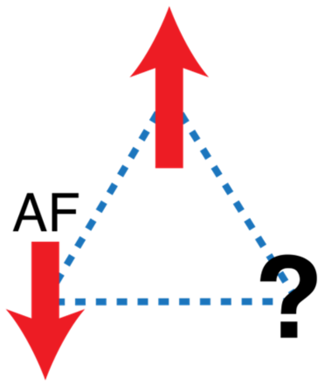
- Background
- Experimental data – Diffraction and Inelastic
- Results – Magnetic ground state and excitations
- Conclusions

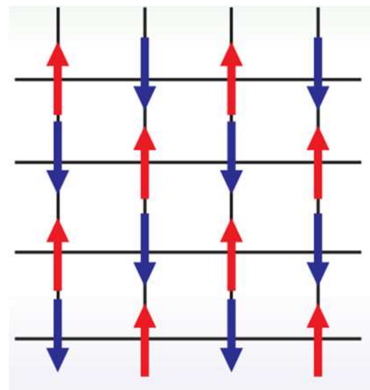
- **CoV_2O_4**

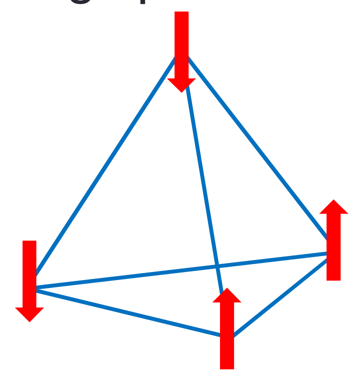
- Background
- Experimental data – Diffraction and Inelastic
- Results – Magnetic Structure and linear spin wave calculation
- Conclusions

What is Frustration?

Antiferromagnetically interacting spins







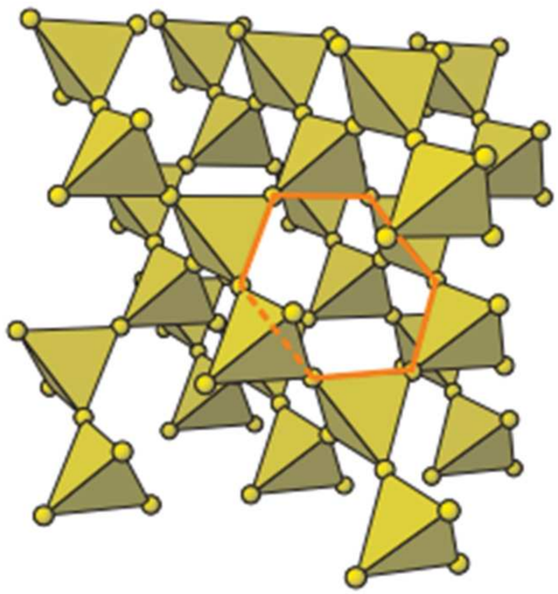
Triangular (2D)

Tetrahedral (3D)

- When a system is geometrically frustrated, absence of a unique ground state gives a finite entropy at absolute zero temperature.
- Some materials may have many nearly-degenerate ground states (a spin glass), or may retain dynamic disorder (a quantum spin liquid).
- Orbital degree of freedom can lift the degeneracy and drive the system into a particular ground state or reduce the frustration.

What is Frustration?

Roderich Moessner and Arthur P. Ramirez
Physics Today / Volume 59 / Issue 2 /



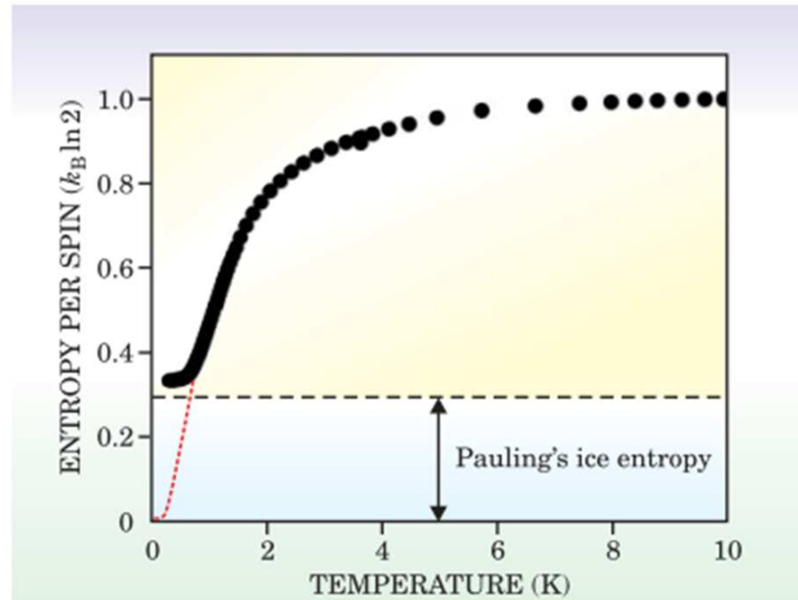
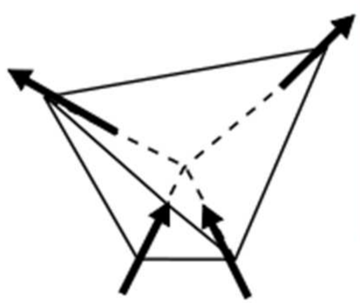


Figure 3. The entropy *S* of the spin-ice compound dysprosium titanate $Dy_2Ti_2O_7$ as a function of temperature *T*. At high *T*, $S = k_B \ln 2$ per spin, the same as for free spins. Cooling the system causes the entropy to drop as correlations develop between spins. An unfrustrated magnet follows the plot's schematic red line down to zero entropy because the system assumes a unique ground state. In spin ice, geometrical frustration creates an exponentially large number of degenerate ground states. The large degeneracy manifests itself in a non-vanishing entropy, which is close to the value that Linus Pauling predicted for ordinary water ice. (Adapted from ref. 5.)

Most degenerate- and thus most frustrated-lattice Readily realizable in three dimensions or less is one made up with corner sharing tetrahedra, the pyrocholre lattice.



Frustrated magnets

- Lies in two fundamental enterprises in condensed matter physics.

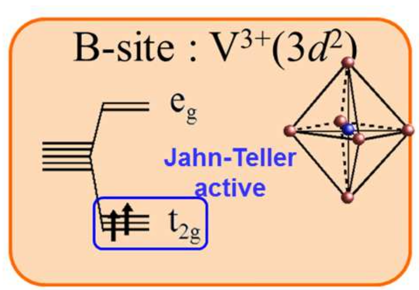
- On the applied side, the instabilities exhibited by frustrated magnets open a window on richness of nature realized in different materials

- On the fundamental side is the search for principles that help organize the variety of behavior we observed around us.

Jahn–Teller effect

- *Any nonlinear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species.*

- The Jahn–Teller effect is most often encountered in octahedral complexes of the transition metals.



Number of d electrons	1	2	3	4	5	6	7	8	9	10
High spin	w	w		s		w	w		s	
Low spin	w	w		w	w		s		s	

w: weak Jahn–Teller effect (t_{2g} orbitals unevenly occupied), **s**: strong Jahn–Teller effect expected (e_g orbitals unevenly occupied), **blank**: no Jahn–Teller

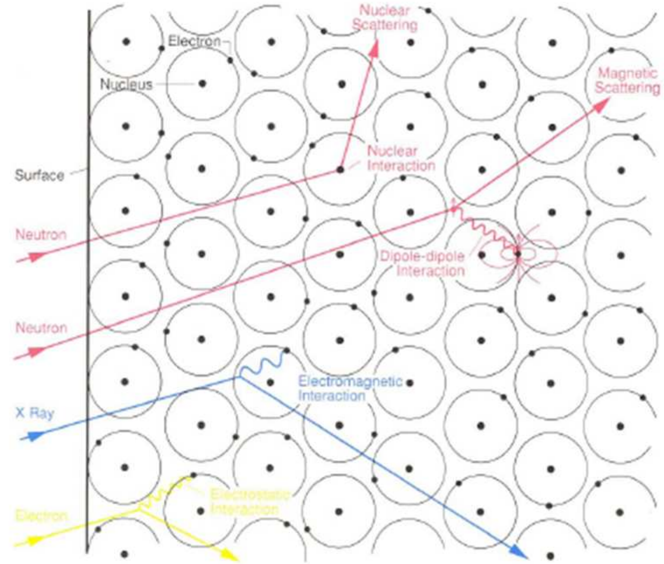
Neutron Scattering

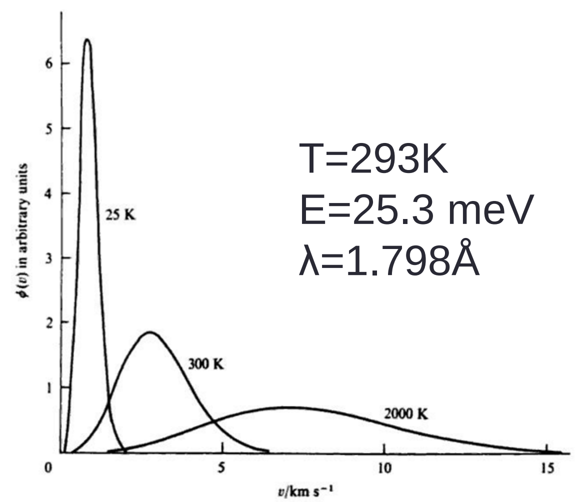
Why neutron?

1. **Zero net charge** makes neutron to penetrate deep inside the sample without being scattered by the electrons like X-ray, hence measuring bulk properties.

2. Its internal **magnetic moment** interact with the unpaired electrons spins in an atom via dipole-dipole interaction enabling direct measurement of magnetic moments.

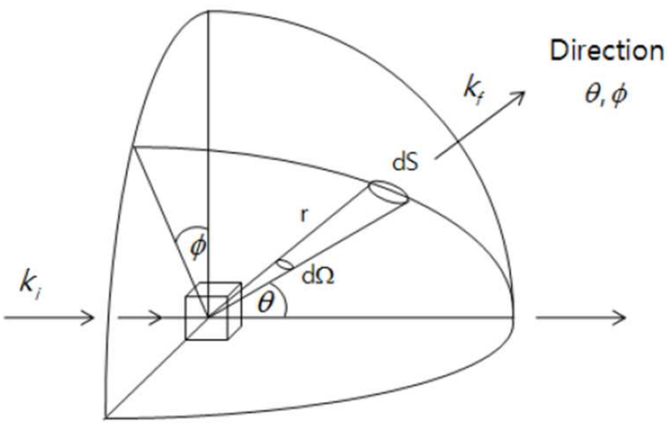
3. Due to **large neutron mass**, when moderated with water or liquid hydrogen, the kinetic energy becomes comparable to that of many elementary excitations in a solid.





Maxwell distribution of thermal neutron

What we measure



The scattering cross section, the actual number measured by the detector, is proportional to the scattering function, S(Q,ω) which is the Fourier transform of time dependent pair correlation function of either atomic density or spin component.

nuclear scattering

$$\frac{d^2\sigma}{d\Omega_f dE_f} = N\frac{k_f}{k_i}b^2 S(\vec{Q},\omega)$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar N}\sum_{ll'}\int_{-\infty}^{\infty} dt\langle e^{-i\vec{Q}\cdot\vec{r}_{l'}(0)}e^{i\vec{Q}\cdot\vec{r}_l(t)}\rangle e^{-i\omega t}$$
$$= \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty} dt\langle \rho_{\vec{Q}}(0)\rho_{-\vec{Q}}(t)\rangle e^{-i\omega t}.$$

$$\rho_{\vec{Q}}(t) = \sum_l e^{i\vec{Q}\cdot\vec{r}_l(t)}$$

magnetic scattering

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{N}{\hbar}\frac{k_f}{k_i}p^2 e^{-2W}\sum_{\alpha,\beta}(\delta_{\alpha,\beta} - \hat{Q}_\alpha\hat{Q}_\beta)S^{\alpha\beta}(\vec{Q},\omega)$$

$$S^{\alpha,\beta}(\vec{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{-i\omega t}\sum_l e^{i\vec{Q}\cdot\vec{r_l}}\langle S_0^\alpha(0)S_l^\beta(t)\rangle$$

$$pS = (\frac{\gamma r_0}{2})gf(\vec{Q})S$$

Neutron scattering

$$\vec{Q} = \vec{k}_i - \vec{k}_f \qquad \hbar\omega = \Delta E = \hbar/(2m_n)\left(k_i^2 - k_f^2\right)$$

- **Elastic Neutron Scattering (Neutron diffraction)**

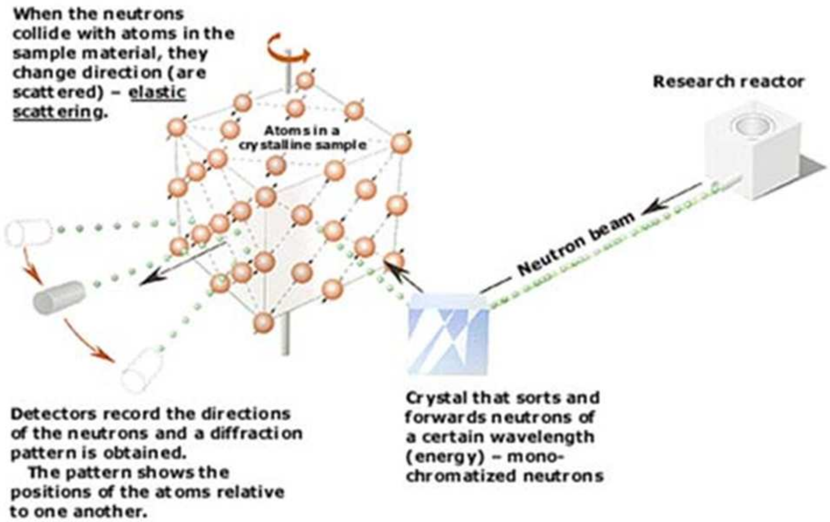
- Reveals the crystal structure.
- Reveals the microscopic magnetic structure

Instruments – Powder and single crystal diffractometer

- **Inelastic Neutron Scattering**

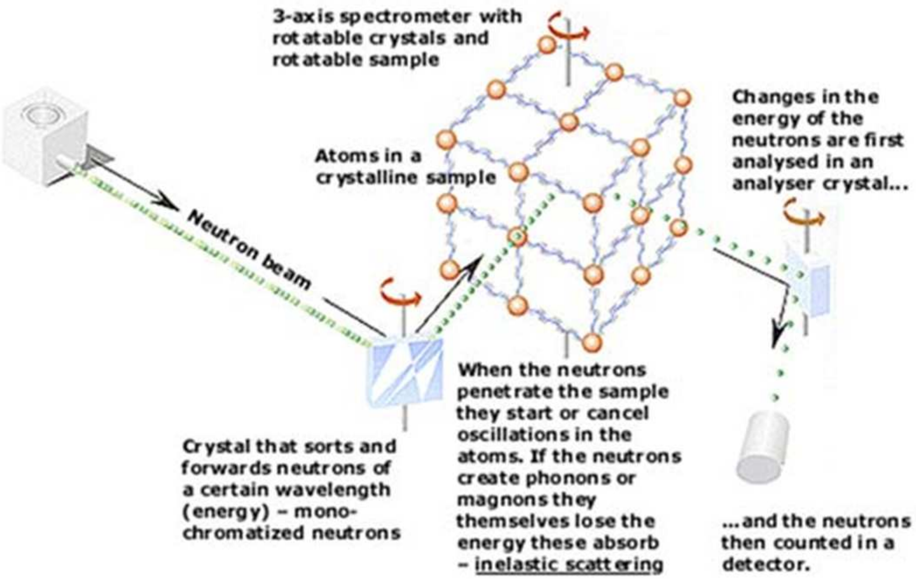
- To study atomic and molecular motion as well as magnetic and crystal field excitations.
-

Instruments – Triple axis spectrometer
Time of flight spectrometer



Elastic Neutron Scattering

Inelastic Neutron Scattering



Source - http://neutron.magnet.fsu.edu/neutron_scattering.html

Neutron diffraction

Powder Diffractometer

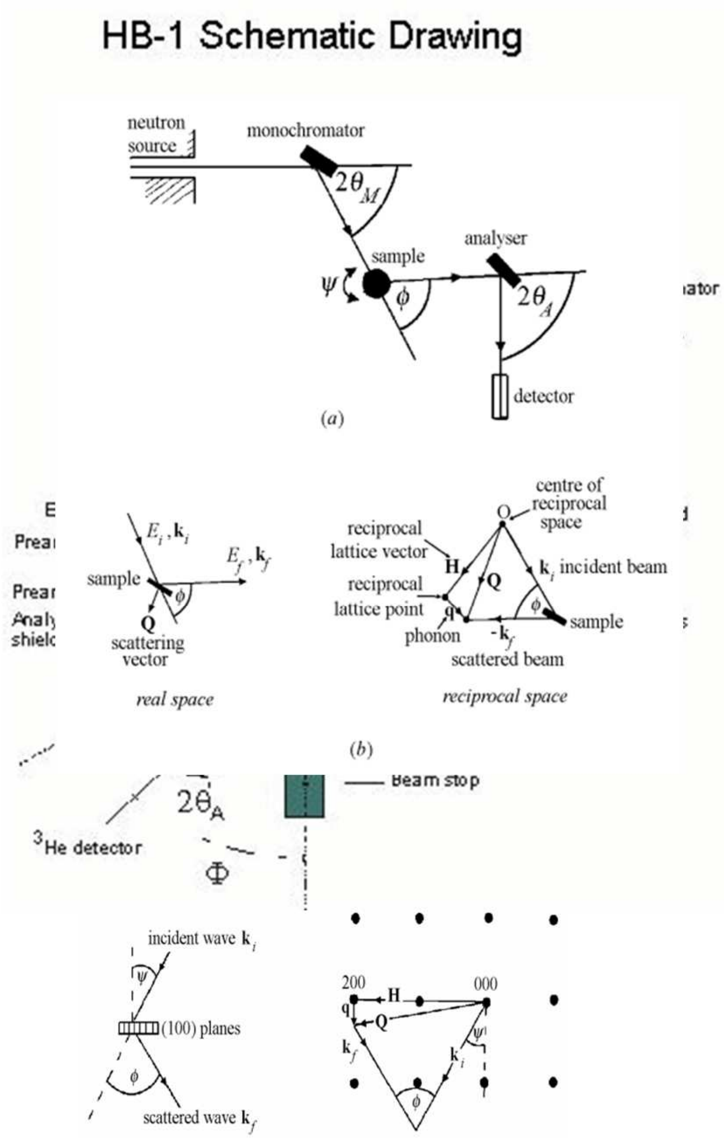
HB2A, HFIR

Single Crystal Diffractometer

RESI, FRM II

Bragg's law $n\lambda = 2d\sin\theta$

Triple axis spectrometer



Real space

reciprocal space

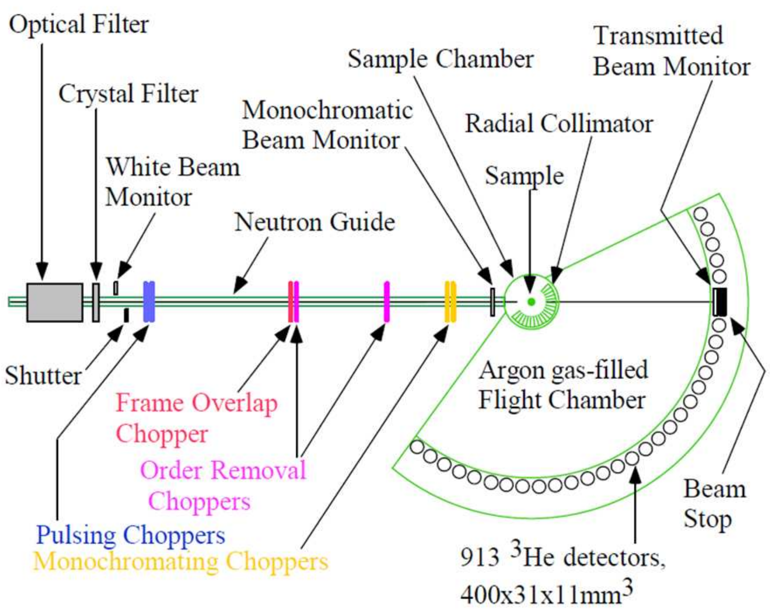
It allows measurement of
the scattering function at any point
in energy and momentum space physically
accessible by the spectrometer.

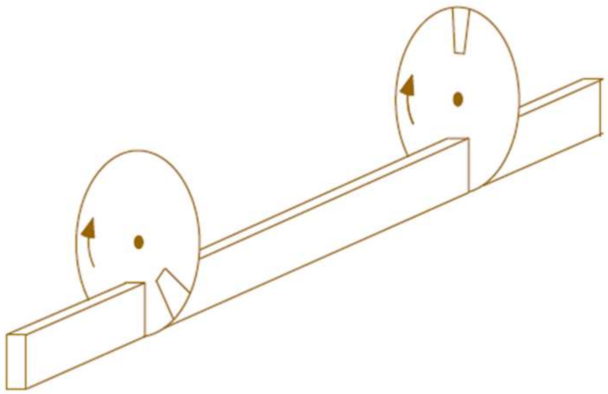
$$|\mathbf{Q}|^2 = |\boldsymbol{k}_i|^2 + |\boldsymbol{k}_f|^2 - 2\,|\boldsymbol{k}_i||\boldsymbol{k}_f|\cos(2\theta)$$

$$\boldsymbol{Q} = \boldsymbol{k}_i - \boldsymbol{k}_f$$

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m_n}\left(k_i^2 - k_f^2\right)$$

Time of Flight measurement





The time of flight spectrometer, as can be expected from its name, determines neutron energy by measuring its time of flight from one point to another.

The beams are monochromated using several choppers rotating at different frequencies allowing only neutrons at certain velocity can pass through.

Since we know the distance between the sample and detectors and can measure the time for neutron to fly from the sample to the detector, we then can calculate the energy of scattered neutrons.

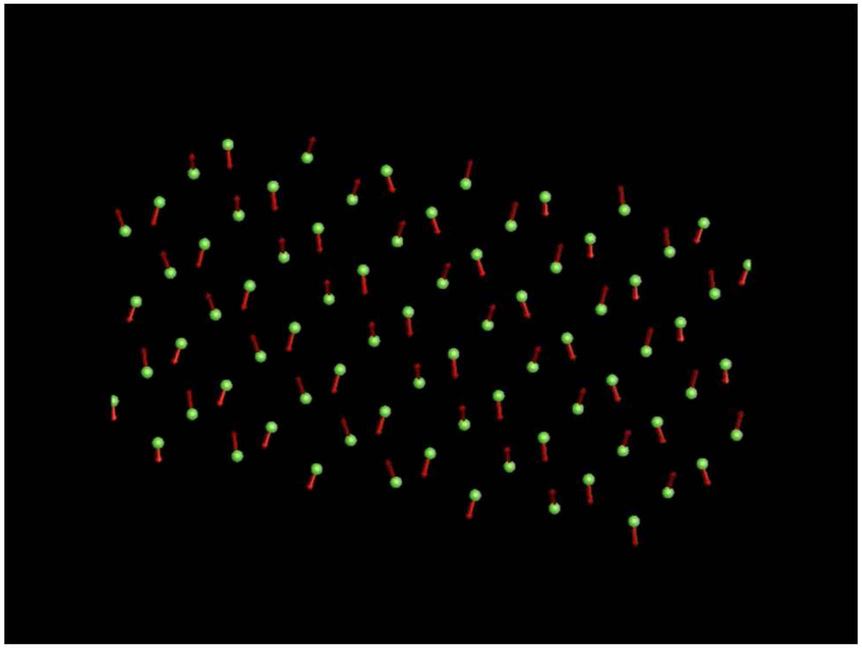
The direction of momentum can be figured out from the detector angle.

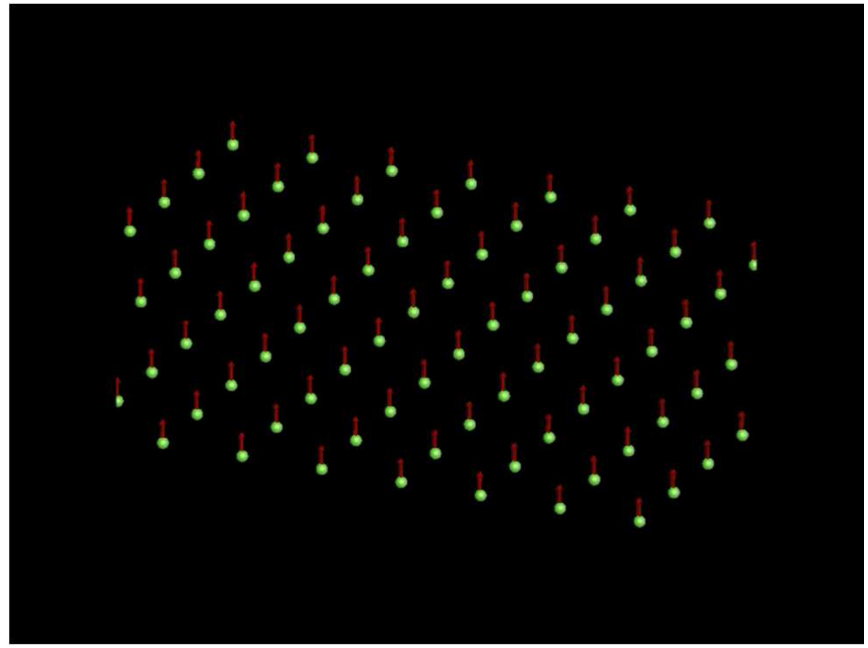
Time-of-flight method is powerful in that it can map out the huge Q-E space at a time.

Spin waves

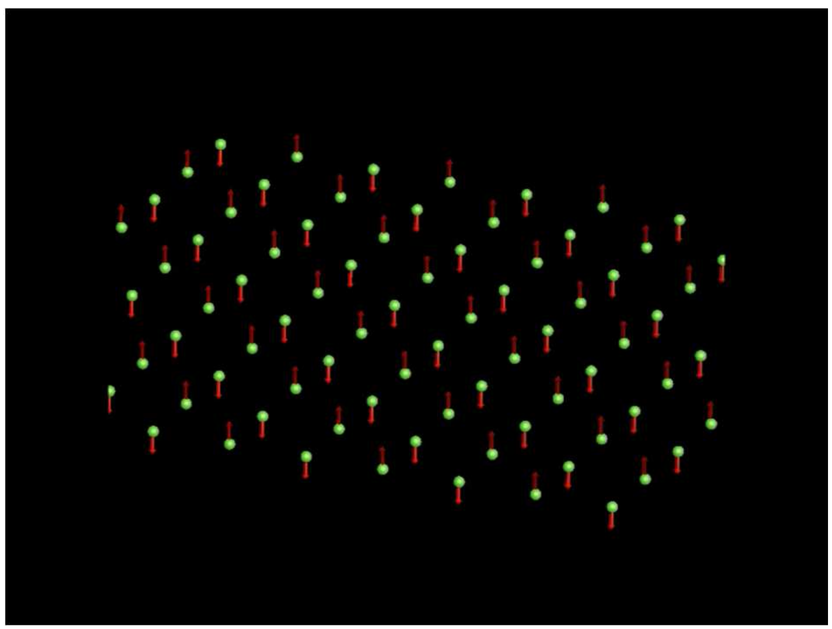
- Propagating disturbances in the ordering of magnetic materials. These low-lying collective excitations occur in magnetic lattices with continuous symmetry.

- Spin waves are the analog for magnetically ordered systems of lattice waves in solid systems; and just as a quantized lattice wave is called a “phonon”, a quantized spinwave is called a “magnon".



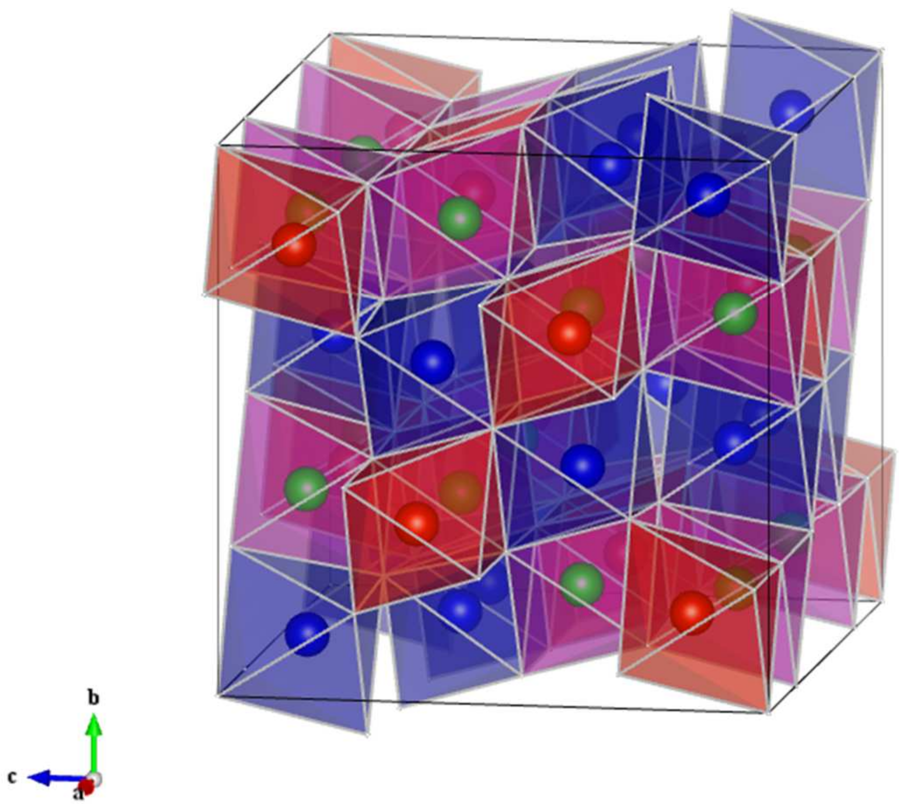


Animations are Created by IDL code written by Prof. Seunghun Lee



Frustrated magnet $BaV_{10}O_{15}$

Introduction – $BaV_{10}O_{15}$



$V^{3+}(3d^2)$ $V^{2+}(3d^3)$

t2g

4 : 1

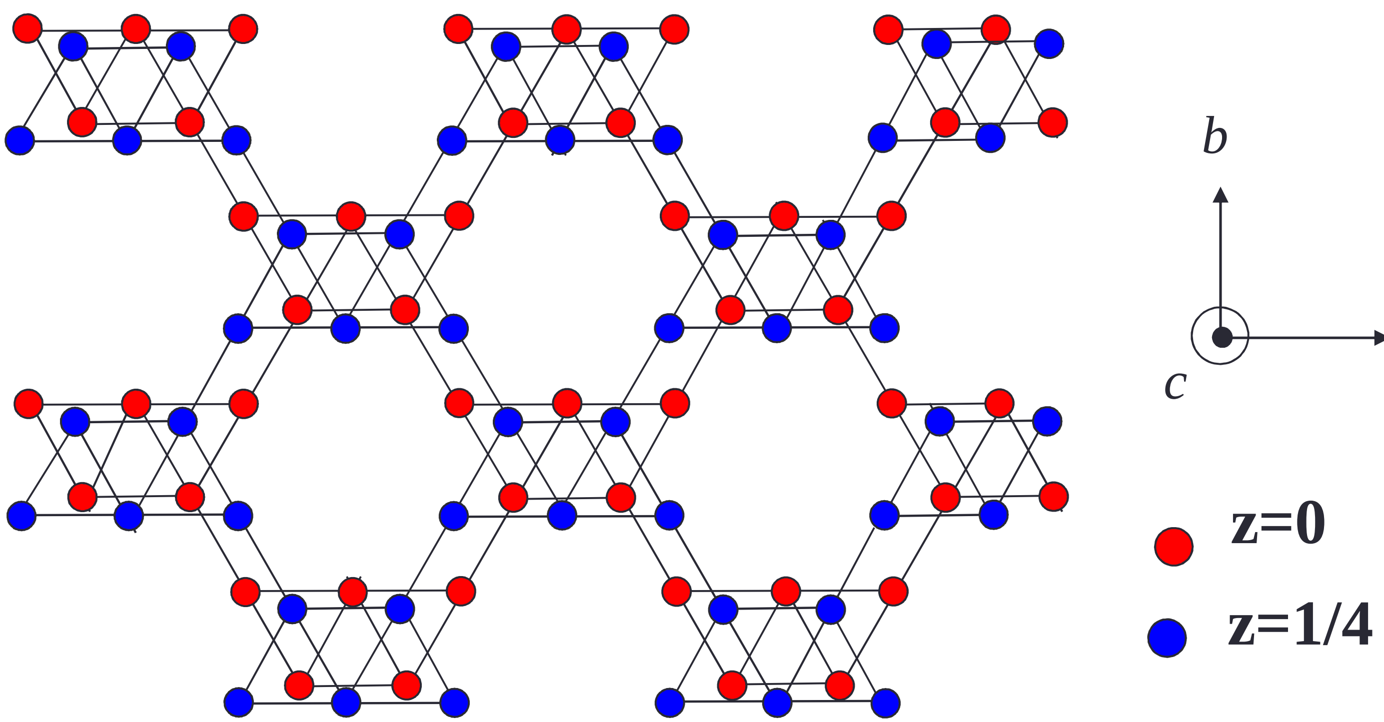
V ions surrounded by oxygen in octahedral fashion

face-, edge-, corner- sharing

mixed valence

t2g orbital ground state

Background : V structure

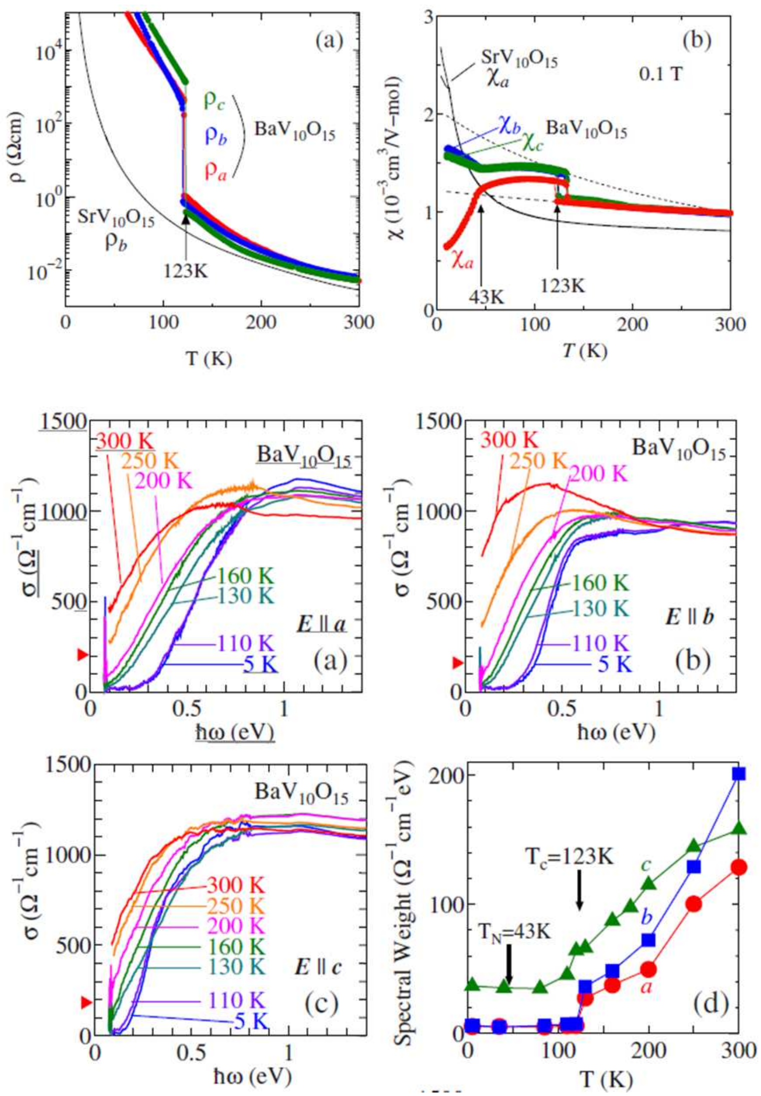


z=0: V5 boat
z=1/4: 180º rotation

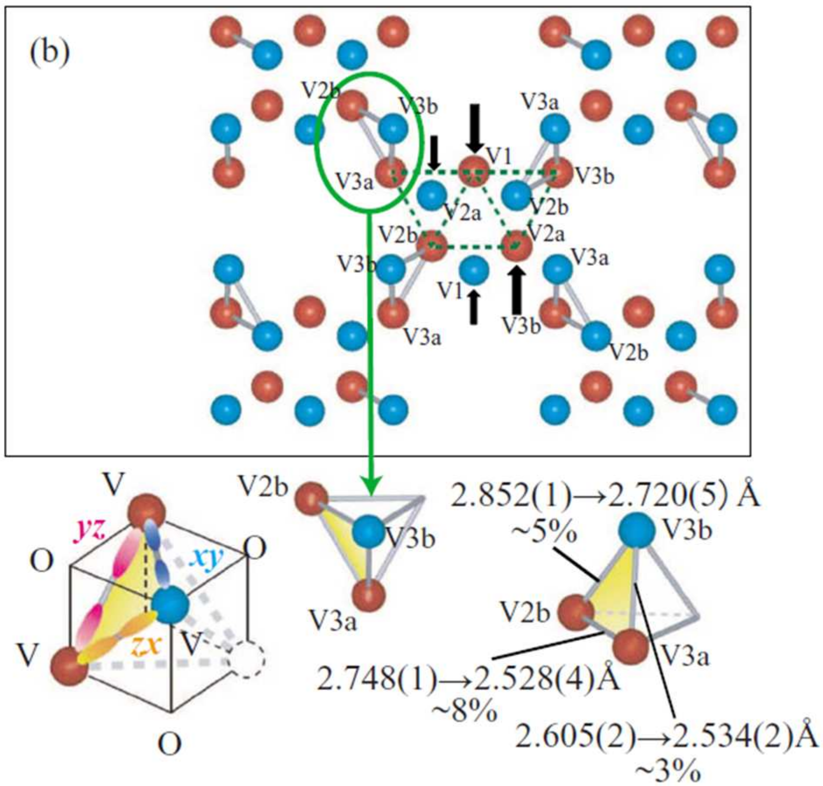
C.Bridges et. al., PRB **74**, 024426 (2006)
J.Miyazaki et. al., PRB **79** 180410(R) (2009)

due to small overlap between z=0 and z=-1/4,
considered as bi-layer structure stacked in ABAB fashion with B shifted along a

Bulk Properties



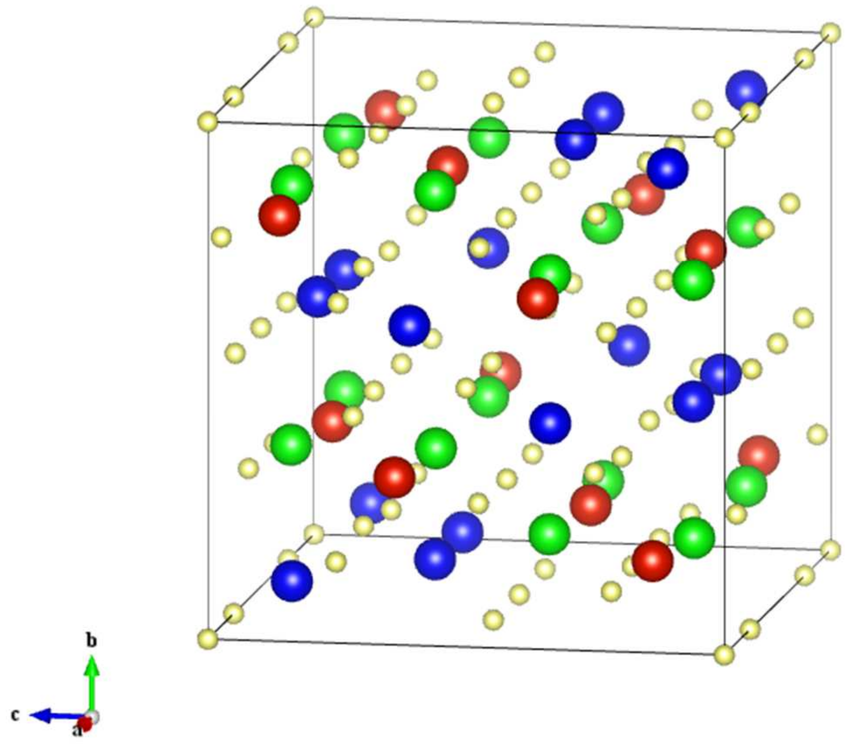
KAJITA et. al., PRB 81, 060405R 2010



-structural phase transition at 123 K
 (Cmce → Pbca)
- -opening of charge gap

-magnetic phase is unknown

Strength of interaction



example of V3 ions interaction

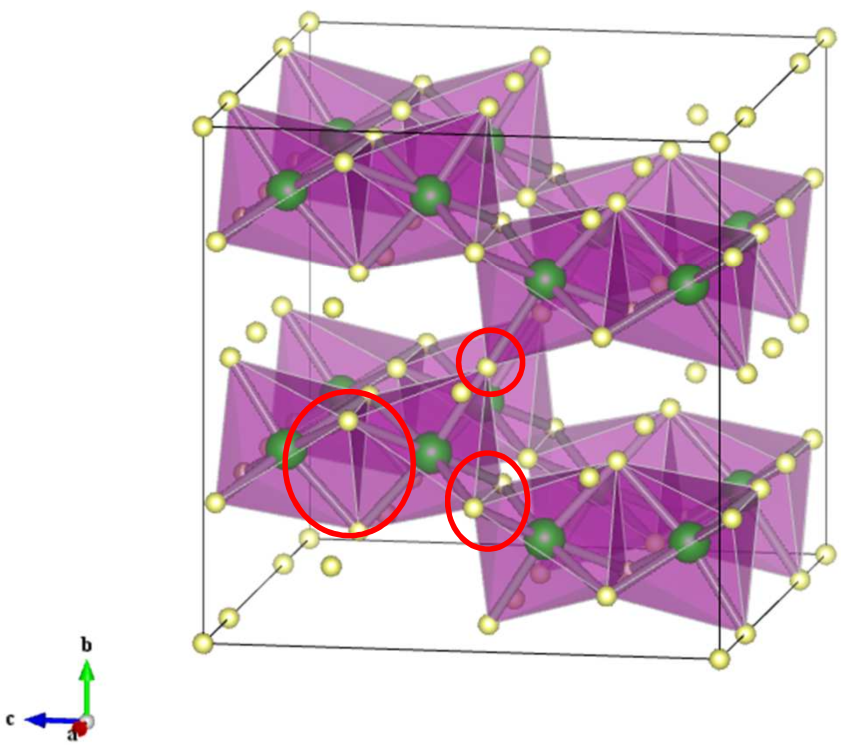
- **which connection is strong?**
  - depends on the amount of orbital overlap

- **In octahedrally coordinated 3d ions case**
  - corner < edge < face

cf.) SCGO, S.-H. Lee et. al., PRL (1996)

*Green ions: V3a(light),V3b(dark)
*Yellow ions: Oxygen

Strength of interaction



example of V3 ions interaction

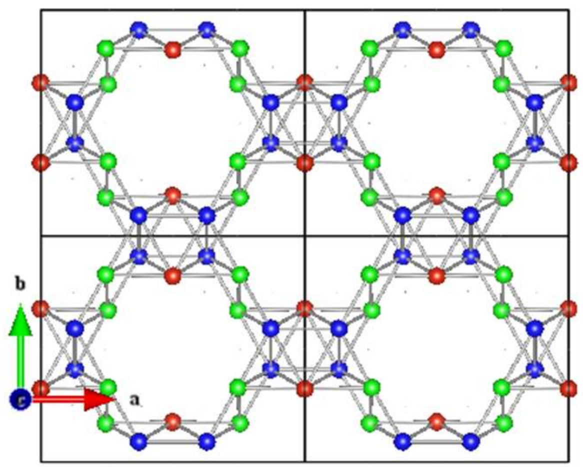
- **which connection is strong?**
  - depends on the amount of orbital overlap
- **In octahedrally coordinated 3d ions case**
  - corner < edge < face

cf.) SCGO, S.-H. Lee et. al., PRL (1996)

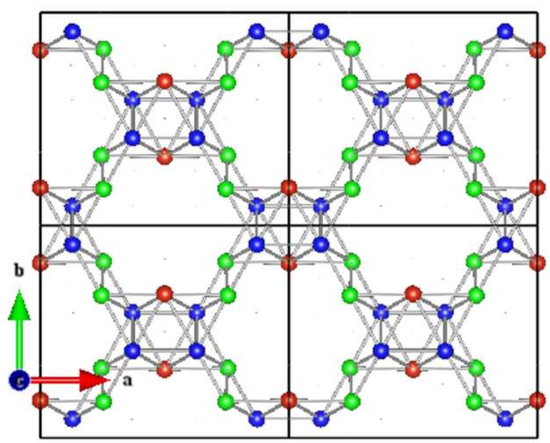
*Green ions: V3a(light),V3b(dark)
*Yellow ions: Oxygen

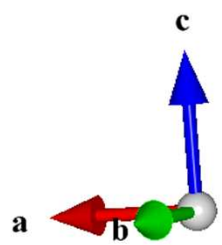
Interactions (face and edge sharing bonds)

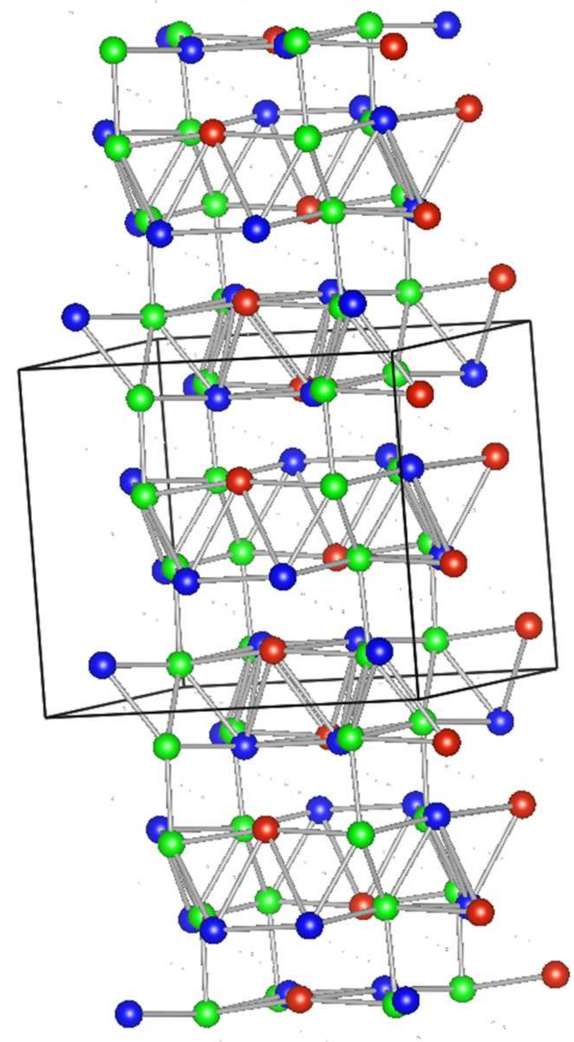
0.3<z<0.7



-0.2<z<0.3







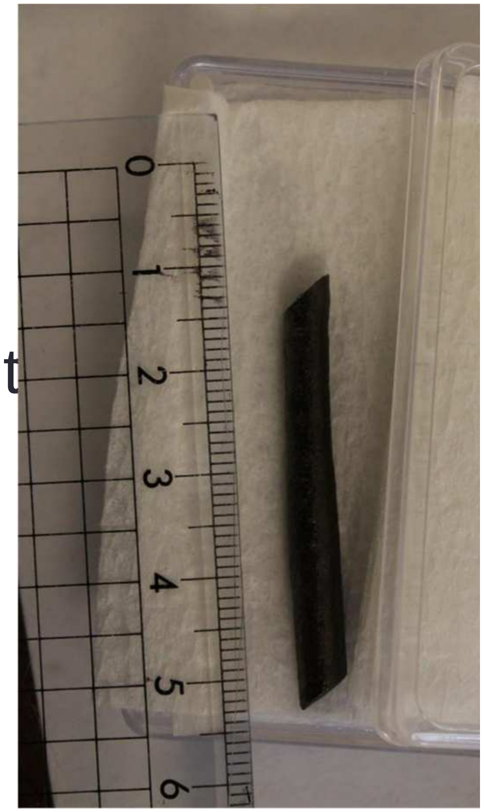
Experiments

- ARCS, SNS

-Time of Flight neutron scattering measurement

-T=4K with Ei=65meV

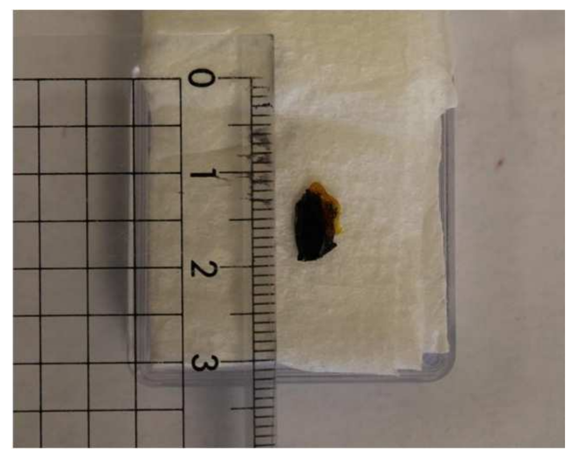
-ki//c with rotation angle -10 to 40 deg.



- HB2A, HFIR

-Neutron powder diffractometer

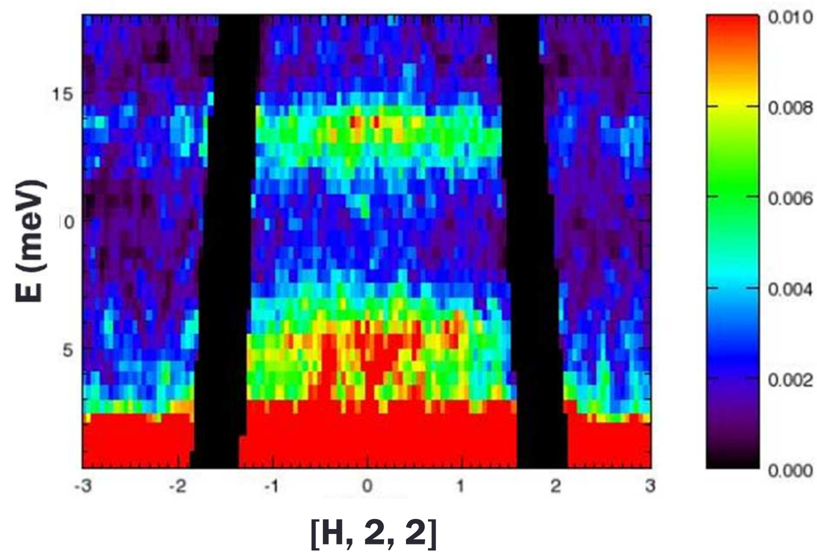
-T=4K with Wavelength 1.538 A



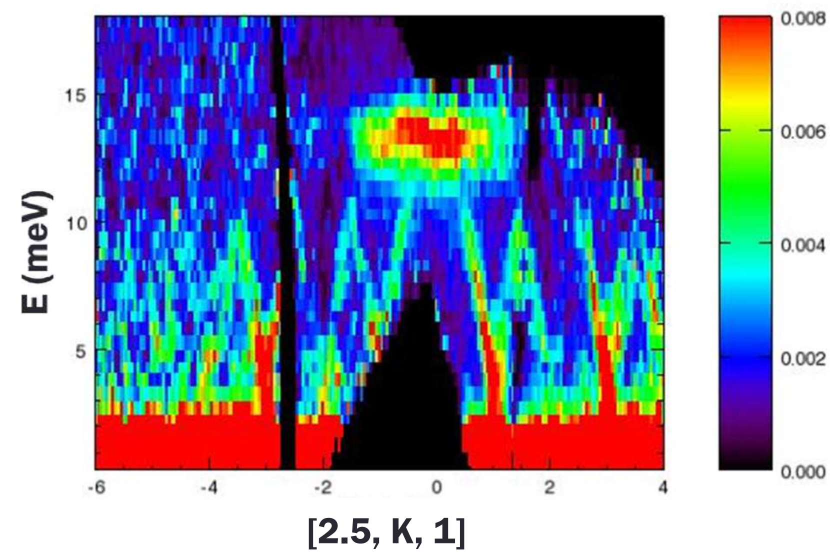
- RESI, FRM II
- Single Crystal Diffractometer
- -T= 4K with wavelength 1 A

Magnetic excitations

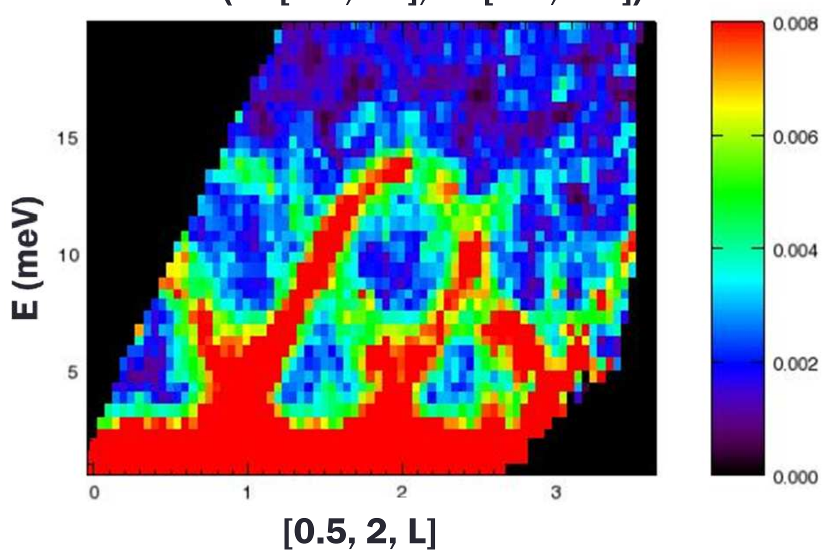
EH cut (K=[1.8,2.2], L=[1.8, 2.2])



EK cut (H=[2.3,2.7], L=[0.8, 1.2])



EL cut (H=[0.3,0.7], K=[1.8, 2.2])



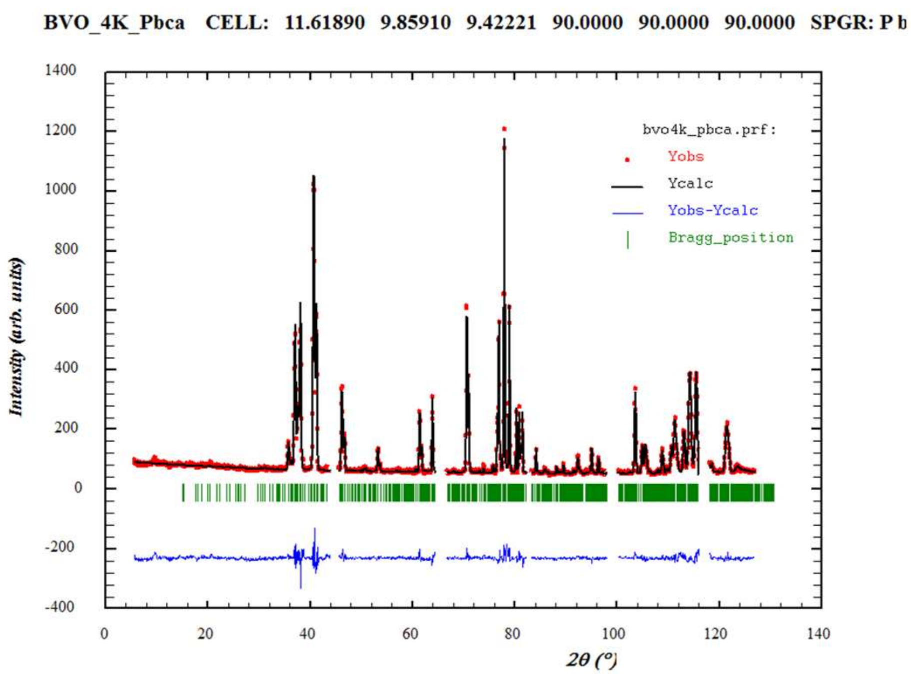
H: Band 1: almost dispersionless, 5~6meV
Band 2: flat, ~13 meV

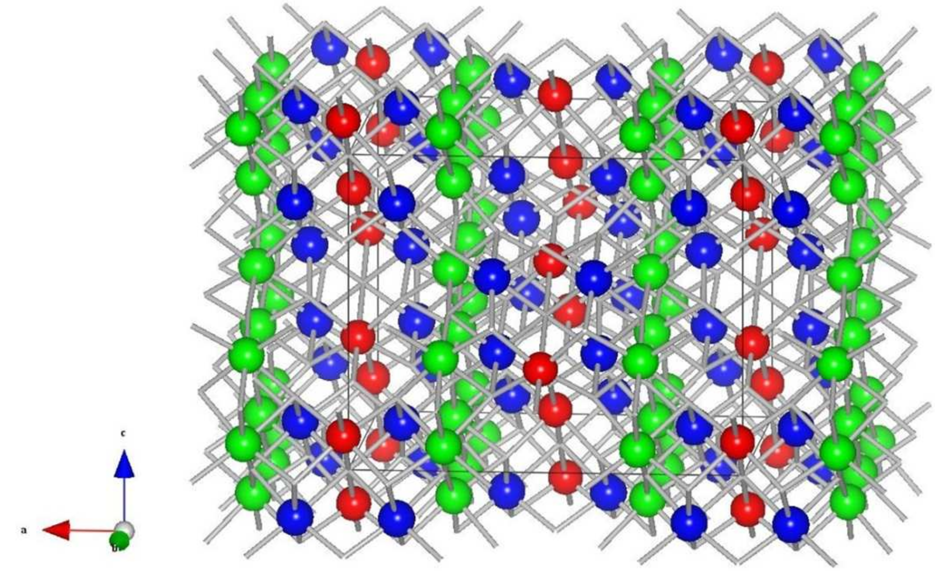
K: Band 1: highly dispersive, 0-10meV
Band 2: flat, ~13 meV

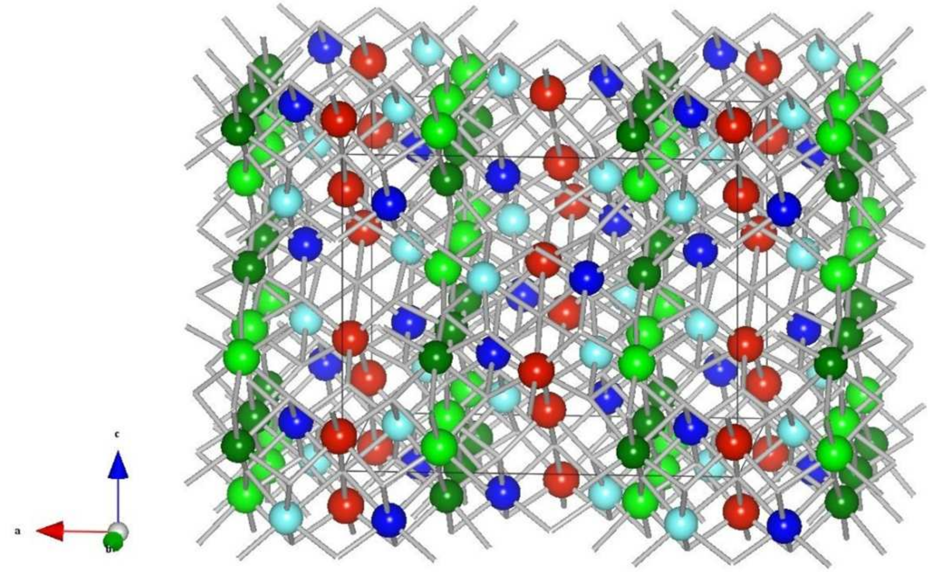
L: Band 1: 0-13 meV, highly dispersive

-not consistent with bi-layer stacked along c

Powder Diffraction







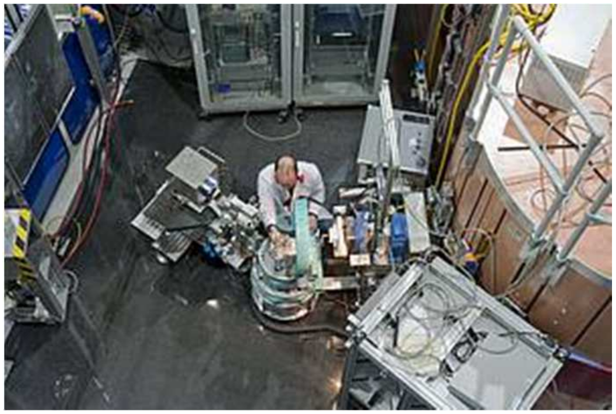
Cmca → Pbca
V1(Red)→V1 (Red)
V2(Blue)→V2a, V2b(Blue, Sky)
V3(Green)→V3a, V3b(Green, Dark Green)

:mirror symmetry is lost

Single Crystal Data

Magnetic peaks					
H	K	L	Q	Observed	Sigma
0.5	-1	0	0.692294	10098.89	252.9
0.5	0	1	0.719572	-177.64	282.46
-0.5	1	1	0.9612	503.91	233.4
0.5	1	1	0.9612	406.75	195.22
1.5	1	0	1.031545	7367.78	137.95
-0.5	0	2	1.360842	2930.91	207.17
-0.5	-2	1	1.463726	15696.28	286.76
0.5	-2	1	1.463726	17409.14	284.03
-0.5	1	2	1.502641	456.01	189.4
0.5	1	2	1.502641	83.16	213.6
1.5	-2	0	1.51084	647.57	205.6
1.5	0	2	1.560982	694.32	226.38
2.5	1	1	1.636639	1084.05	235.15
-1.5	2	1	1.651446	2442.92	206.92
1.5	2	1	1.651446	1989.52	127.95
-0.5	2	2	1.864512	4621.35	189.72
0.5	2	2	1.864512	3919.91	189.21
-1.5	3	1	2.181297	2053.82	242.04
1.5	-3	1	2.181297	2055.34	208.58
-1.5	1	3	2.250818	446.08	205.26
1.5	1	3	2.250818	573.47	234.38
0.5	3	2	2.346745	-406.49	187.29

RESI, FRM II
-Single Crystal Diffractometer
--T= 4K with wavelength 1 A



Representational Analysis

$$\boxed{\Gamma_{mag} = \sum_{\Gamma_i} n_i \Gamma_i} \qquad \Gamma_i \ - Irreducible\ representation$$

$$\mathbf{S}^{\mathbf{k}v} = \sum_{L} \sum_{\lambda} C_{\lambda}^{k_L v} \psi_{\lambda}^{k_L v}$$

Spin of the n^{th} cell $\quad S_{ni} = \exp(ikt_n)\, S_{oi}$

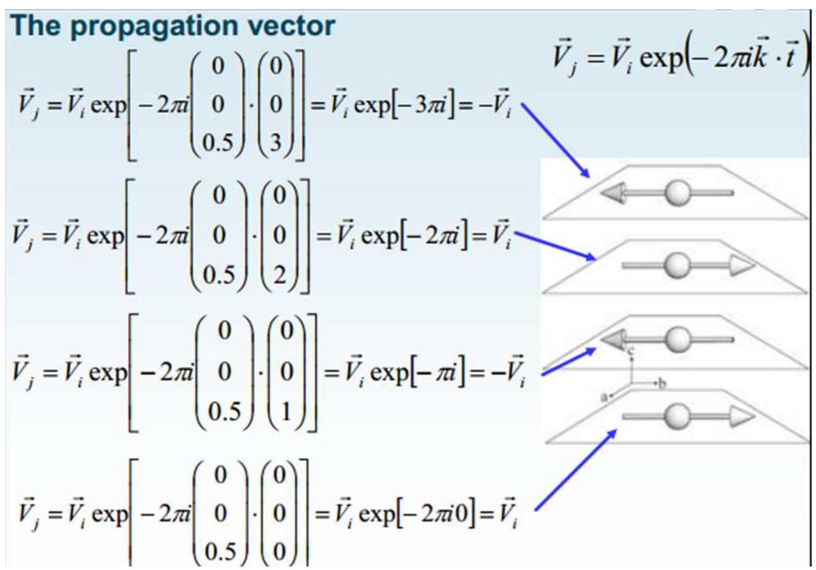
Representational Analysis

$$\boxed{\Gamma_{mag} = \sum_{\Gamma_i} n_i \Gamma_i}$$

Γ_i $- \mathit{Irreducible\ representation}$

Magnetic structure

$$m_j = \sum_L \sum_\lambda C_\lambda^{k_L v} \psi_\lambda^{k_L v} e^{-2\pi i k \cdot t}$$



Refining the magnetic structure - Basis functions

80 Magnetic V atoms $\Gamma_{mag} = 6\Gamma_1 + 6\Gamma_2$ Γ_1, Γ_2- 2 Dimensional

Table B.3: The basis functions of the irreducible representations for the space group Pbca with **k** = (1/2, 0, 0)

	BV	Atom 1			Atom 2			Atom 3			Atom 4			Atom 5			Atom 6			Atom 7			Atom 8		
		m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z
Γ_1	ψ_1	1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0
	ψ_2	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0
	ψ_3	0	0	1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0
	ψ_4	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0
	ψ_5	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0
	ψ_6	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	1
	ψ_7	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0
	ψ_8	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0
	ψ_9	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	1
	ψ_{10}	1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0
	ψ_{11}	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0
	ψ_{12}	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0
Γ_2	ψ_{13}	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0
	ψ_{14}	0	1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0
	ψ_{15}	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0
	ψ_{16}	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0
	ψ_{17}	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	-1	0
	ψ_{18}	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	-1
	ψ_{19}	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0
	ψ_{20}	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0
	ψ_{21}	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	-1
	ψ_{22}	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0	0	0
	ψ_{23}	0	1	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0
	ψ_{24}	0	0	1	0	0	0	0	0	-1	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	0

- C. Bridges Thesis 2002

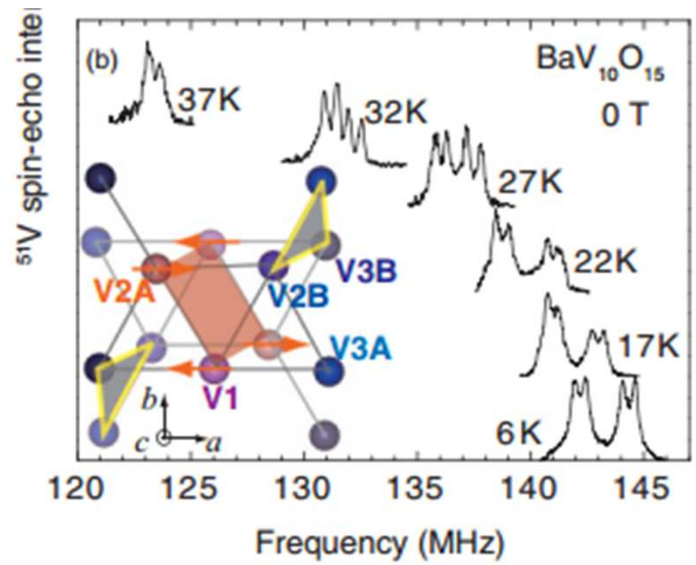
Refining the magnetic structure

- Refining the Magnetic structure by carrying out all the possibilities is very hard, due to enormous possibilities

- We approached the refinement in two ways.

Refining the magnetic structure

Shimizu et. al. **PRB** 84, 064421 (2011)



1. Trimer with tetramer

There are 4 basis vectors that is pointing in a-direction. BV1, BV4, BV7, BV10

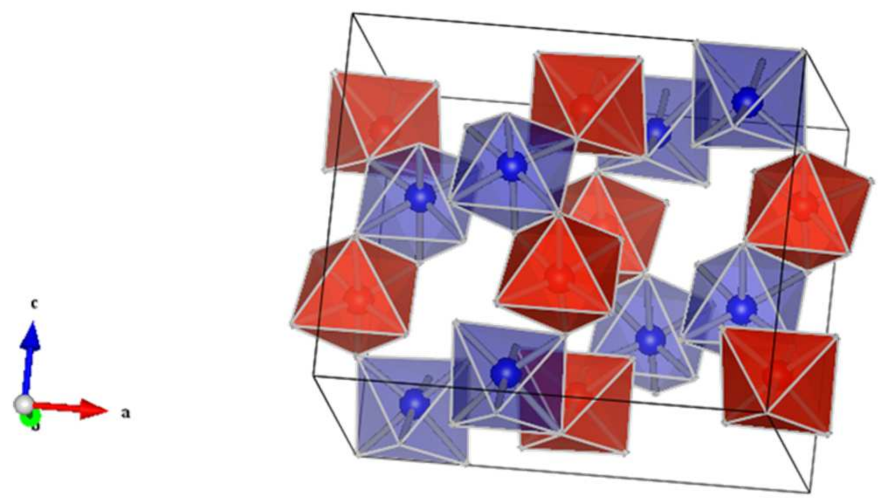
a.) All bonds with in all tetramers in unit cell are satisfied

Γ_1 - BV1 and BV 10

Γ_2 - BV4 and BV 7

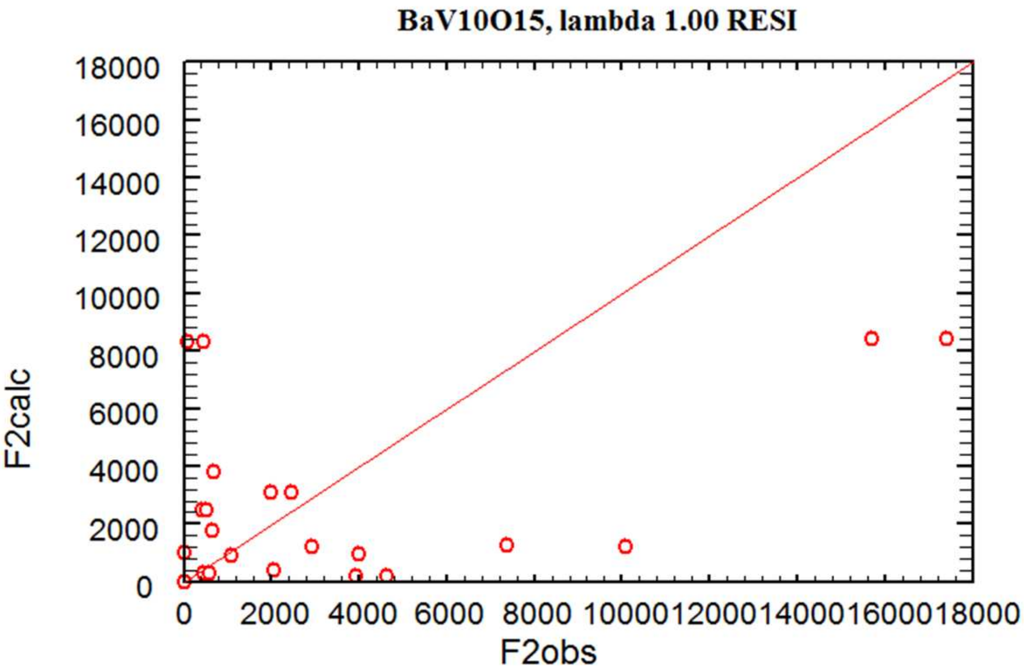
b.) Some bonds within tetramers does not satisfy

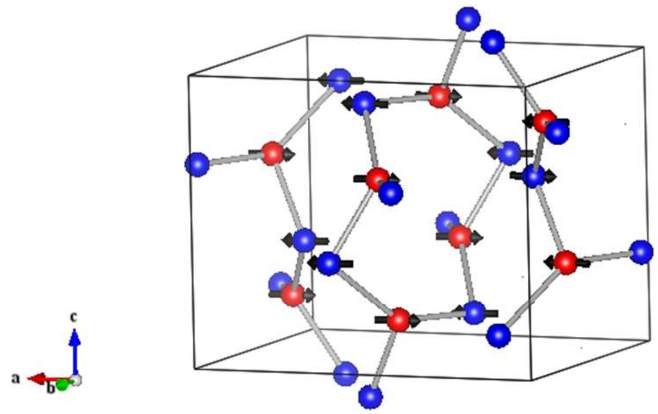
Other combinations of BV1, BV4, BV7, BV10

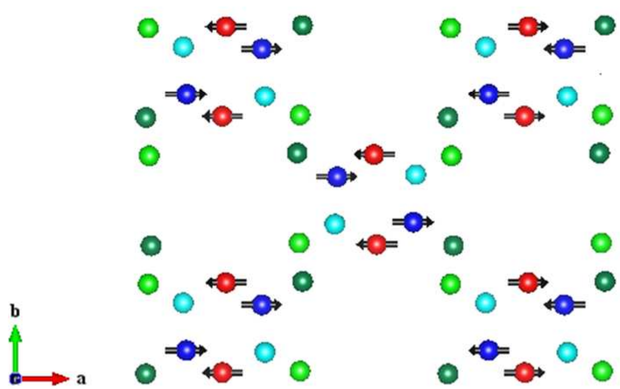


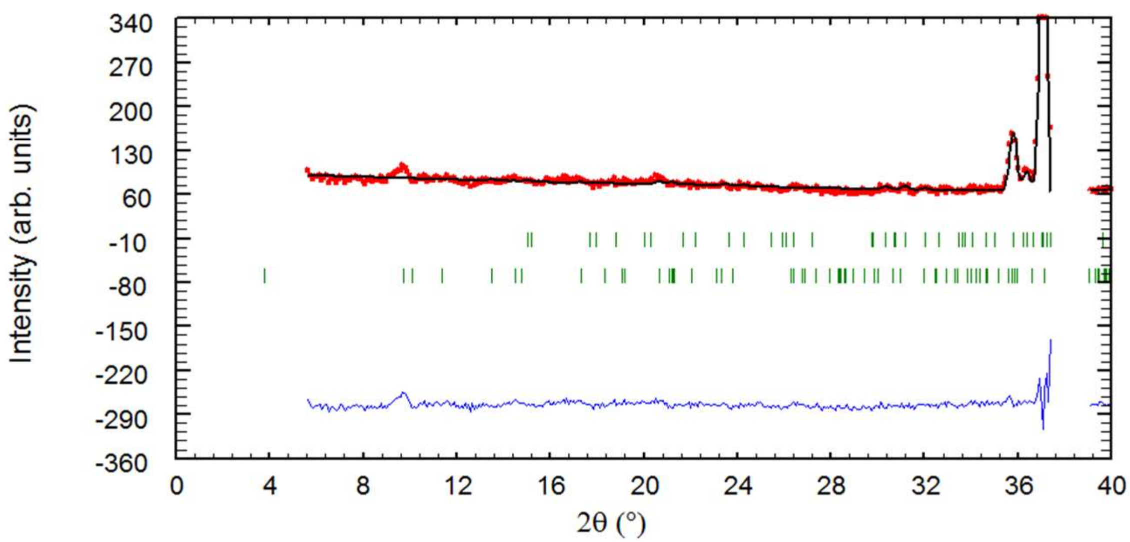
Trimer with tetramer - All bonds with in all tetramers in unit cell are satisfied

Γ_2



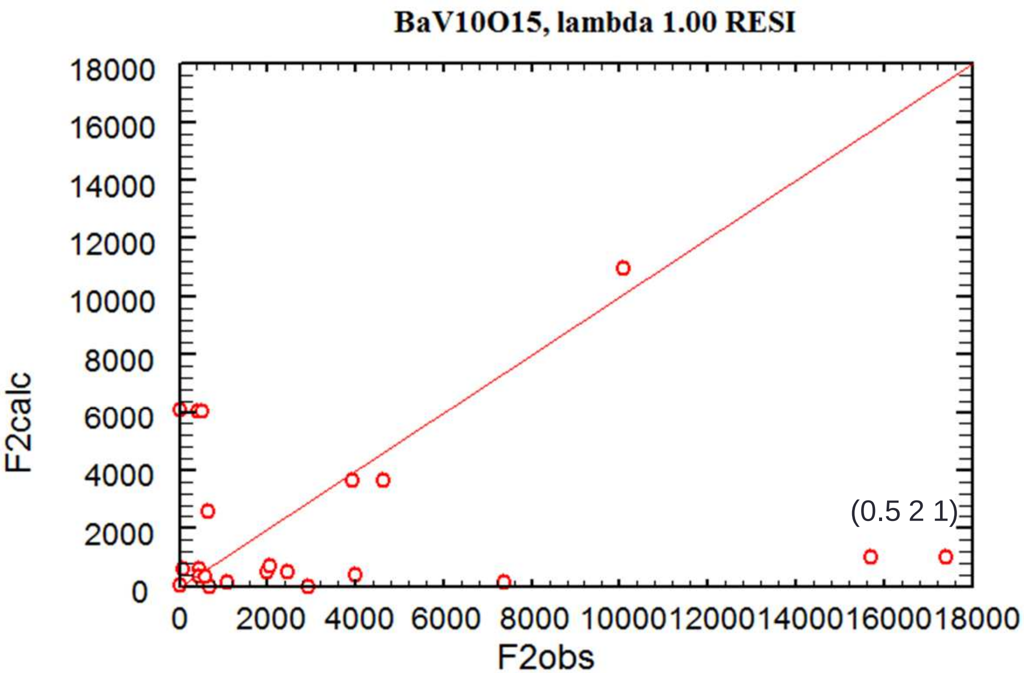




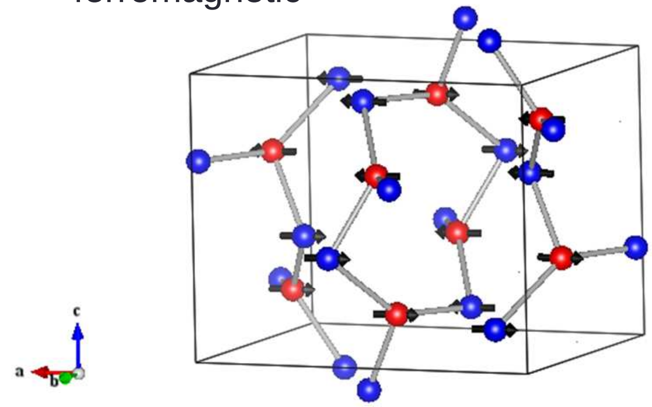


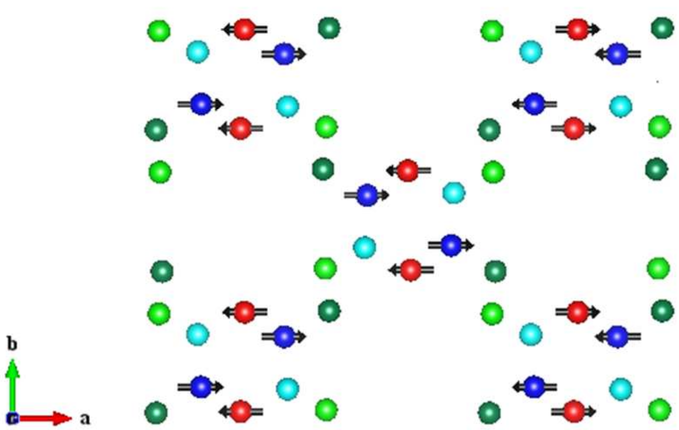
Trimer with tetramer - All bonds with in all tetramers in unit cell are satisfied

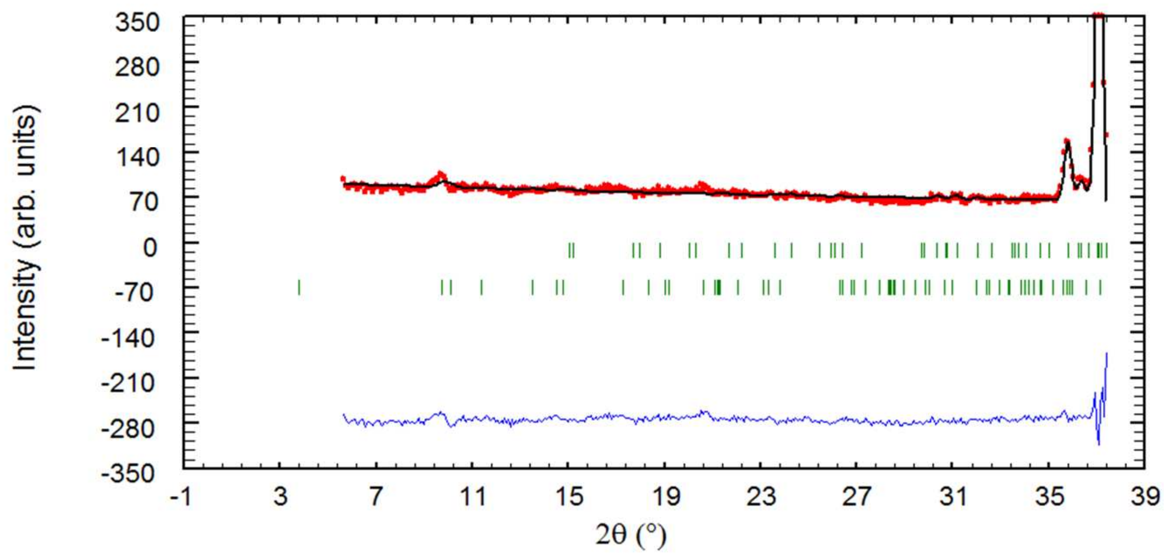
Γ_1



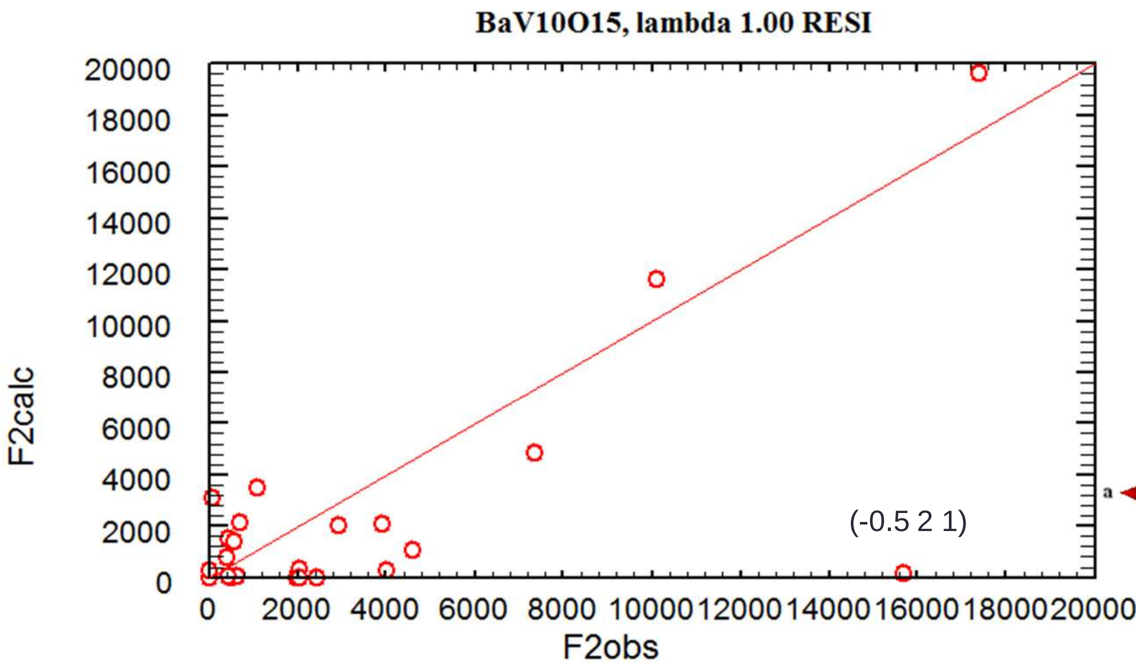
Corner sharing bond along C, not satisfied or ferromagnetic

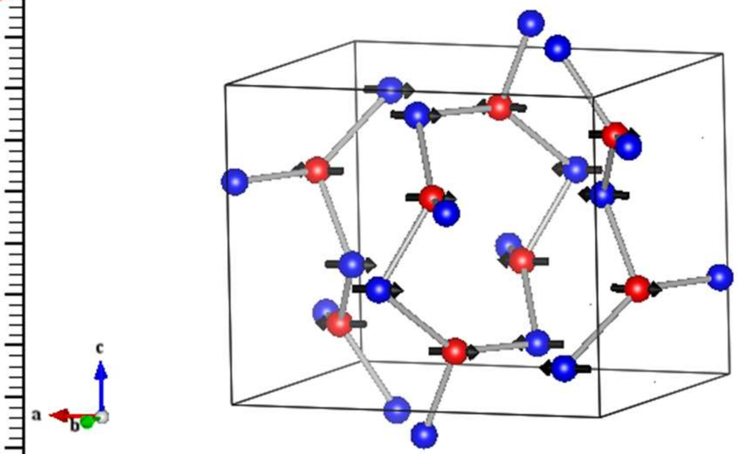


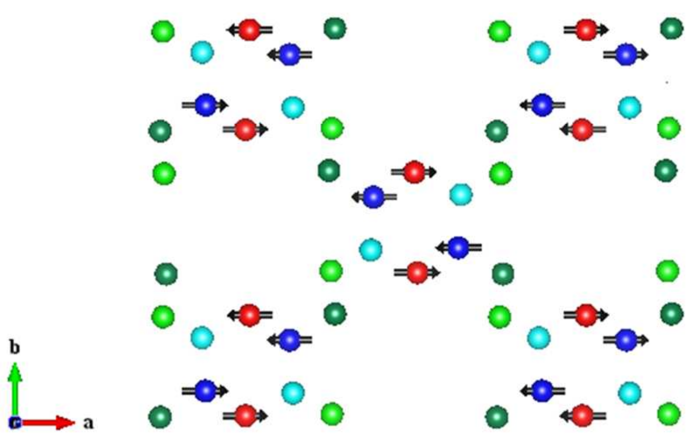


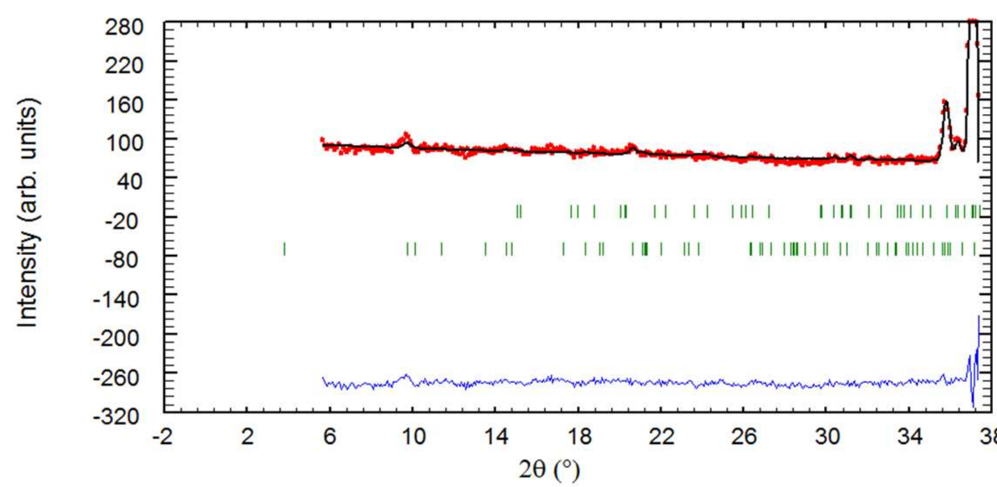


Trimer with tetramer - Some bonds with in tetramers does not satisfy









Refining the magnetic structure

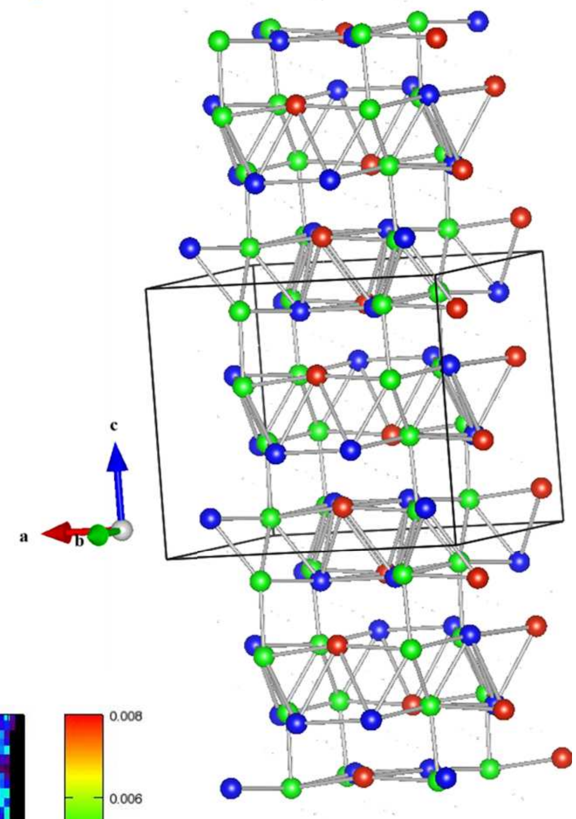
2. Non trimer model – All five V atoms are ordered

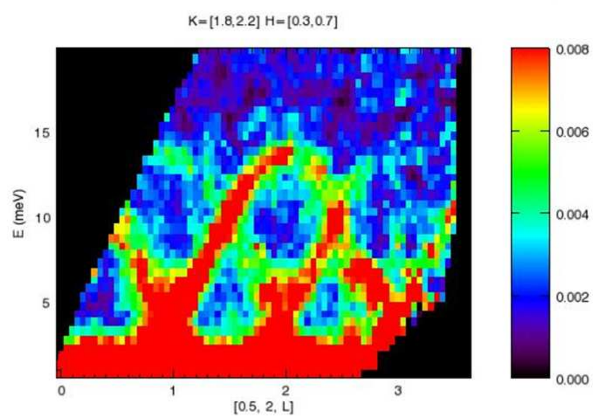
Here we assumed that chain along c-direction is always satisfied.

This allows us to restrict number of combinations
in the basis vectors.

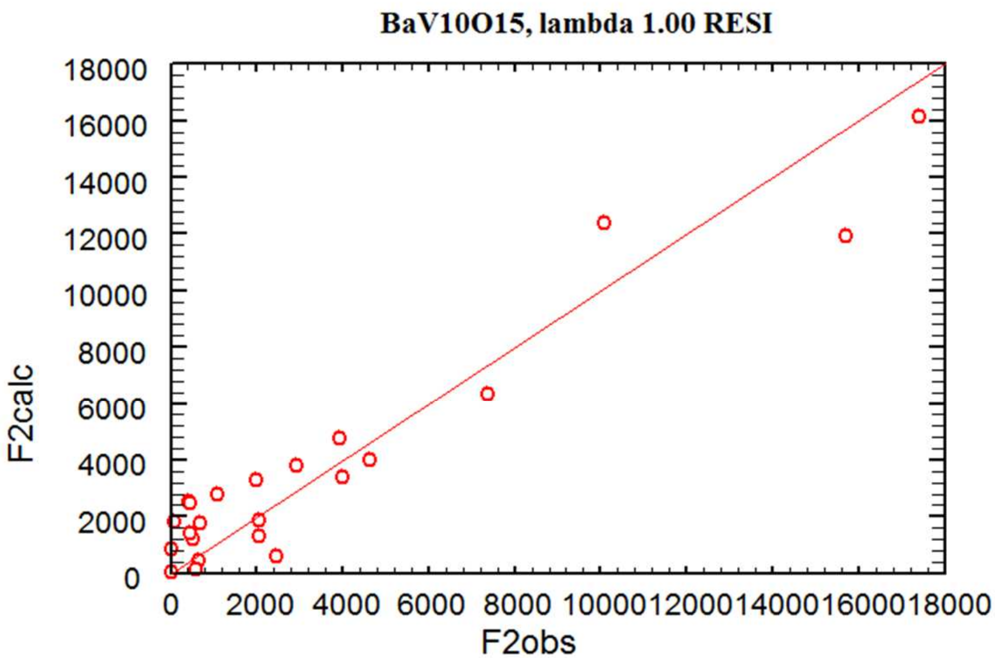
For eg. :

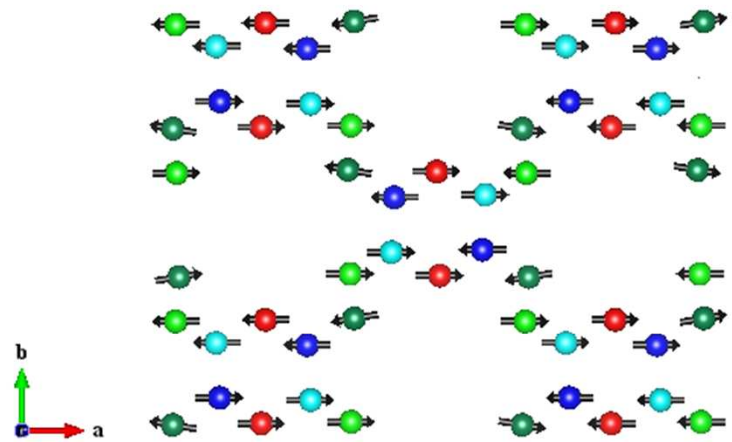
	Γ_1, Γ_2
a direction	V3 (BV1) + V3B(BV4) + V3 (BV7) + V3B (BV10)
b direction	V3 (BV5) + V3B (BV2) + V3 (BV11) + V3B (BV8)
c direction	V3 (BV6) + V3B (BV3) + V3 (BV12) + V3B (BV9)

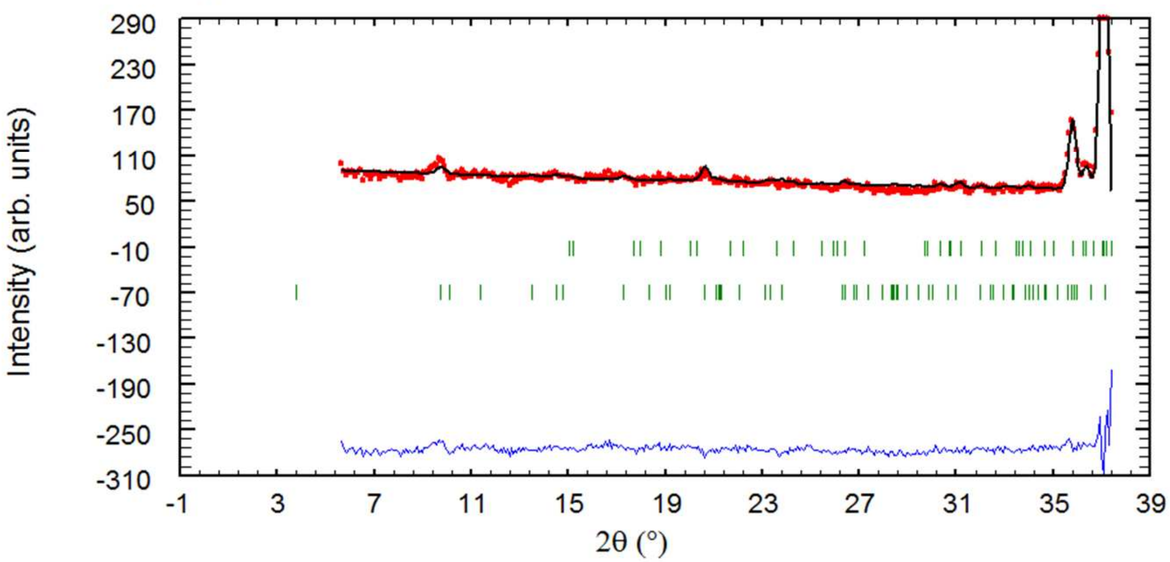




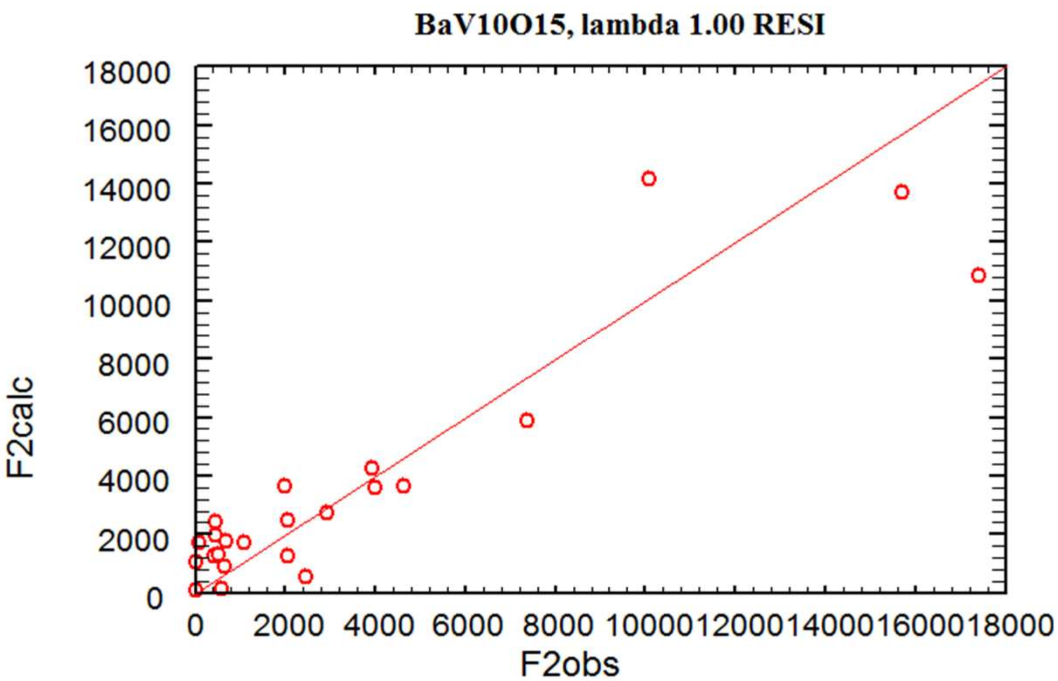
Non Trimer models – All five V atoms are ordered

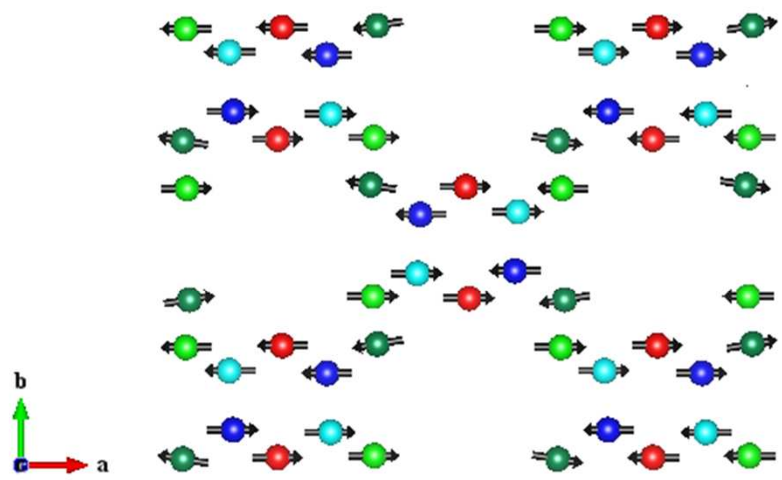


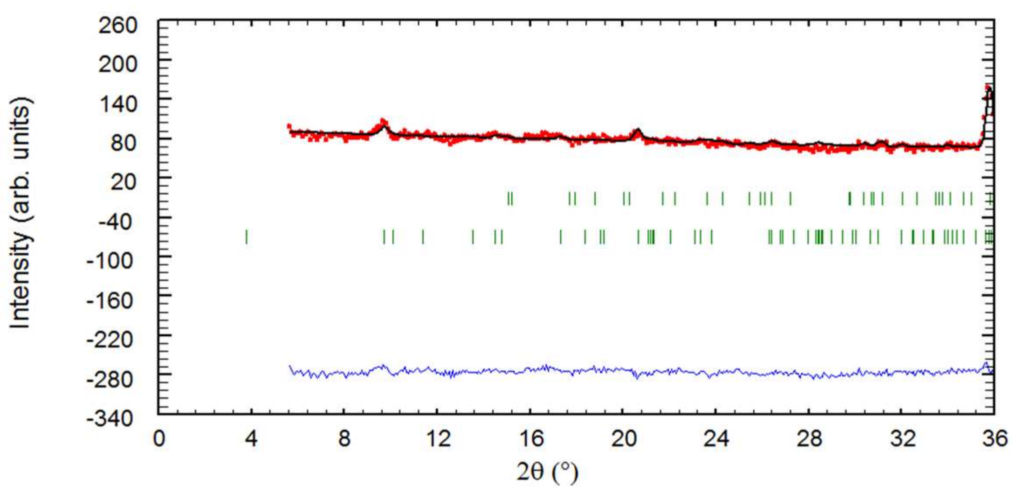




Non Trimer models – All five V atoms are ordered







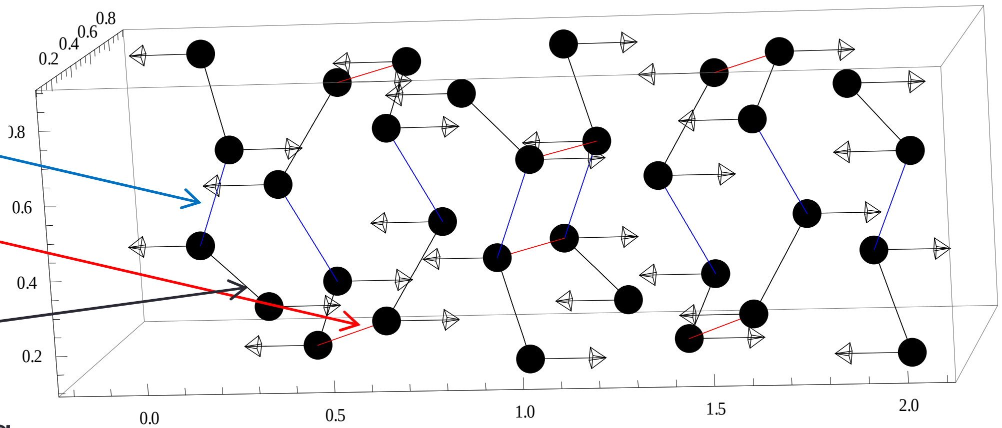
Linear spinwave calculation - Tetramer

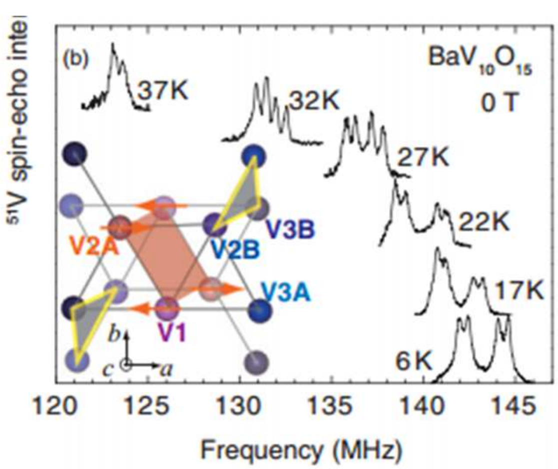
$$H = \sum J_{ij} S_i \cdot S_j$$

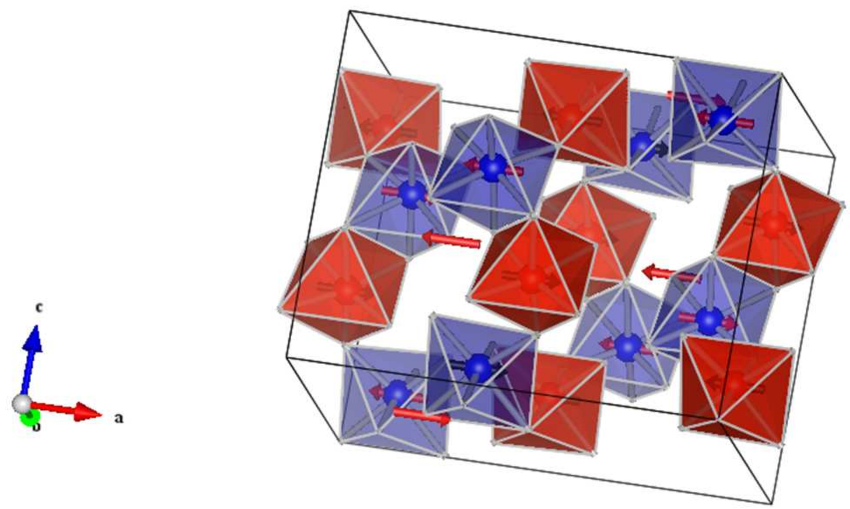
J_2
Edge Sharing

J_1
Edge Sharing

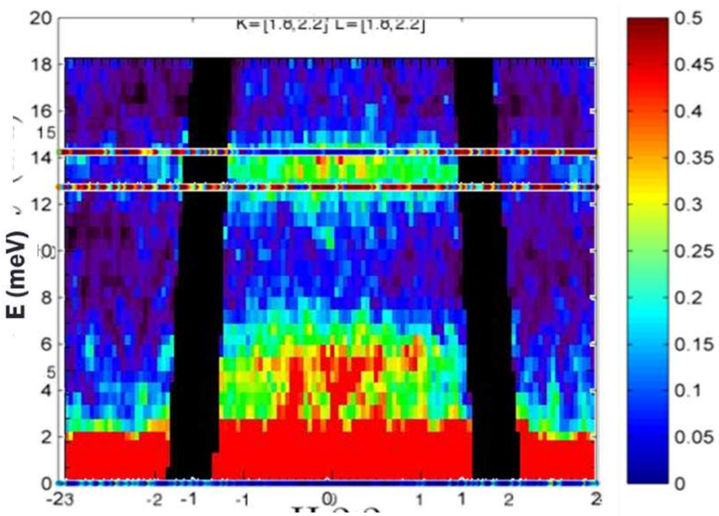
J_3
Corner Sharing



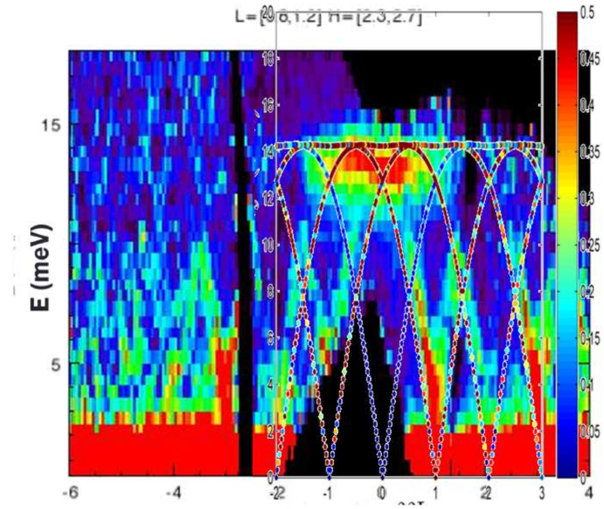




Linear spinwave calculation - Tetramer

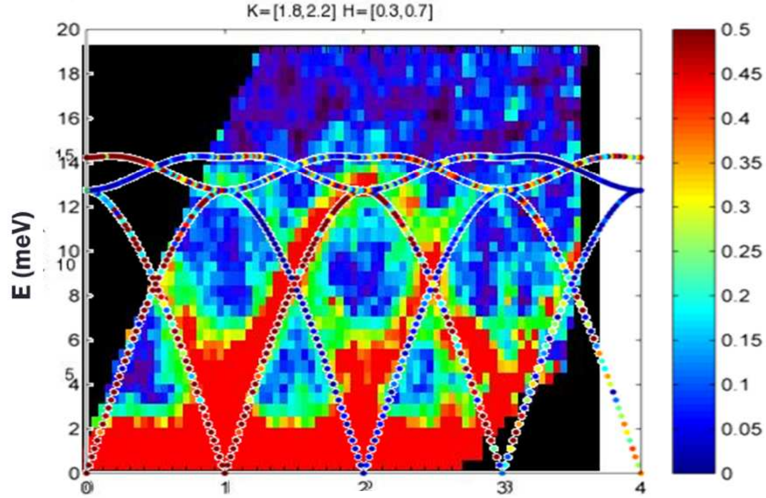


[H, 2, 2]



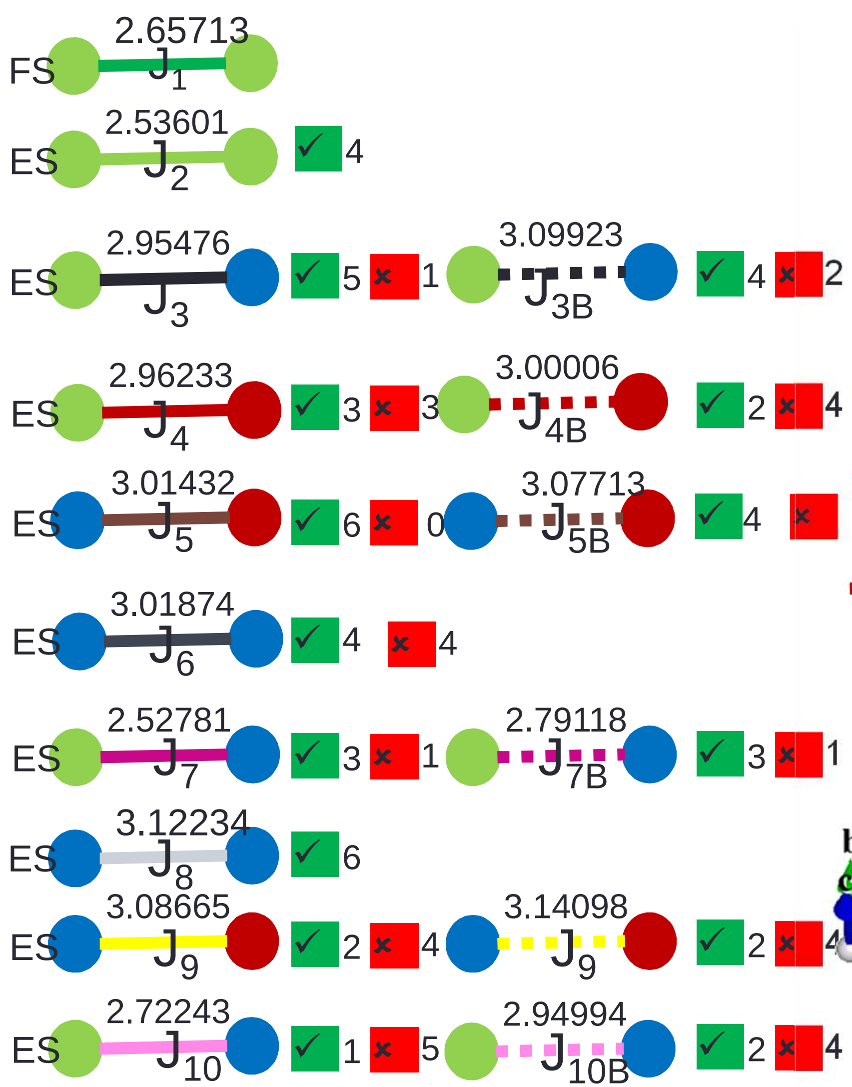
[2.5, K, 1]

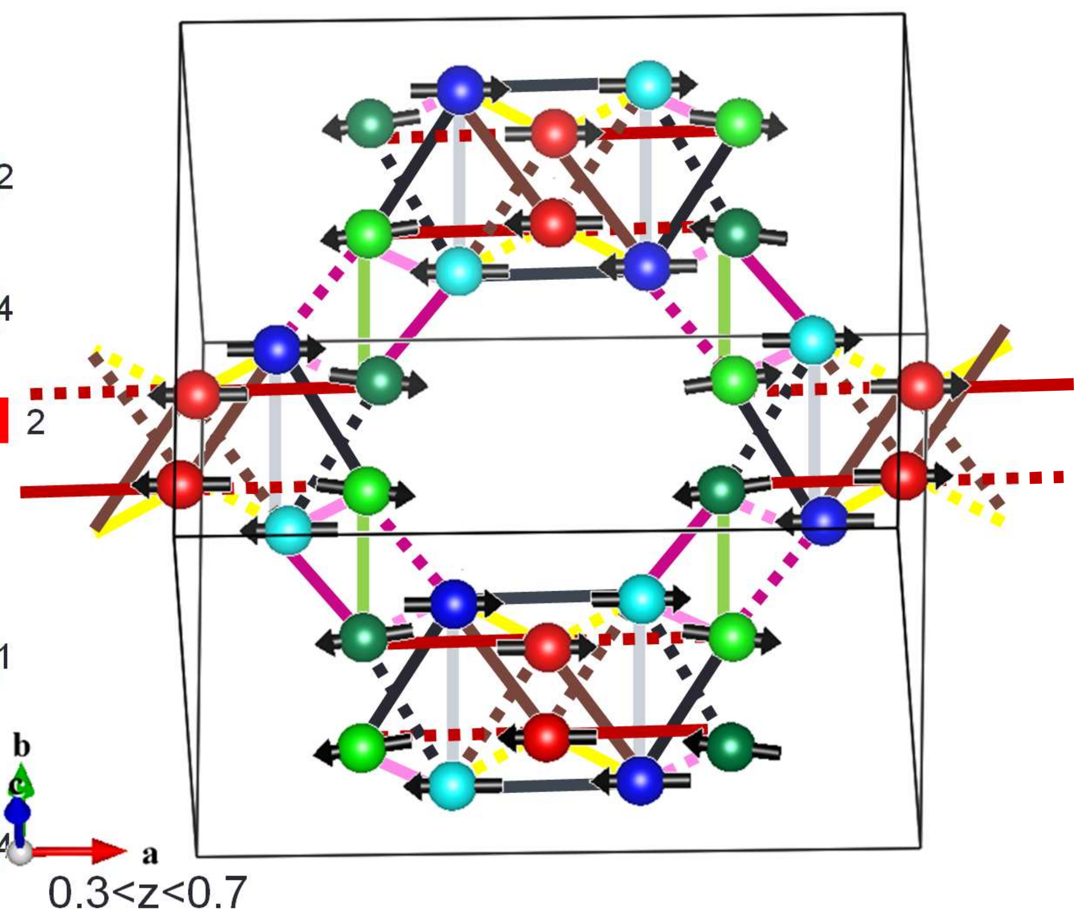
J2=7.5 meV;
J1=0.3*J2;
J3=0.6*J2;



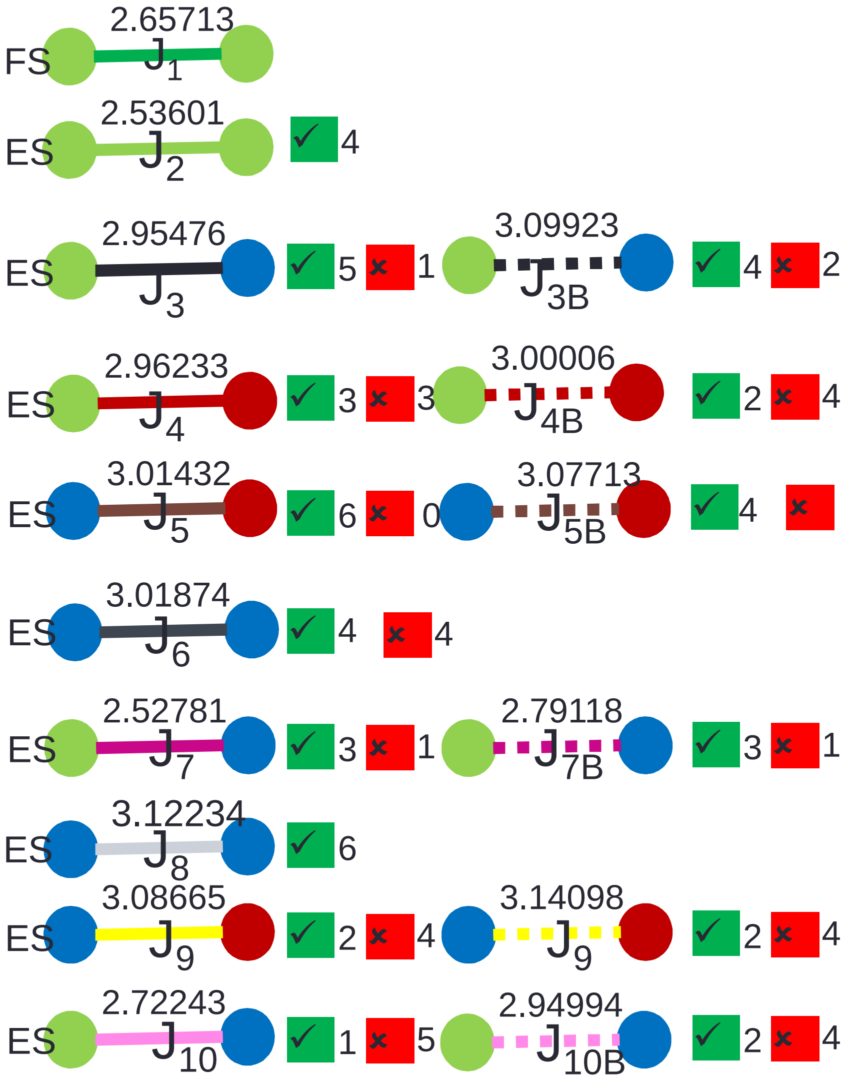
[0.5, 2, L]

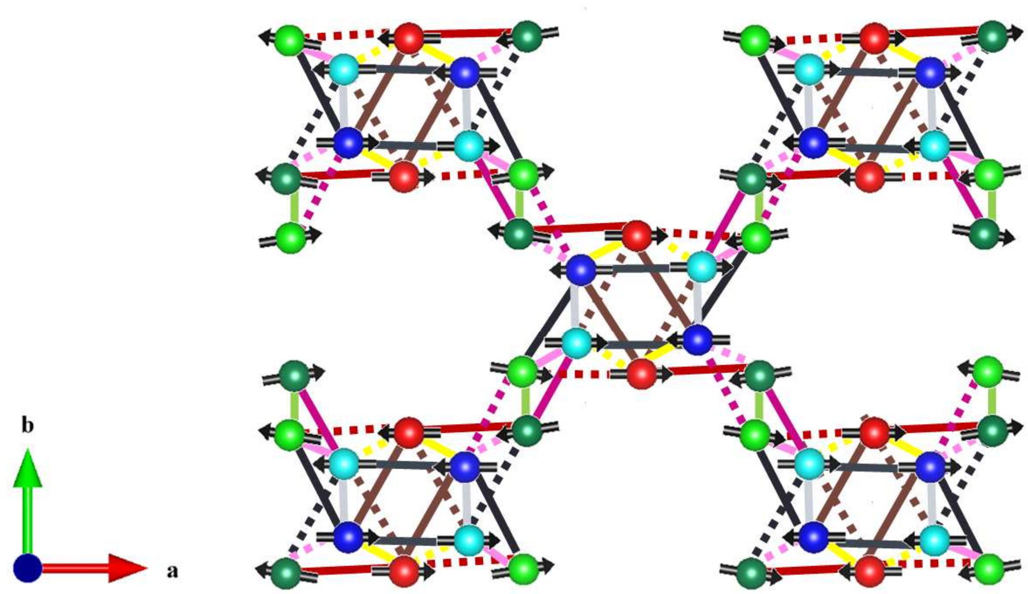
Interactions – Non Trimer





Interactions – Non Trimer

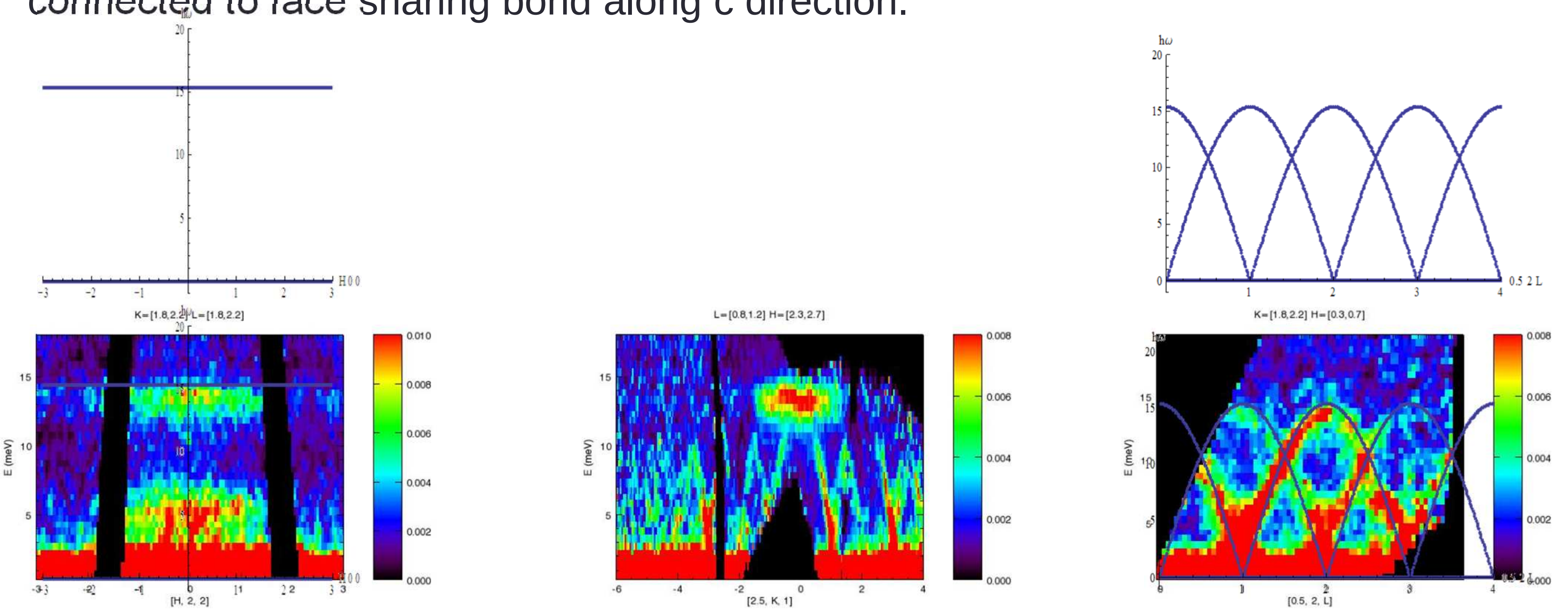




-0.2 <z < 0.3

Non Trimer models – All five V atoms are ordered – Spin waves

- Chain along c-direction with one face sharing and one edge sharing bonds can satisfy the L dependence of the excitations.
- Also, along a-direction it is mostly disconnected and thus can produce the flat modes observed along H.
- The reason for highly dispersive mode along K, is still a question and our hypothesis is frustrated bonds some how create a similar chain along b direction which might be connected to face sharing bond along c direction.



Summary and future work

- We have examined the magnetic structure of BaV10O15 using Single Crystal and powder diffraction data.

- Our analysis shows that Trimer model with only V1 and V2a atoms ordered, cannot reproduce our diffraction data.

- Frustrated model with all five atoms ordered can reasonably reproduce our both single crystal and powder diffraction data.

- We will continue our analysis to find the best Hamiltonian for this system.
- Our future experiments consists of,

1. Field dependence of the excitations
2. Inelastic experiment to see whether there is any high energy modes.

Spinel CoV_2O_4

Spinel Family

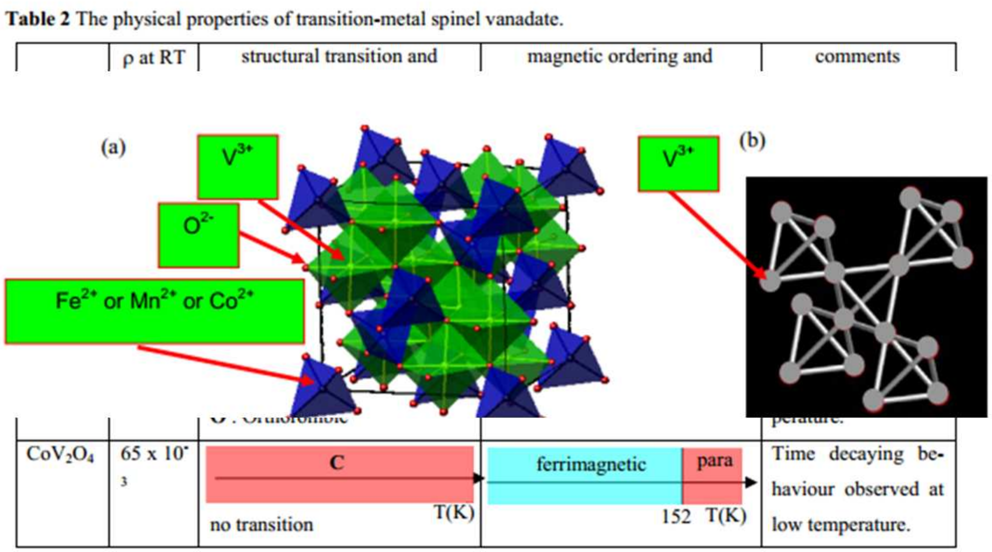
- Spinel is an important class of mixed-metal oxides, which has the general chemical composition of AB_2O_4.

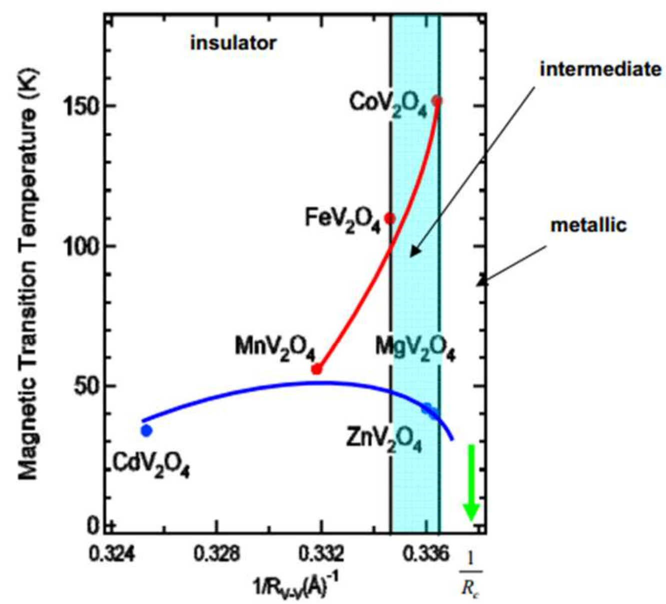
- When the shape of the orbital is changed by an external stimulus, the magnetic, electric, elastic, and optical properties may also be altered.

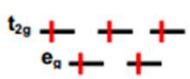
- Spinel oxides with the general formula AB_2O_4 provide a fertile playground for studying the interplay between these degrees of freedom.

Spinel Family

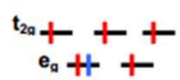
Kismarahardja, Dissertation 2010



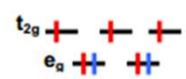




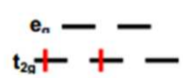
Mn^{2+}, tetrahedral, high spin, e_g2, t_{2g} 3
Magnetic moment = 5.91 μ_B,
free electrons = 5



Fe^{2+}, tetrahedral, high spin, e_g3, t_{2g} 3
Magnetic moment = 4.89 μ_B,
free electrons = 4



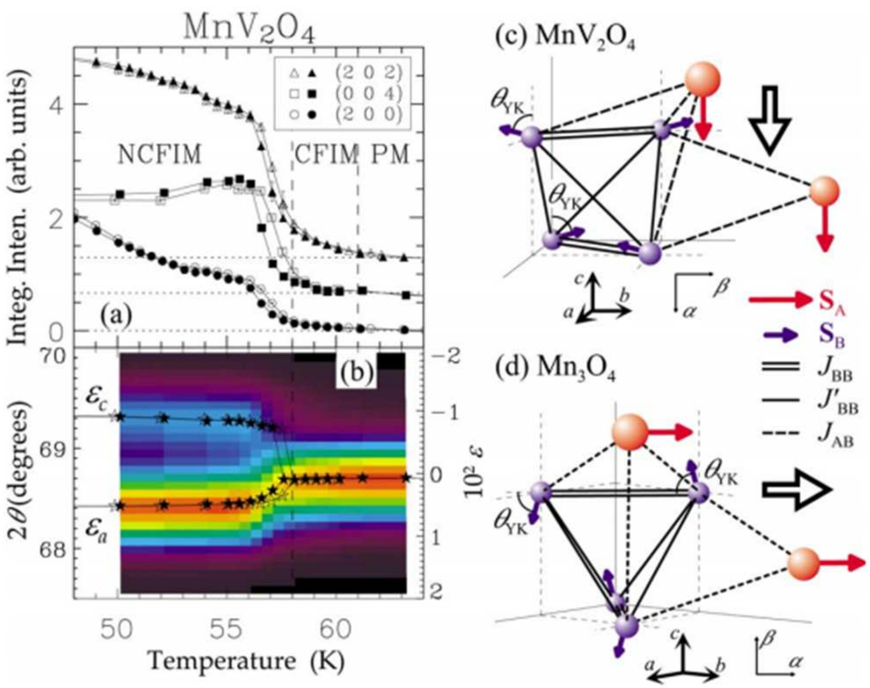
Co^{2+}, tetrahedral, high spin, e_g4, t_{2g} 3
Magnetic moment = 3.87μ_B,
free electrons = 3



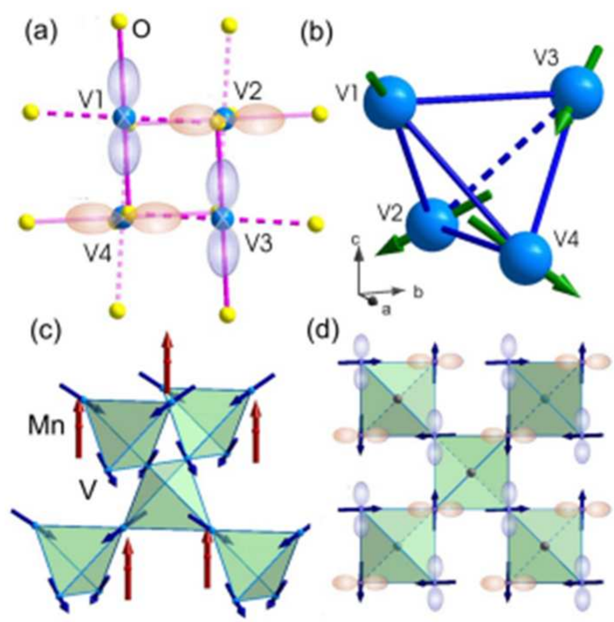
V^{3+}, octahedral, high spin, e_g0, t_{2g} 2
Magnetic moment = 2.82 μ_B,
free electrons = 2

MnV_2O_4: Magnetic structure

PHYSICAL REVIEW B **77**, 054412 (2008)

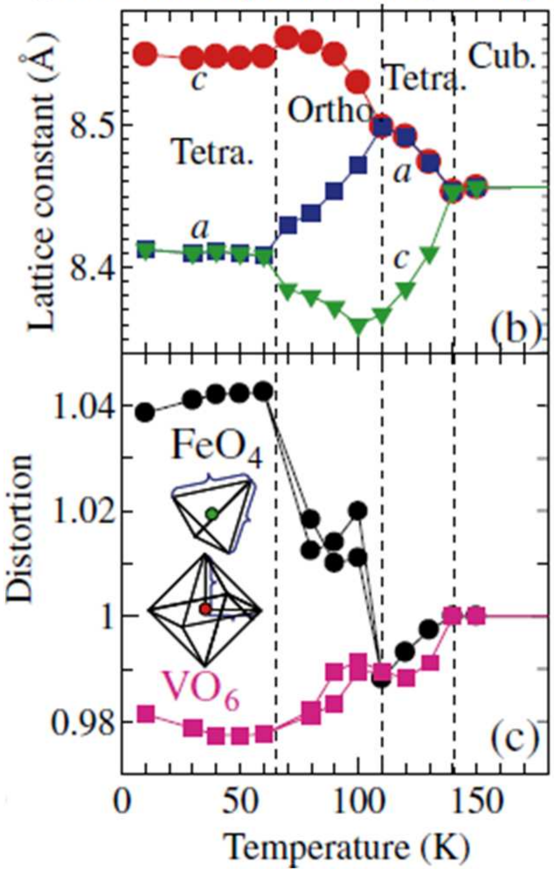


PRL **100**, 066404 (2008)



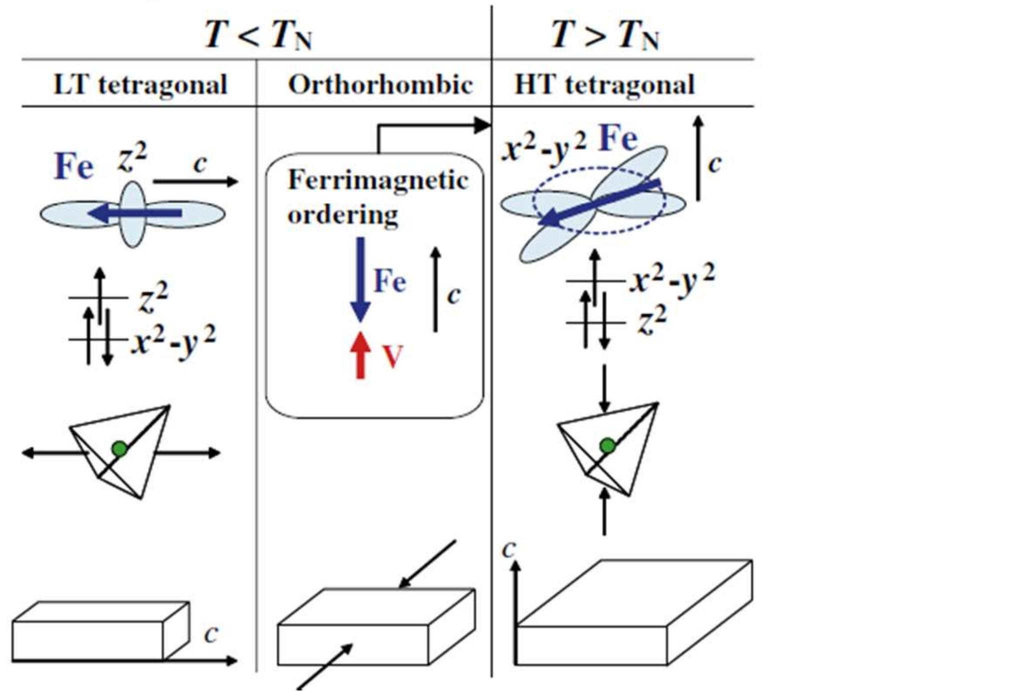
FeV_2O_4: Magnetic structure

Journal of the Physical Society of Japan
Vol. 77, No. 5, May, 2008, 053708



Structural and Magnetic Properties of Spinel FeV_2O_4 with Two Ions Having Orbital Degrees of Freedom

Takuro KATSUFUJI[1,2,3], Takehito SUZUKI[1], Haruki TAKEI[1], Masao SHINGU[1], Kenichi KATO[4,5,6], Keiichi OSAKA[5], Masaki TAKATA[4,5,6], Hajime SAGAYAMA[7], and Taka-hisa ARIMA[7]



Magnetic excitations in MnV_2O_4

PHYSICAL REVIEW B **77**, 054412 (2008)

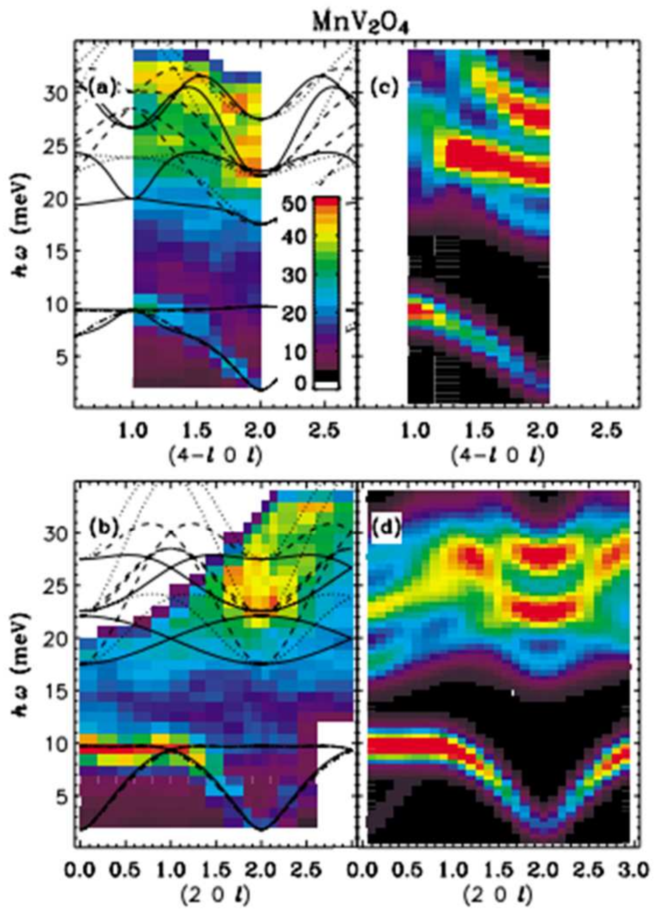
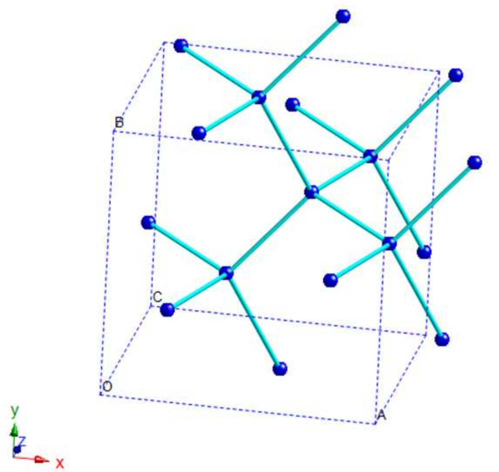


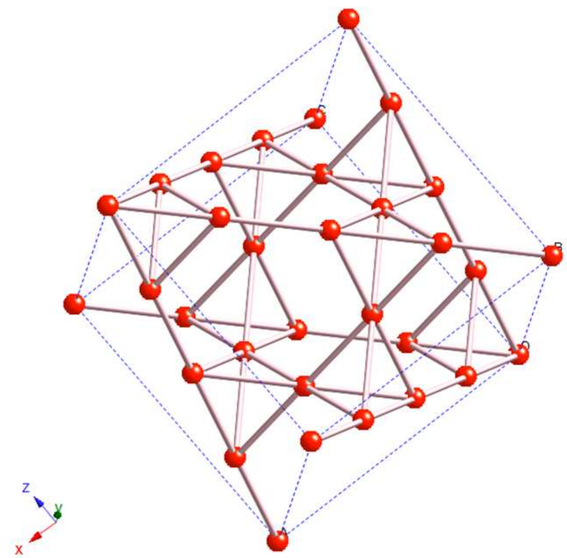
TABLE I. The optimal parameters used to calculate spin wave dispersions of Mn_3O_4 [Fig. 2(b)] and MnV_3O_4 (Fig. 3) ($\tilde{J}$ and $\tilde{D}$ are in meV).

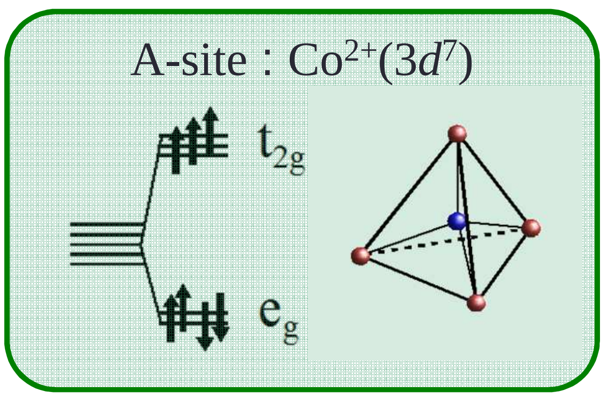
	$\tilde{J}_{AB}$	$\tilde{J}_{BB}$	$\tilde{J}'_{BB}$	$\tilde{D}_A^{1\bar{1}0}$	$\tilde{D}_B^z$	
Mn_3O_4	2.7(1)	19(1)	−1.1(7)	−0.1(3)	−0.28(3)	
	$\tilde{J}_{AB}$	$\tilde{J}_{BB}$	$\tilde{J}'_{BB}$	$\tilde{D}_A^z$	$\tilde{D}_B^y$	$\tilde{D}_B^z$
MnV_2O_4	2.8(2)	9.8(9)	3.0(8)	−0.6(4)	−4.0(4)	2.7(9)

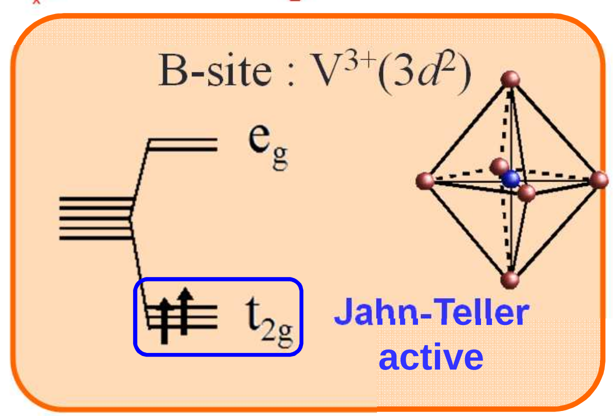
CoV_2O_4: Structure (Cubic with *a* = 8.41 Å)

A-site (Co^{2+}, S=3/2) forms a diamond lattice while B-site (V^{3+}, S=1) forms a pyrochlore lattice. V^{3+} ions are Jahn-Teller active.







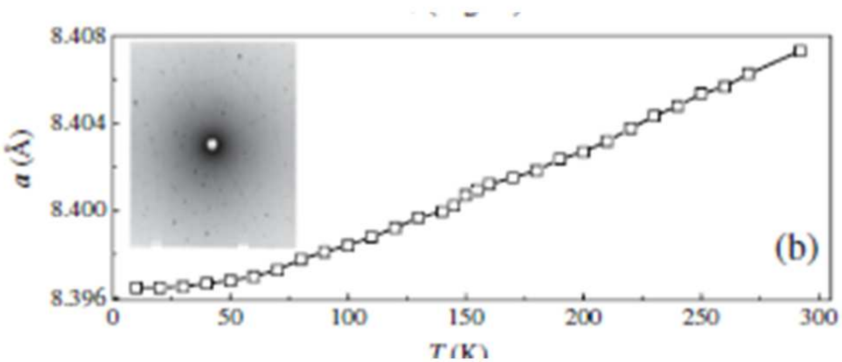


CoV_2O_4: Detailed structure

PRL 106, 056602 (2011) PHYSICAL REVIEW LETTERS week ending 4 FEBRUARY 2011

$Co[V_2]O_4$: A Spinel Approaching the Itinerant Electron Limit

A. Kismarahardja,[1,2] J. S. Brooks,[1,2] A. Kiswandhi,[1,2] K. Matsubayashi,[3] R. Yamanaka,[3] Y. Uwatoko,[3] J. Whalen,[1]
T. Siegrist,[1,4] and H. D. Zhou[1,*]



$Fd\bar{3}m$ O_h^7 $m\bar{3}m$ Cubic

No. 227 $F\ 4_1/d\ \bar{3}\ 2/m$ Patterson symmetry $Fm\bar{3}m$

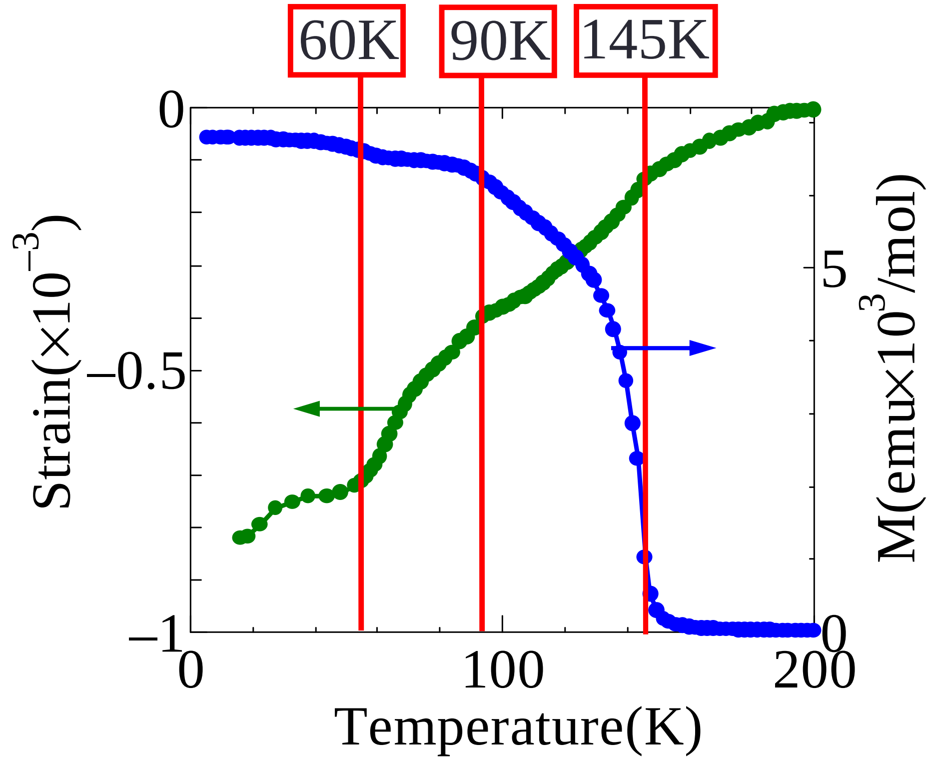
ORIGIN CHOICE 2

TABLE I. Room temperature crystallographic data for $Co[V_2]O_4$. (a) $R_1 = \sum || F_o | - | F_c || / \sum | F_o |$, (b) $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (A \cdot p)^2 + B \cdot p]^{-1}$, and $p = (F_o^2 + 2F_c^2)/3$; $A = 0.0067$, $B = 0$.

Space Group	$Fd\bar{3}m$ (No. 227)
a (Å)	8.4073(1)
Z	8
Atom Positions, U_{iso}	Co 0.375, 0.006 70(13)
($x = y = z$)	V 0, 0.005 68(12)
	O 0.239 79(10), 0.0071(2)
V (Å^3)	594.251(12)
ρ_{cal} (g/cm^3)	5.026
μ (mm^{-1})	11.497
Data Collection Range (deg)	$8.06 < \theta < 61.47$
Reflections Collected	7124
Independent Reflections	260[$R_{int} = 0.097$]
Parameter Refined	8
R_1, wR_2 ($F_o > 4\sigma F_o$)	0.0370, 0.1035
R_1, wR_2 (All Data)	0.0398, 0.1015
Goodness-of-Fit	1.112

CoV_2O_4: Magnetism

CoV_2O_4 shows a ferrimagnetic transition at T = 145 K. And there may be two additional transitions at T = 60 and 90 K (spin re-orientation ?).



Experiments

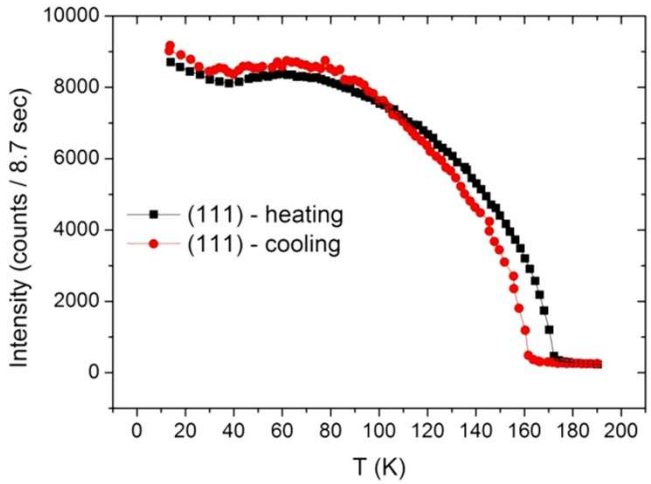
- E5, HZB
- Single Crystal Diffractometer
- -T= 4K with wavelength 1 A

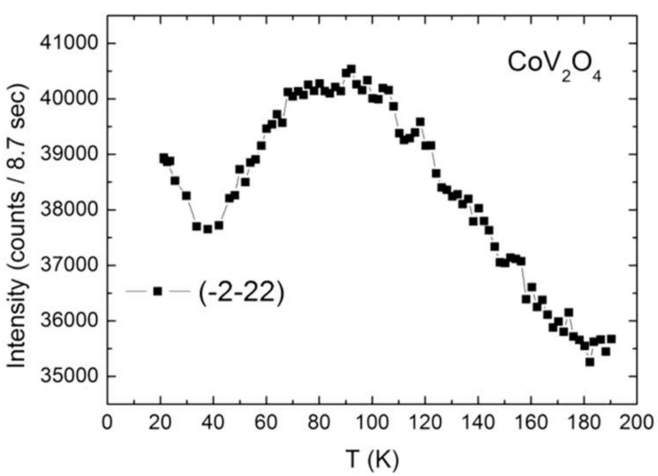
- HB1A, HFIR

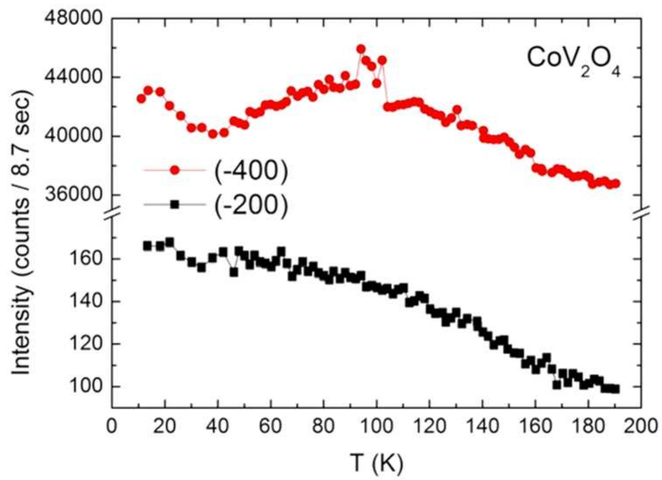
-Thermal Triple axis spectrometer

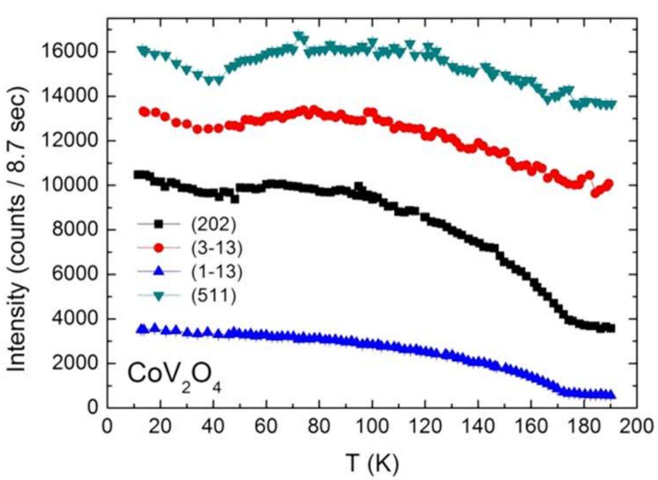
-T=4K with E_f=65meV

Temperature dependence of nuclear + magnetic peaks

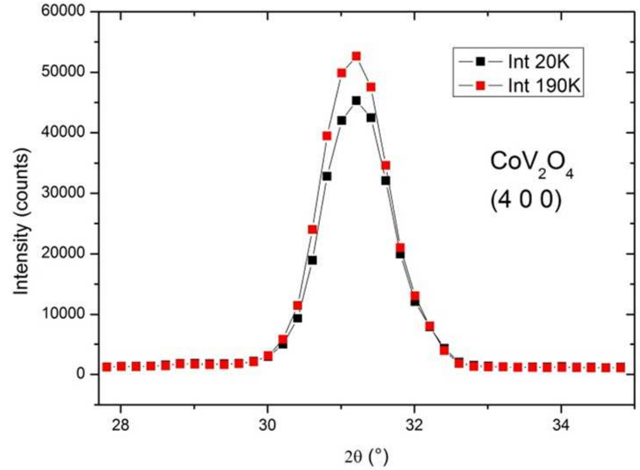


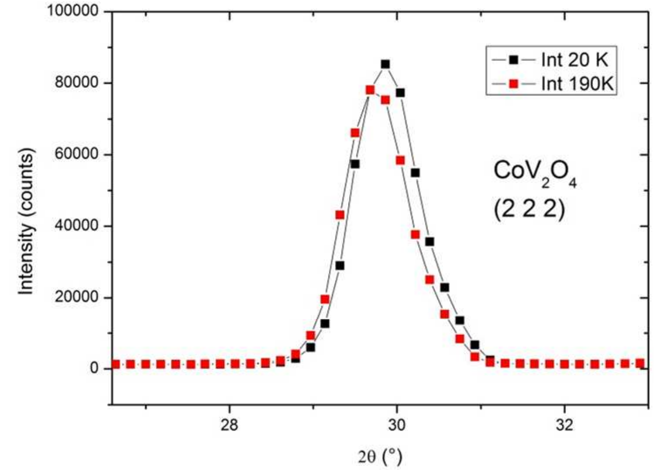




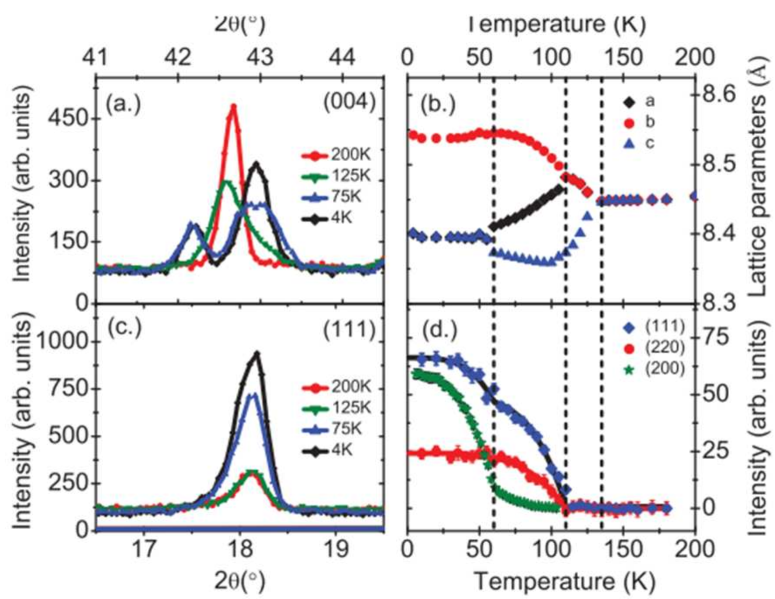


No structural transistion

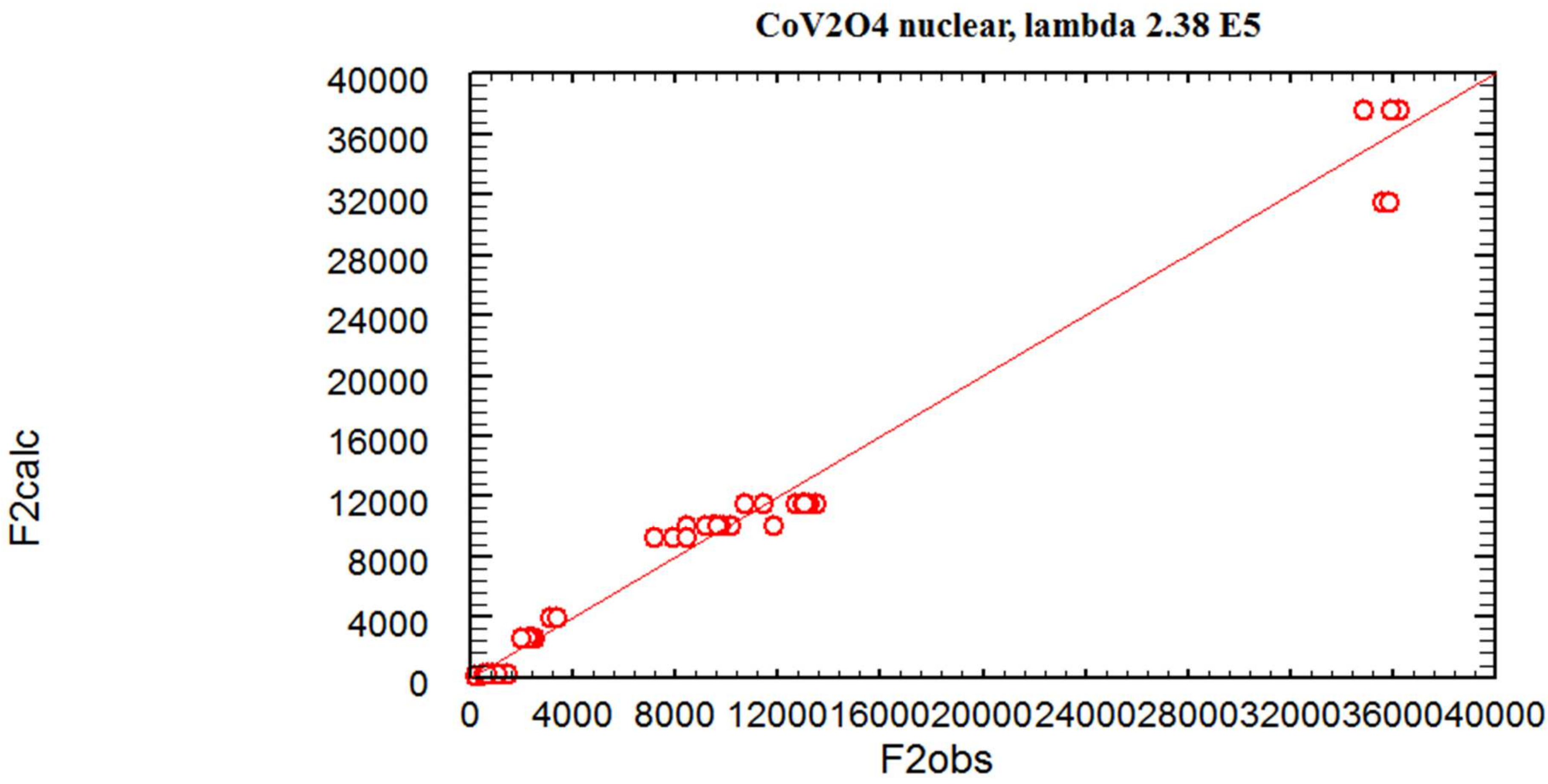




FeV_2O_4

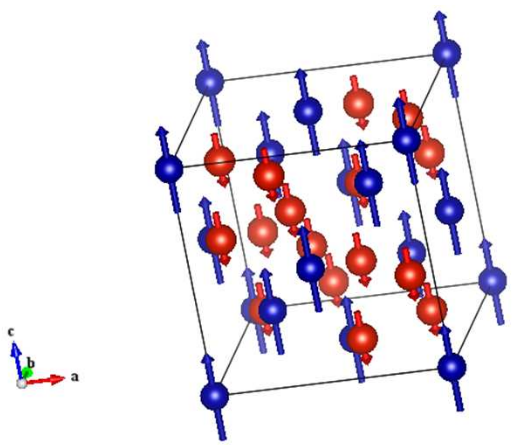


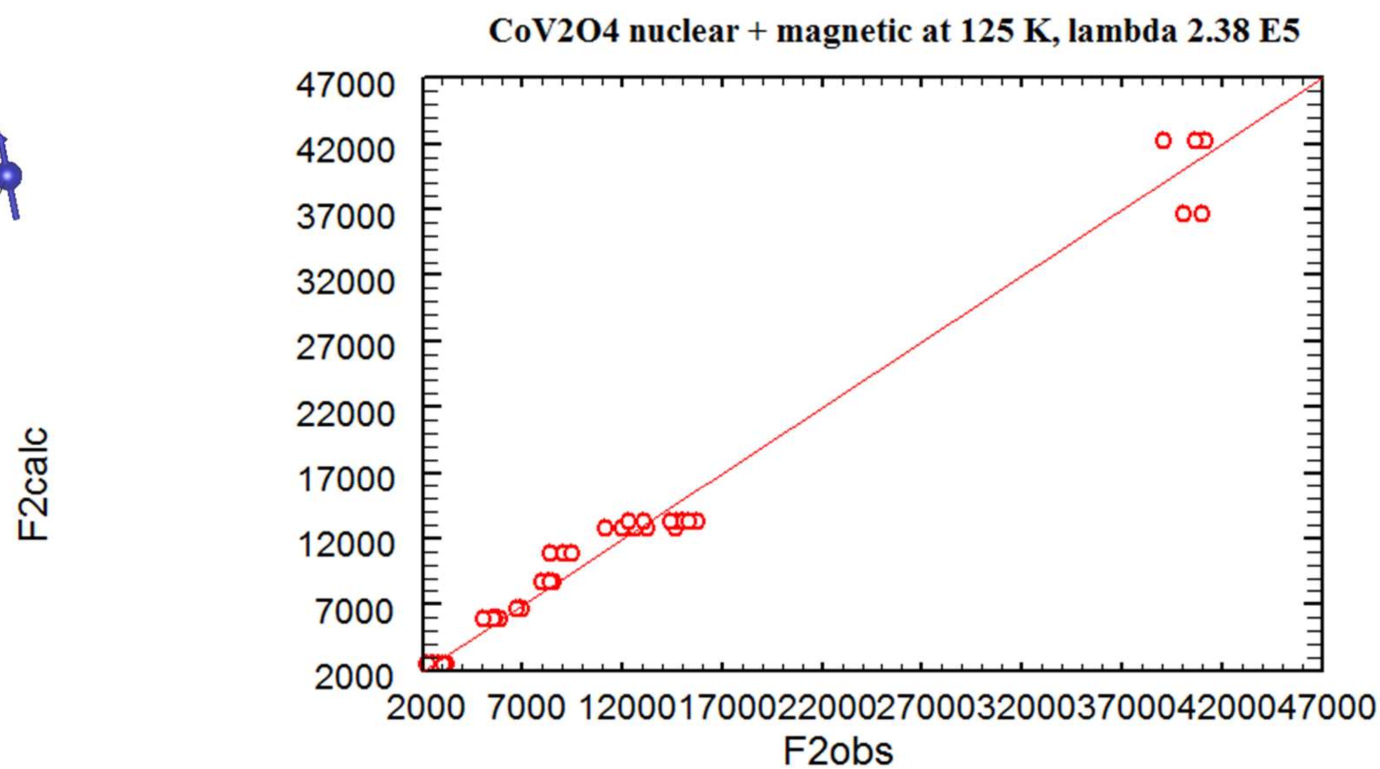
Refinement – 200 K (nuclear)



Refinement – 115 K (magnetic)

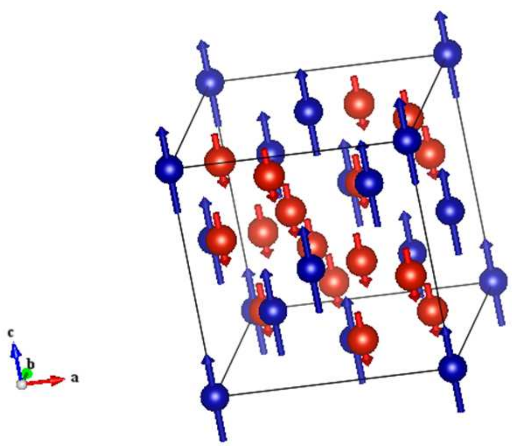
Co	V
2.58227 μ_B	-0.68620 μ_B

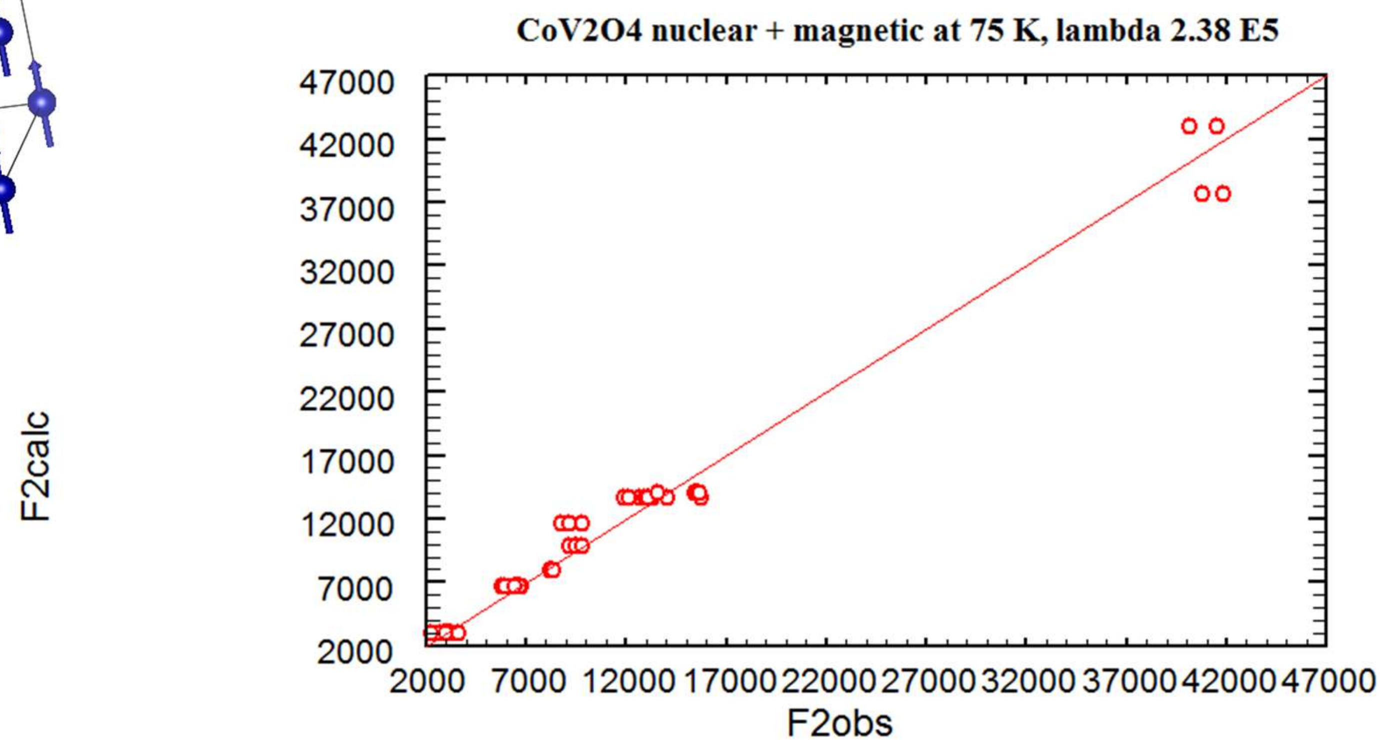




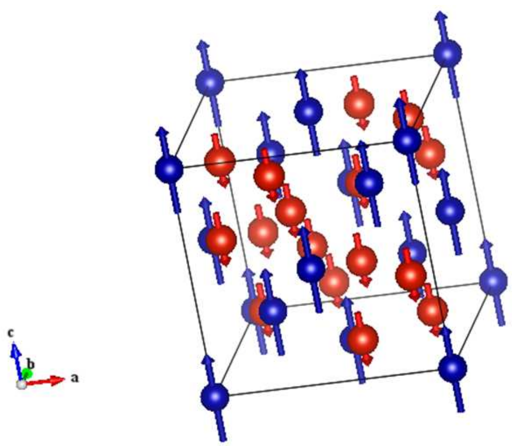
Refinement – 75 K (magnetic)

Co	V
2.95270 μ_B	-0.82596 μ_B

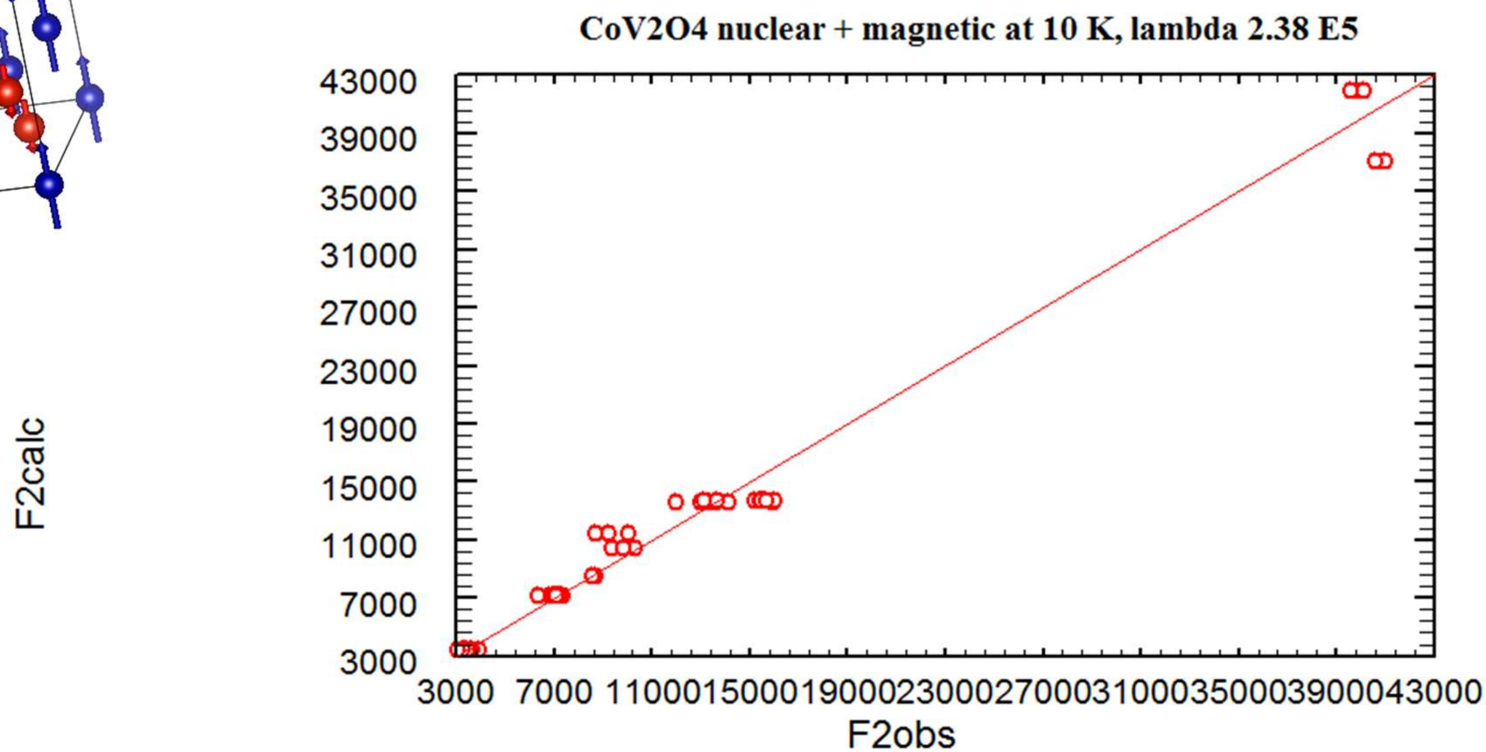




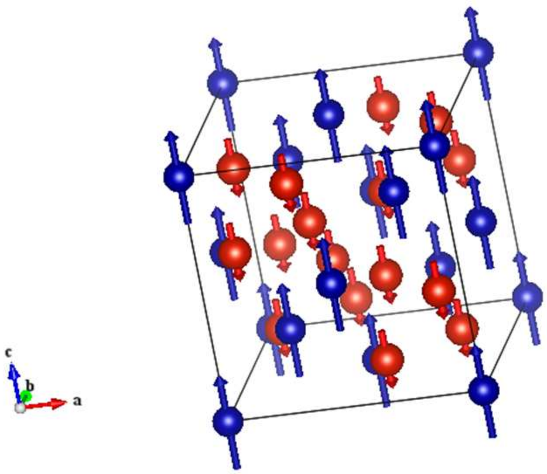
Refinement – 10 K (magnetic)



Co	V
3.27383 μ_B	-0.87081 μ_B

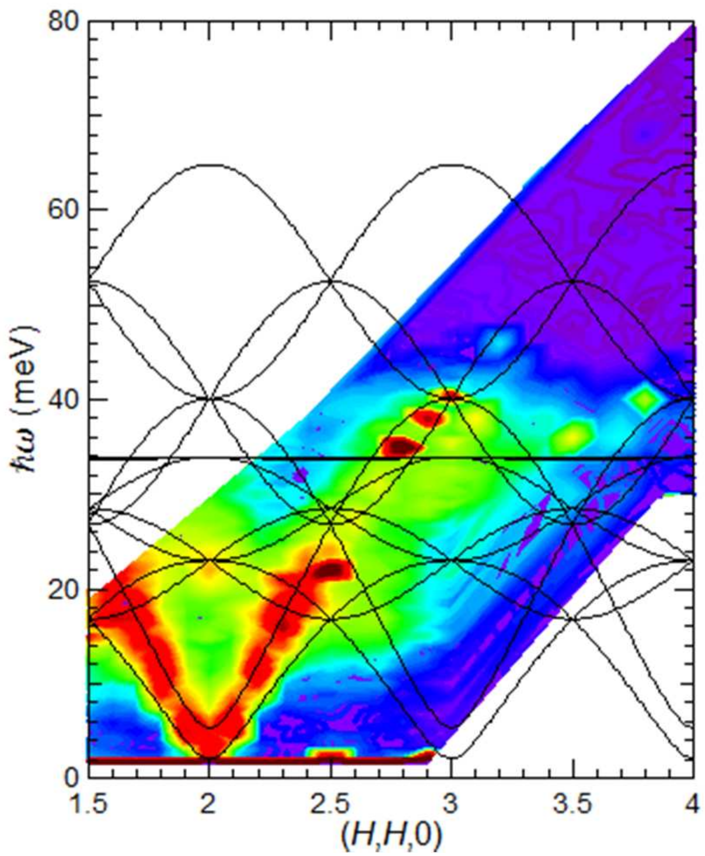


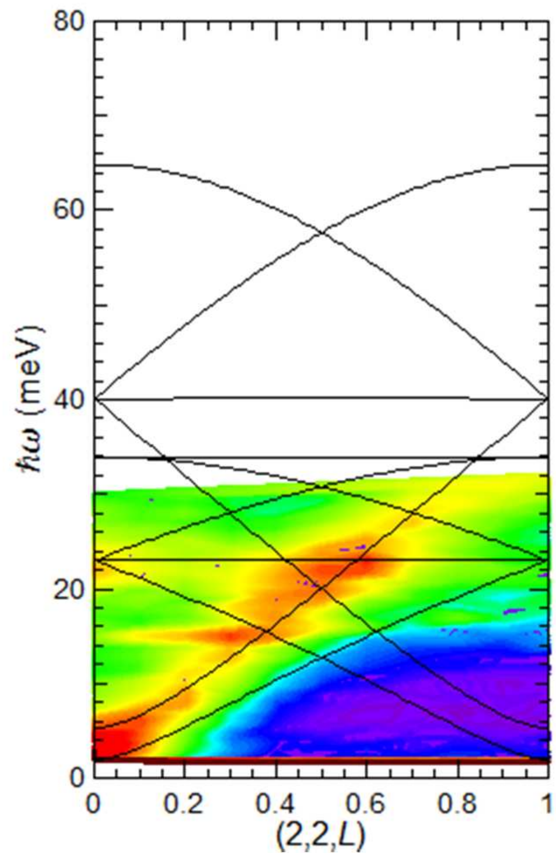
Refinement – Magnetic Structure



Temp (K)	Co Moment (μ_B)	V Moment (μ_B)
115 K	2.582(1)	0.686(1)
75 K	2.952(2)	0.825(1)
10 K	3.273(2)	0.870(1)

Magnetic excitations





Linear Spinwave calculation

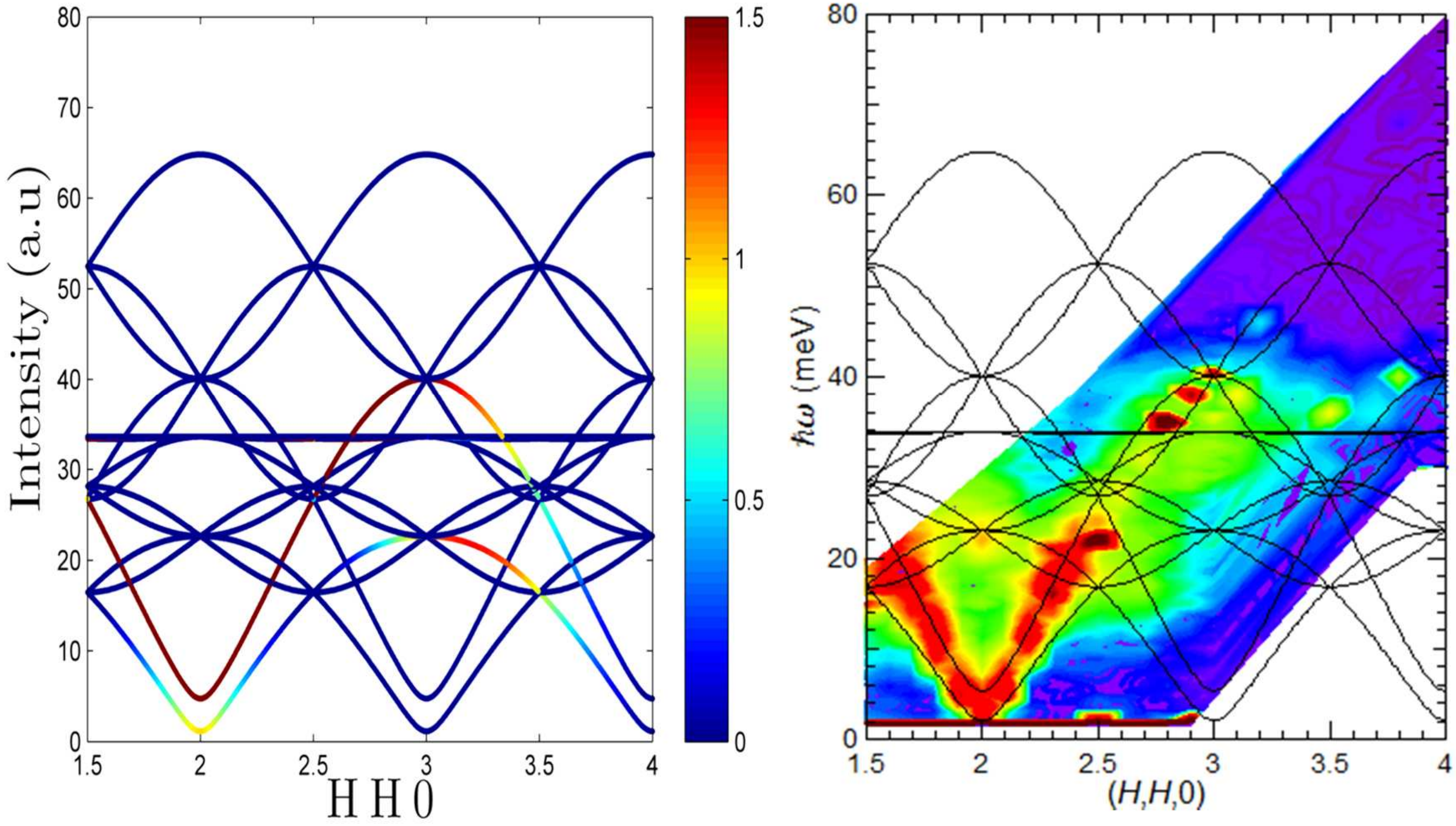
$$\mathcal{H} = \sum_{i,j} J_{Co-V}\, \boldsymbol{S}_{i,Co}.\boldsymbol{S}_{j,V} + \sum_{i,j} J_{Co-Co}\, \boldsymbol{S}_{\boldsymbol{i},\boldsymbol{Co}}.\boldsymbol{S}_{j,Co} + \sum_{i,j} J_{V-V}\, \boldsymbol{S}_{i,V}.\boldsymbol{S}_{j,V} + \sum_{i} D_{Co}\, (S^{z}{}_{i,Co})^2 + \sum_{i} D_V\, (Sz_{i,V})^2$$

J_{Co-Co} ,J_{V-V} and J_{Co-V} are nearest neighbor interactions. D_{Co} and D_V are the single ion anisotropy for Co and V along z direction.

A good fit with the observed magnetic excitations were obtained when J_{Co-V}= 1.3 meV , J_{V-V} = - 2.7 meV, J_{Co-Co} = -4.1 meV, D_V = -0.32 meV and D_{Co} = -0.02 meV.

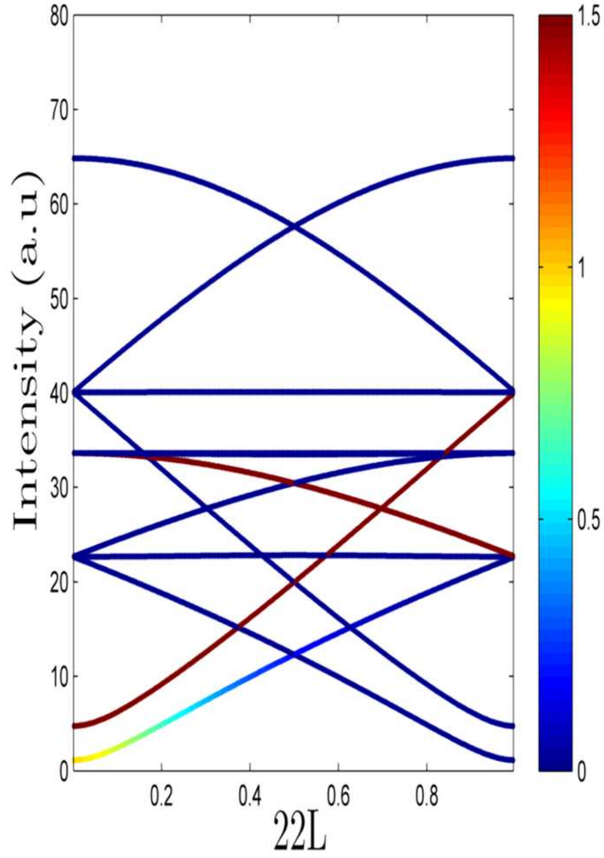
Linear Spinwave calculation

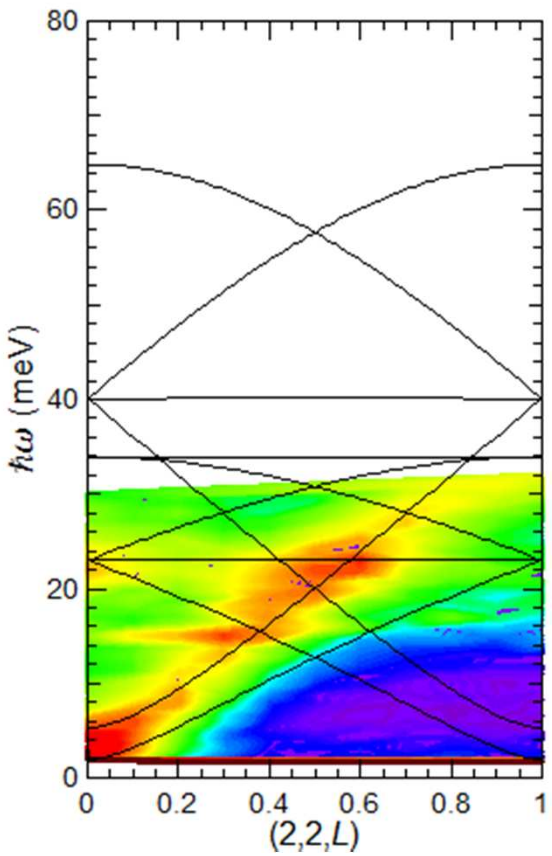
J_{Co-V}= 1.3 meV , J_{V-V} = - 2.7 meV, J_{Co-Co} = -4.1 meV
D_V = -0.32 meV , D_{Co} = -0.02 meV.



Linear Spinwave calculation

J_{Co-V}= 1.3 meV , J_{V-V} = - 2.7 meV, J_{Co-Co} = -4.1 meV
D_V = -0.32 meV , D_{Co} = -0.02 meV.





Summary and future work

- CoV_2O_4 does not show any structural transition as observed in MnV_2O_4 and FeV_2O_4.

- Single crystal data can be successfully refined with a collinear ferrimagnetic structure.

- Collinear ferrimagnetic structure can be used to reproduce inelastic data using a Hamiltonian with nearest neighbor interactions and single ion anisotropy.

- Origin of the anomaly around 40 K is yet to be understood.

THANK YOU !