

Interpretation of magnetic structures of insulators with the help of the computing programs SIMBO and ENERMAG

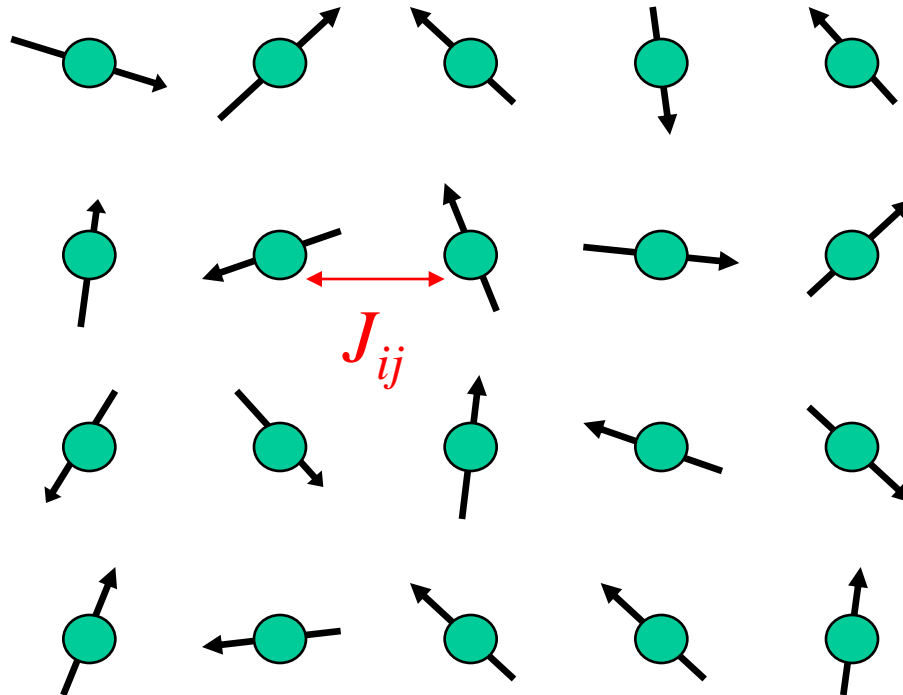
*Juan Rodríguez-Carvajal
Institut Laue-Langevin
Diffraction Group*

What is a magnetic structure? (1)

Paramagnetic state:
Snapshot of magnetic moment configuration

$$E_{ij} = -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

$$\langle \mathbf{S}_i \rangle = 0$$

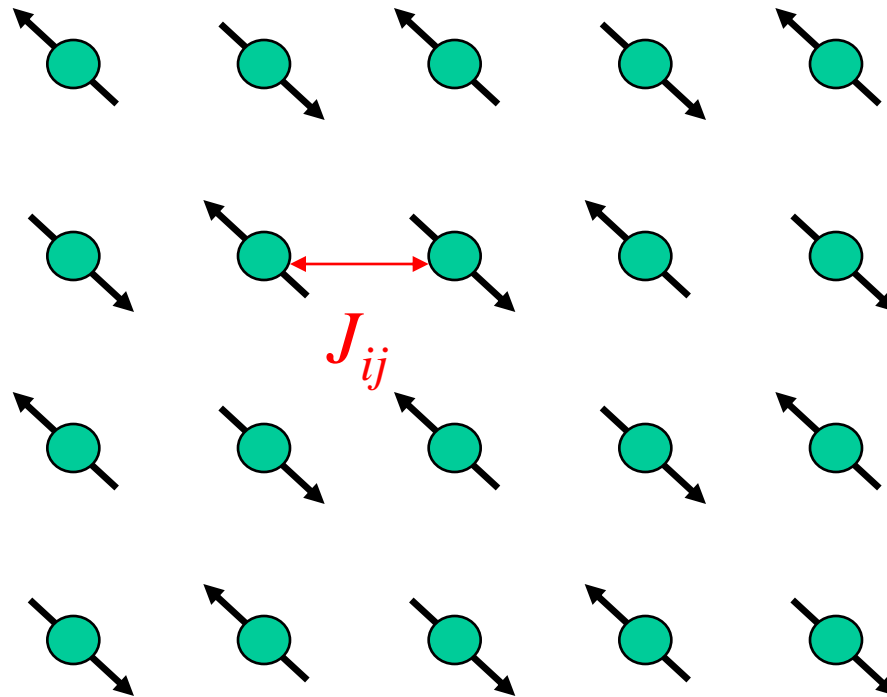


What is a magnetic structure? (2)

Ordered state: Anti-ferromagnetic
Small fluctuations (spin waves) of static configuration

$$E_{ij} = -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

$$\langle \mathbf{S}_i \rangle \neq 0$$



Magnetic structure:
Quasi-static configuration of magnetic moments

Magnetic structures

Magnetic moment \rightarrow Fourier series



$$\mathbf{m}_{lj} = \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} e^{-2\pi i \mathbf{k} \mathbf{R}_l}$$

General expression of the Fourier coefficients (complex vectors) for an arbitrary site (drop of j indices) when \mathbf{k} and $-\mathbf{k}$ are not equivalent:

$$\mathbf{S}_{\mathbf{k}} = \frac{1}{2} (\mathbf{R}_{\mathbf{k}} + i \mathbf{I}_{\mathbf{k}}) \exp\{-2\pi i \phi_{\mathbf{k}}\}$$

Only six parameters are independent. The writing above is convenient when relations between the vectors \mathbf{R} and \mathbf{I} are established (e.g. when $|\mathbf{R}| = |\mathbf{I}|$, or $\mathbf{R} \cdot \mathbf{I} = 0$)

Magnetic structures

Magnetic moment \rightarrow Fourier series



$$\mathbf{m}_{lj} = \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} e^{-2\pi i \mathbf{k} \mathbf{R}_l}$$

The program **FullProf Studio** performs the above sum and represents graphically the magnetic structure.
 This program can help to learn about this formalism because the user can write manually the Fourier coefficients and see what is the corresponding magnetic structure immediately.

Web site: <http://www.ill.eu/sites/fullprof/>

According to the Landau theory of phase transitions, **it is expected that the configuration of the magnetic moments can be described in terms of the basis functions of the Irreps of the propagation vector group** $G_{\mathbf{k}}$ (subgroup of the SG formed by those elements that leave \mathbf{k} invariant). The Irreps of $G_{\mathbf{k}}$ are tabulated or can be calculated independently of the problem

But, knowing the classical Hamiltonian of the spin system, the ground state (magnetic structure at $T = 0$ K) should minimize the energy

$$H = \sum_{j\alpha, im\beta} J_{jl,im}^{\alpha\beta} S_{jl\alpha} S_{im\beta} + \dots O(S^n)$$

The symmetry of the Hamiltonian may be higher than the space group symmetry (e.g. isotropic exchange interactions)

Relation of Fourier coefficients and basis functions of Irreps



$$\mathbf{S}_{\mathbf{k}j} = \sum_{n\lambda\nu} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(j)$$

Fourier coeff. $\mathbf{S}_{\mathbf{k}j}$ Basis vectors $\mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(j)$

The coefficients $C_{n\lambda}^{\nu}$ are the free parameters of the magnetic structure (order parameters of the phase transition in the Landau theory)

Indices:

\mathbf{k} : reference to the propagation vector

ν : reference to the irreducible representation

n : index running from 1 up to $n_{\nu} \Rightarrow$

λ : index running from 1 up to $\dim(\Gamma_{\nu})$

$$\Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu} \Gamma_{\nu}$$

Basic Calculations (1)



The interaction energy between the spins i and j located respectively in the unit cells n and m , is supposed to be of the form:

$$E_{ij}(\mathbf{R}_n, \mathbf{R}_m) = -J_{ij}(\mathbf{R}_n, \mathbf{R}_m) \mathbf{S}_i(\mathbf{R}_n) \cdot \mathbf{S}_j(\mathbf{R}_m)$$

The translation symmetry implies :

$$J_{ij}(\mathbf{R}_n, \mathbf{R}_m) = J_{ij}(\mathbf{R}_n - \mathbf{R}_p, \mathbf{R}_m - \mathbf{R}_p)$$

$$J_{ij}(\mathbf{R}_n, \mathbf{R}_m) = J_{ij}(\mathbf{R}_n - \mathbf{R}_m)$$

Basic Calculations (2)



The classical internal field approximation (H.M. James and T.A. Keenan, J. Chem. Phys. 31, 12, (1959)) assumes that the orientation distribution function for spin i is $p_i(\omega_i)$, which is normalized over all solid angle

$$\int p_i(\omega_i) d\omega_i = 1 \quad \omega_i = (\theta_i, \phi_i)$$

The internal energy and the entropy of the spin system are:

$$U = \frac{1}{2} \sum_{ij} \int d\omega_i \int d\omega_j p_i(\omega_i) p_j(\omega_j) E_{ij}(\omega_i, \omega_j)$$

$$S = -k_B \sum_i \int d\omega_i p_i(\omega_i) \ln p_i(\omega_i)$$

Basic Calculations (3)

The minimisation of the free energy with respect to all p_i subject to the normalisation condition yields:

$$p(\omega_i) = \frac{e^{-\beta \sum_j \int d\omega_j p_j(\omega_j) E_{ij}(\omega_i, \omega_j)}}{\int d\omega_i e^{-\beta \sum_j \int d\omega_j p_j(\omega_j) E_{ij}(\omega_i, \omega_j)}}$$

Anisotropic
exchange

$$E_{ij}(\omega_i, \omega_j, \mathbf{R}_n, \mathbf{R}_m) = -\mathbf{S}_i(\mathbf{R}_n) \mathbf{J}_{ij}(\mathbf{R}_n, \mathbf{R}_m) \mathbf{S}_j(\mathbf{R}_m) = -\sum_{\alpha\beta} S_i^\alpha(\mathbf{R}_n) J_{ij}^{\alpha\beta}(\mathbf{R}_n, \mathbf{R}_m) S_j^\beta(\mathbf{R}_m)$$

in terms of the average spins: $\sigma_i(\mathbf{R}_n) = \int d\omega_i^{\mathbf{R}_n} p_i(\omega_i^{\mathbf{R}_n}) \mathbf{S}_i(\mathbf{R}_n)$

$$\sigma_i(\mathbf{R}_n) = \int d\omega_i^{\mathbf{R}_n} p_i(\omega_i^{\mathbf{R}_n}) \mathbf{S}_i(\mathbf{R}_n) = \frac{\int d\omega_i^{\mathbf{R}_n} \mathbf{S}_i(\mathbf{R}_n) e^{\beta \mathbf{S}_i(\mathbf{R}_n) \mathbf{H}_i}}{\int d\omega_i^{\mathbf{R}_n} e^{\beta \mathbf{S}_i(\mathbf{R}_n) \mathbf{H}_i}}$$

With the molecular field: $\mathbf{H}_i = -\sum_{jm} \mathbf{J}_{ij}(\mathbf{R}_n - \mathbf{R}_m) \sigma_j(\mathbf{R}_m)$

$$H_i^\alpha = -\sum_{jm\beta} J_{ij}^{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) \sigma_j^\beta(\mathbf{R}_m)$$

Basic Calculations (4)



The mean-field equation for all temperatures:

$$\sigma_i(\mathbf{R}_n) = \frac{\int d\omega_i^{\mathbf{R}_n} S_i(\mathbf{R}_n) e^{-\beta S_i(\mathbf{R}_n) \sum_{jm} \mathbf{J}_{ij}(\mathbf{R}_n - \mathbf{R}_m) \sigma_j(\mathbf{R}_m)}}{\int d\omega_i^{\mathbf{R}_n} e^{-\beta S_i(\mathbf{R}_n) \sum_{jm} \mathbf{J}_{ij}(\mathbf{R}_n - \mathbf{R}_m) \sigma_j(\mathbf{R}_m)}}$$

has the solution $\sigma_i(\mathbf{R}_n) = 0$ representing the disordered state

At low temperature, the equation presents different solutions with

$$\sigma_i(\mathbf{R}_n) \neq 0 \quad T \uparrow \rightarrow \sigma_i(\mathbf{R}_n) = \vec{0}$$

all of which evolves towards the disordered state as soon as the temperature increases.

Basic Calculations (5)



The temperature at which a solution disappears is called « branching temperature » T_b . In the neighborhood of T_b , the exponential function of the mean-field equation can be written in a linear form for the spin . When the average spin is small only the first non-null term is retained. We obtain the equations:

$$\sum_{jm} \mathbf{J}_{ij}(\mathbf{R}_n - \mathbf{R}_m) \boldsymbol{\sigma}_j(\mathbf{R}_m) = \lambda \boldsymbol{\sigma}_i(\mathbf{R}_n) = -3k_B T_b \boldsymbol{\sigma}_i(\mathbf{R}_n)$$

$$\sum_{jm\beta} J_{ij}^{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) \sigma_j^{\beta}(\mathbf{R}_m) = \lambda \sigma_i^{\alpha}(\mathbf{R}_n)$$

This equation can be simplified when taking into account the translational symmetry (Fourier transform).

Basic Calculations (6)

Using the Fourier expansion:

$$\sigma_i^\alpha(\mathbf{R}_n) = \sum_{\mathbf{k}} \sigma_{\mathbf{k}i}^\alpha e^{-2\pi i \mathbf{k} \cdot \mathbf{R}_n}$$

We obtain the equation:

$$\sum_{j\beta} \sigma_{\mathbf{k}j}^\beta \sum_m J_{ij}^{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) e^{-2\pi i \mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)} = \lambda(\mathbf{k}) \sigma_{\mathbf{k}i}^\alpha$$

$$\sum_{j\beta} \xi_{ij}^{\alpha\beta}(\mathbf{k}) \sigma_{\mathbf{k}j}^\beta = \lambda(\mathbf{k}) \sigma_{\mathbf{k}i}^\alpha = 3kT_b(\mathbf{k}) \sigma_{\mathbf{k}i}^\alpha$$

Which is an eigen-value equation with: $\lambda(\mathbf{k}) = 3kT_b(\mathbf{k})$

Basic Calculations (7)



The final eigen-value/eigen-vector equation is:

$$\sum_{j\beta} \xi_{ij}^{\alpha\beta}(\mathbf{k}) \sigma_{\mathbf{k}j}^{\beta} = \lambda(\mathbf{k}) \sigma_{\mathbf{k}i}^{\alpha} = 3kT_b(\mathbf{k}) \sigma_{\mathbf{k}i}^{\alpha}$$

If the equation is satisfied by the Fourier coefficients: $\sigma_{\mathbf{k}i}^{\alpha}$
The first magnetically ordered state corresponds to the highest eigen-value (maximum branching temperature) of the Hermitical matrix representing the Fourier transform of the exchange interactions:

$$\xi_{ij}^{\alpha\beta}(\mathbf{k}) = \sum_p J_{ij}^{\alpha\beta}(\mathbf{R}_p) e^{-2\pi i \mathbf{k} \cdot \mathbf{R}_p}$$

Interpretation of the magnetic structure
as the ground state (first ordered state)
of a classical spin system

Classical magnetic energy: $E = -\sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$

First ordered state corresponds to the **lowest eigenvalue** of the **negative** Fourier matrix of the exchange interactions:

$$\xi_{ij}(\mathbf{k}) = -\sum_p J_{ij}(\mathbf{R}_p) e^{-2\pi i \mathbf{k} \cdot \mathbf{R}_p}$$

Summary: SIMBO (1)



We have developed two programs (SIMBO and ENERMAG) that provide an important help for interpreting experimental magnetic structures in terms of relative exchange interactions

The program SIMBO analyses the crystal structure of an insulator in terms of super-exchange M_1-X-M_2 and super-super-exchange $M_1-X_1-X_2-M_2$ paths from the knowledge of the space group, atom coordinates in the asymmetric unit, ionic charges, magnetic moments and cell parameters.

Summary: SIMBO (2)



The program uses this information for calculating distances, angles and exchange paths. SIMBO provides a first file containing the list of paths connecting the magnetic atoms of the structure and attribute them the appropriate symbols for gathering the exchange interactions as a function of inter-atomic distances.

SIMBO provides also a formal description of the Fourier transform of the isotropic exchange interactions in a matrix form (exchange matrix) of dimension $n \times n$, where n is the number of magnetic ions in the primitive cell.

This information is summarized in a file that is used by the program ENERMAG.

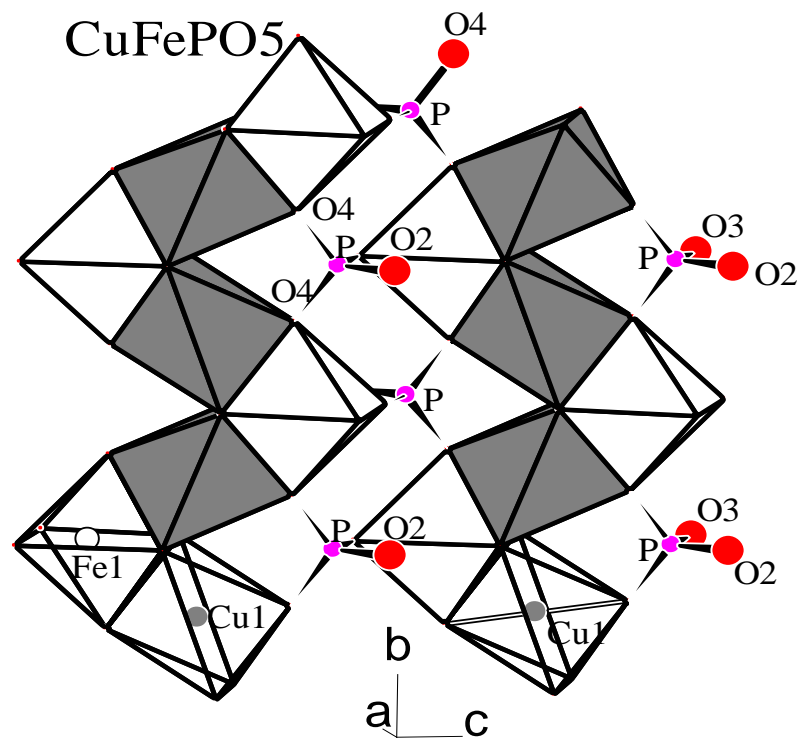
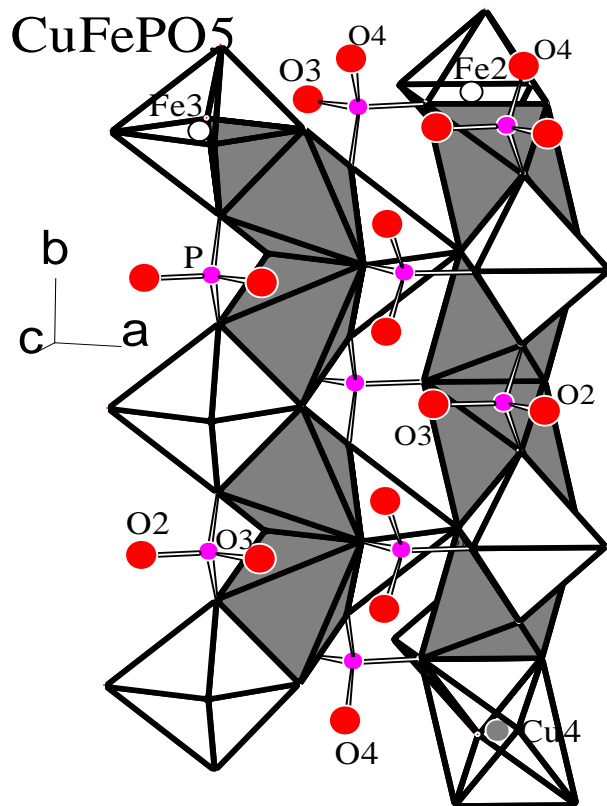
Input file: My_file.cfl

Example:

```

Title  NiFePO5
Cell   7.1882    6.3924    7.4847    90.000    90.000    90.000
Spgr   P n m a
!
!           x           y           z           occ   B   Spin Charge
Atom  Ni   NI   0.0000    0.0000    0.0000    0.74   0.5   2.0    2.0
Atom  Fe   FE   0.1443    0.2500    0.7074    0.63   0.5   5.0    3.0
Atom  P    P    0.3718    0.2500    0.1424    0.79   0.5   0.0    5.0
Atom  O1   O    0.3988    0.2500    0.64585   0.71   0.5   0.0   -2.0
Atom  O2   O    0.19415   0.2500    0.0253    0.70   0.5   0.0   -2.0
Atom  O3   O    0.0437    0.2500    0.4728    0.83   0.5   0.0   -2.0
Atom  O4   O    0.3678    0.0566    0.2633    0.77   1.0   0.0   -2.0
  
```

Phase diagram for the topology of $M\text{FePO}_5$



Output files:

My_file.nei	⇒	General output file
My_file.exc	⇒	Input file for ENERMAG
My_file.mcm	⇒	Input file for MCMAG

SIMBO running

C:\ProgCFML\Testing\Enermag>simbo mfepo5

```
----- PROGRAM SIMBO -----
---- Version 2.0 Oct-2003----
```

```
*****
* Generates neighboring files for magnetic simulations *
*****
(JRC- October 2003 )
```

```
=> Maximum bond-distance (Dmax) : 6.000
=> Maximum distance for direct exchange (Direct) : 0.000
=> Maximum distance for angle calculation(Dangl) : 0.000
=> Maximum distance for anion-anion bond (Dbond)
    (also for cation-anion bonds) : 3.000
=> Maximum angle M-M'^M(M')-A(A') for S-E paths (Angm): 89.500
=> Minimum angle M-A-A'/M'-A'-A for S-E paths (Angn): 89.500
    (if Dangl=0 no angles are calculated)
```

any change ? (Y/N=<cr>):

SIMBO running

```
any change ? (Y/N=<cr>): y
=> Give new values for Dmax, Direct, Dangl, Dbond, Angm and Angn :
    5 0 0 3 90 90
=> List all distances & angles (y/n)? (def=n):
=> List detailed exchange paths (y/n)? (def=n):
```

Total CPU-Time

CPU-seconds:	0.45
CPU-minutes:	0.01
CPU-hours :	0.00

=> Results in files:

```
mfepo5.nei
mfepo5.exc -> input for ENERMAG
mfepo5.mcm -> input for MCMAG
```

SIMBO output (1)

```
=====
=====>  LIST OF INDEPENDENT EXCHANGE INTERACTIONS  <=====
=====
```

```
=> Exchange interaction: J1  between Ni    and Fe    -> Distance:    2.9028
```

```
S-Exchange (d1,d2,theta): Ni_2-O1_3-Fe_4(0,0,0)  (  2.0676  2.0786  88.87 )
```

```
S-Exchange (d1,d2,theta): Ni_2-O2_4-Fe_4(0,0,0)  (  2.1301  2.4062  79.31 )
```

```
S-Exchange (d1,d2,theta): Ni_2-O4_7-Fe_4(0,0,0)  (  2.0427  2.0060  91.61 )
```

```
=> Exchange interaction: J2  between Ni    and Ni    -> Distance:    3.1962
```

```
S-Exchange (d1,d2,theta): Ni_1-O1_4-Ni_3(0,-1,0)  (  2.0676  2.0676 101.24 )
```

```
S-Exchange (d1,d2,theta): Ni_1-O2_3-Ni_3(0,-1,0)  (  2.1301  2.1301  97.22 )
```

```
SS-Exchange (d1,d2,d3,ang1,ang2,dihed): Ni_1-O4_4-O4_6-Ni_3(0,-1,0)  (  2.0427  2.4726  2.0427
100.20 100.20    0.00 )
```

```
=> Exchange interaction: J3  between Ni    and Fe    -> Distance:    3.3913
```

```
S-Exchange (d1,d2,theta): Ni_1-O1_2-Fe_2(-1,0,-1) (  2.0676  1.8865 118.04 )
```

```
SS-Exchange (d1,d2,d3,ang1,ang2,dihed): Ni_1-O2_3-O4_5-Fe_2(-1,0,-1) (  2.1301  2.5019  2.0060
91.11 108.22  34.14 )
```

```
=> Exchange interaction: J4  between Fe    and Fe    -> Distance:    3.6502
```

```
S-Exchange (d1,d2,theta): Fe_1-O1_2-Fe_2(-1,0,0)  (  2.0786  1.8865 133.97 )
```

```
SS-Exchange (d1,d2,d3,ang1,ang2,dihed): Fe_1-O3_1-O2_2-Fe_2(-1,0,0)  (  1.8990  2.5127  2.4062
112.06  98.89    0.00 )
```

```
=> Exchange interaction: J5  between Fe    and Fe    -> Distance:    4.9151
```

```
SS-Exchange (d1,d2,d3,ang1,ang2,dihed): Fe_1-O3_1-O4_8-Fe_3(-1,-1,0)  (  1.8990  2.5000  2.0060
147.80 110.96  15.72 )
```

```
SS-Exchange (d1,d2,d3,ang1,ang2,dihed): Fe_1-O4_4-O3_3-Fe_3(-1,-1,0)  (  2.0060  2.5000  1.8990
110.96 147.80 -15.72 )
```

SIMBO output (2)

Effective Neighbouring matrix

	1	2	3	4	5	6	7	8
1	0	0	2	0	1	1	1	1
2	0	0	0	2	1	1	1	1
3	2	0	0	0	1	1	1	1
4	0	2	0	0	1	1	1	1
5	1	1	1	1	0	2	2	0
6	1	1	1	1	2	0	0	2
7	1	1	1	1	2	0	0	2
8	1	1	1	1	0	2	2	0

SIMBO output (3)

Terms of the Fourier transform of exchange interactions

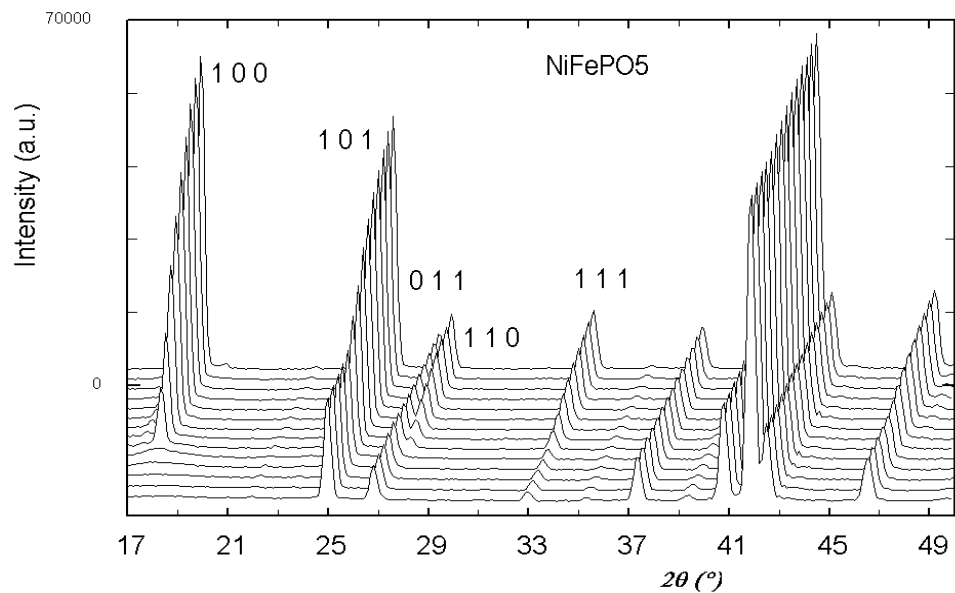
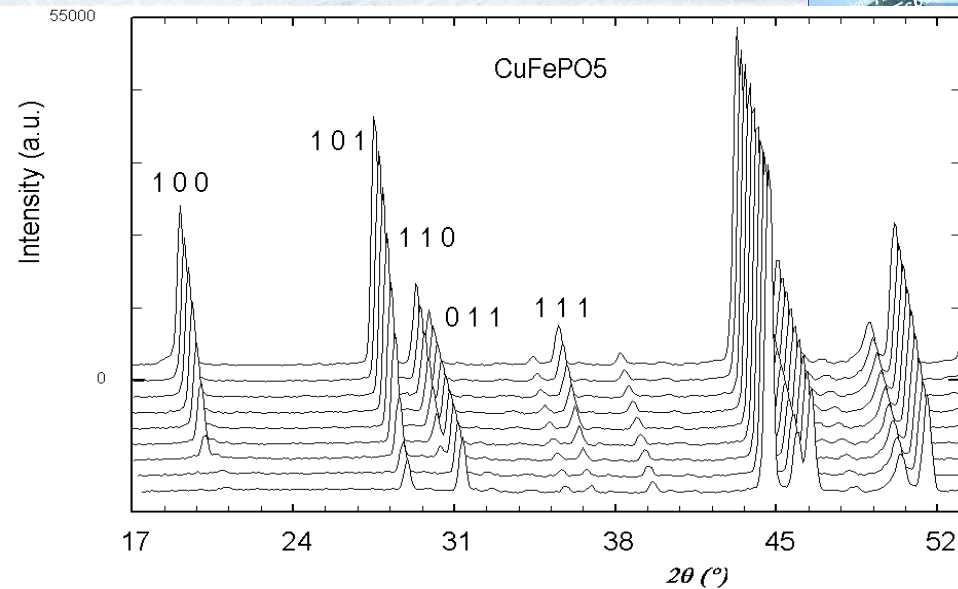
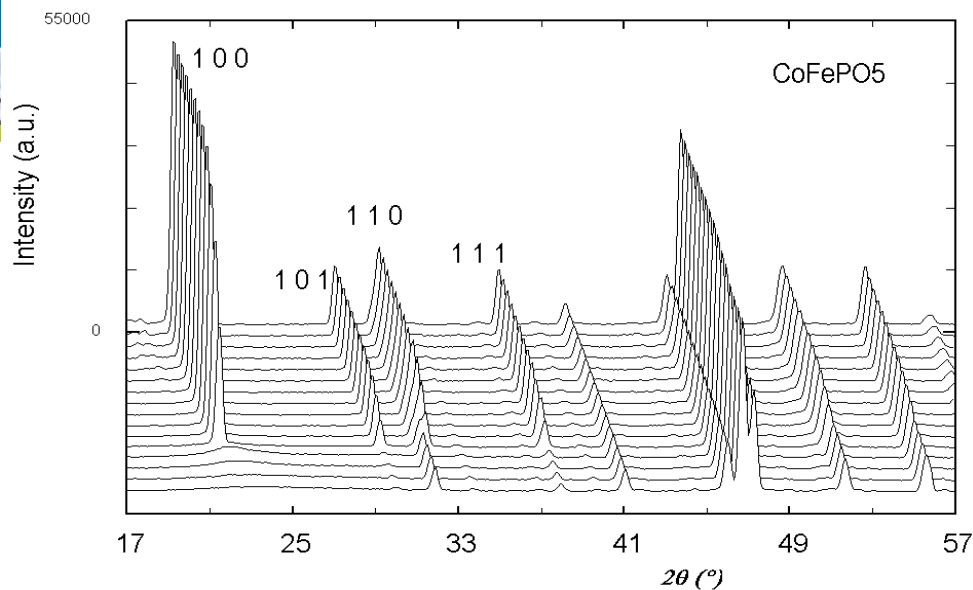
```

=> J( 1, 1) [K]      ( 0 terms)
=> J( 1, 2) [K]      ( 0 terms)
=> J( 1, 3) [K]      ( 2 terms)
      Rn=(0,-1,0)      dist= 3.1962 --> J2 exp{-2pi(-Y)}
      Rn=(0,0,0)      dist= 3.1962 --> J2
=> J( 1, 4) [K]      ( 0 terms)
=> J( 1, 5) [K]      ( 1 terms)
      Rn=(0,0,-1)      dist= 2.9028 --> J1 exp{-2pi(-Z)}
=> J( 1, 6) [K]      ( 1 terms)
      Rn=(-1,0,-1)      dist= 3.3913 --> J3 exp{-2pi(-X-Z)}
=> J( 1, 7) [K]      ( 1 terms)
      Rn=(-1,-1,0)      dist= 2.9028 --> J1 exp{-2pi(-X-Y)}
. . .
=> J( 5, 5) [K]      ( 0 terms)
=> J( 5, 6) [K]      ( 2 terms)
      Rn=(-1,0,0)      dist= 3.6502 --> J4 exp{-2pi(-X)}
      Rn=(0,0,0)      dist= 3.6502 --> J4
=> J( 5, 7) [K]      ( 2 terms)
      Rn=(-1,-1,0)      dist= 4.9151 --> J5 exp{-2pi(-X-Y)}
      Rn=(-1,0,0)      dist= 4.9151 --> J5 exp{-2pi(-X)}
=> J( 5, 8) [K]      ( 0 terms)

```

SIMBO output (4)

$$\xi(\vec{k}) = \begin{pmatrix} 0 & 0 & J_2(1+e^{2\pi i Y}) & 0 & J_1 e^{2\pi i Z} & J_3 e^{2\pi i(X+Z)} & J_1 e^{2\pi i(X+Y)} & J_3 e^{2\pi i Y} \\ 0 & 0 & 0 & J_2(1+e^{-2\pi i Y}) & J_3 & J_1 & J_3 & J_1 \\ J_2(1+e^{-2\pi i Y}) & 0 & 0 & 0 & J_1 e^{2\pi i Z} & J_3 e^{2\pi i(X+Z)} & J_1 e^{2\pi i X} & J_3 \\ 0 & J_2(1+e^{2\pi i Y}) & 0 & 0 & J_3 & J_1 & J_3 e^{2\pi i Y} & J_1 e^{2\pi i Y} \\ J_1 e^{-2\pi i Z} & J_3 & J_1 e^{-2\pi i Z} & J_3 & 0 & J_4(1+e^{2\pi i X}) & 0 & 0 \\ J_3 e^{-2\pi i(X+Z)} & J_1 & J_3 e^{-2\pi i(X+Z)} & J_1 & J_4(1+e^{-2\pi i X}) & 0 & 0 & 0 \\ J_1 e^{-2\pi i(X+Y)} & J_3 & J_1 e^{-2\pi i X} & J_3 e^{-2\pi i Y} & 0 & 0 & 0 & J_4(1+e^{-2\pi i X}) \\ J_3 e^{-2\pi i Y} & J_1 & J_3 & J_1 e^{-2\pi i Y} & 0 & 0 & J_4(1+e^{2\pi i X}) & 0 \end{pmatrix}$$



Similar magnetic structures
 $\mathbf{k}=(0,0,0)$, two sites M and Fe
 of four sublattices

$$\mathbf{G}_M + \mathbf{G}_{Fe} = (+ - + - ; + - + -)$$

The program ENERMAG



$$\xi_{ij}(\mathbf{k}) = - \sum_p J_{ij}(\mathbf{R}_p) e^{-2\pi i \mathbf{k} \cdot \mathbf{R}_p}$$

The program handles the diagonalization of the Fourier matrix solving the parametric equation:

$$\xi(\mathbf{k}, \mathbf{J}) \mathbf{v}(\mathbf{k}, \mathbf{J}) = \lambda(\mathbf{k}, \mathbf{J}) \mathbf{v}(\mathbf{k}, \mathbf{J})$$

- For a given set $\mathbf{J} = \{J_{ij}\}$, and no degeneracy, the lowest eigenvalue $\lambda_{\min}(\mathbf{k}_0, \mathbf{J})$ occurs for a particular \mathbf{k}_0 .
- The corresponding eigenvector $\mathbf{v}_{\min}(\mathbf{k}_0, \mathbf{J})$ (that may be complex for incommensurate structures), describes the spin configuration of the first ordered state

ENERMAG (running)

```
C:\CrysFML\enermag>enermag
```

```
*****
****                                ****
*****

      *** Version 1.5 ***

*****
* Calculates the Magnetic Energy for k-vectors in BZ*
*      Uses a Classical Heisenberg Hamiltonian      *
*      and isotropic exchange interactions          *
*****

      (JRC August-2001, LLB)
```

```
=> Code of the file xx.exc (give xx): mfepo5
=> Code of the .out file ( <cr>= mfepo5) :
=> Do you want to save data in *.res file (y/n)? : y
=> Code of the .res file ( <cr>= mfepo5) :
=> Give a comment for the .res file: Phase diagram of MFePO5
```

ENERMAG (running)

```
=> Input file read!!!
=> Do you want to calculate a phase diagram (y/n)?: y
=> Phase diagram will be calculated
=> Enter a target k-vector (3 reals): 0 0 0
=> Number of J's TO BE VARIED (<=15): 3
-> Number & Range of varied J-parameter 1 & No of points: 2 -100 100 15
-> Number & Range of varied J-parameter 2 & No of points: 3 -100 100 15
-> Number & Range of varied J-parameter 3 & No of points: 4 -100 100 15
=> Phase diagram for:      3375 sets of exchange integrals
    Vectors k in BZ, components in [-1,1]
=> Options:
    0: Special k-vectors
    1: Give individual k-vectors
    2: k-vectors along a line
    3: k-vectors in a plane
    4: General + Special k-vectors
    5: Grid inside the Brillouin Zone
=> Give the option: 4
=> Number of k-vectors (<125000): 2000
=> Give region of k-vectors (in r.l.u.)
    (kx1,kx2,ky1,ky2,kz1,kz2): 0 0.5 0 0.5 0 0.5
```

Once the program finishes the job, several files are generated and they can be analyzed by auxiliary programs.

Example:

The program PHASDIAG reads the file « *.res » generated by ENERMAG and gathers the solutions in two general types: commensurate and incommensurate (or not order at all), it generates a binary file that can be read by GFOURIER for graphical visualization of the phase diagram.

```
C:\ProgCFML\Testing\Enermag>phas
=> Code of the *.res file: mfepo5
=> Number of Js (only the first 3 Js may be varied!): 3
=> Number of Sites: 2
=> Number of atoms for site: 1: 4
=> Number of atoms for site: 2: 4
=> List of magnetic structure types:
```

Type	Code	Vk-Sign seq.	J-domains	Frequency	
1	17222	(1: + - + - + - + -) k = (0 , 0 , 0)	-100.0 100.0	-100.0 -14.3	-100.0 -14.3	689
2	16442	(1: + + + + - - - -) k = (0 , 0 , 0)	-100.0 100.0	-100.0 0.0	-14.3 100.0	936
3	56700	(4: + - - + 0 0 0 0) k = (0 , 0 , 1/2)	-100.0 -71.4	-42.9 28.6	0.0 0.0	7
4	0	(10: 0 0 0 0 0 0 0 0) k = (0 , 1/4, 0)	-100.0 100.0	-28.6 42.9	-85.7 85.7	61
5	82944	(6: + - - + 0 0 0 0) k = (1/2, 0 , 1/2)	-100.0 -57.1	-28.6 14.3	-14.3 0.0	6
6	13174	(1: 0 0 0 0 + - - +) k = (0 , 0 , 0)	-100.0 14.3	-14.3 -14.3	-100.0 -85.7	5
7	95470	(7: + + - - + - - +) k = (0 , 1/2, 1/2)	-100.0 -85.7	-14.3 -14.3	-57.1 -57.1	2
8	17242	(1: + - + - - + - +) k = (0 , 0 , 0)	-100.0 100.0	0.0 100.0	-100.0 14.3	936
9	16686	(1: + + - - 0 0 0 0) k = (0 , 0 , 0)	-100.0 -100.0	0.0 0.0	0.0 0.0	1
10	42646	(3: + + + + + + + +) k = (0 , 1/2, 0)	-100.0 -85.7	14.3 14.3	57.1 57.1	2
11	13198	(1: 0 0 0 0 - - + +) k = (0 , 0 , 0)	-100.0 100.0	14.3 14.3	100.0 100.0	10
12	16402	(1: + + + + + + + +) k = (0 , 0 , 0)	-100.0 100.0	14.3 100.0	14.3 100.0	688
13	13190	(1: 0 0 0 0 - + + -) k = (0 , 0 , 0)	-85.7 100.0	-14.3 -14.3	-100.0 -100.0	11
14	82296	(6: + + - - 0 0 0 0) k = (1/2, 0 , 1/2)	-85.7 -85.7	0.0 0.0	0.0 0.0	1
15	96146	(7: + - - + - - - -) k = (0 , 1/2, 1/2)	-85.7 -42.9	14.3 14.3	71.4 71.4	4
16	43468	(3: + - + - + - - +) k = (0 , 1/2, 0)	-71.4 -71.4	-14.3 -14.3	-71.4 -71.4	1
17	13166	(1: 0 0 0 0 + + - -) k = (0 , 0 , 0)	-42.9 85.7	14.3 14.3	85.7 100.0	6
18	56581	(4: + - + - + + - +) k = (0 , 0 , 1/2)	-14.3 71.4	0.0 0.0	0.0 0.0	2
19	17224	(1: + - + - + - - +) k = (0 , 0 , 0)	0.0 71.4	-14.3 -14.3	-100.0 -85.7	3
20	16438	(1: + + + + - - + +) k = (0 , 0 , 0)	0.0 0.0	14.3 14.3	85.7 85.7	1
21	55781	(4: + + + + + - - -) k = (0 , 0 , 1/2)	14.3 57.1	0.0 0.0	0.0 0.0	2
22	16406	(1: + + + + + + - -) k = (0 , 0 , 0)	14.3 71.4	14.3 14.3	85.7 100.0	2

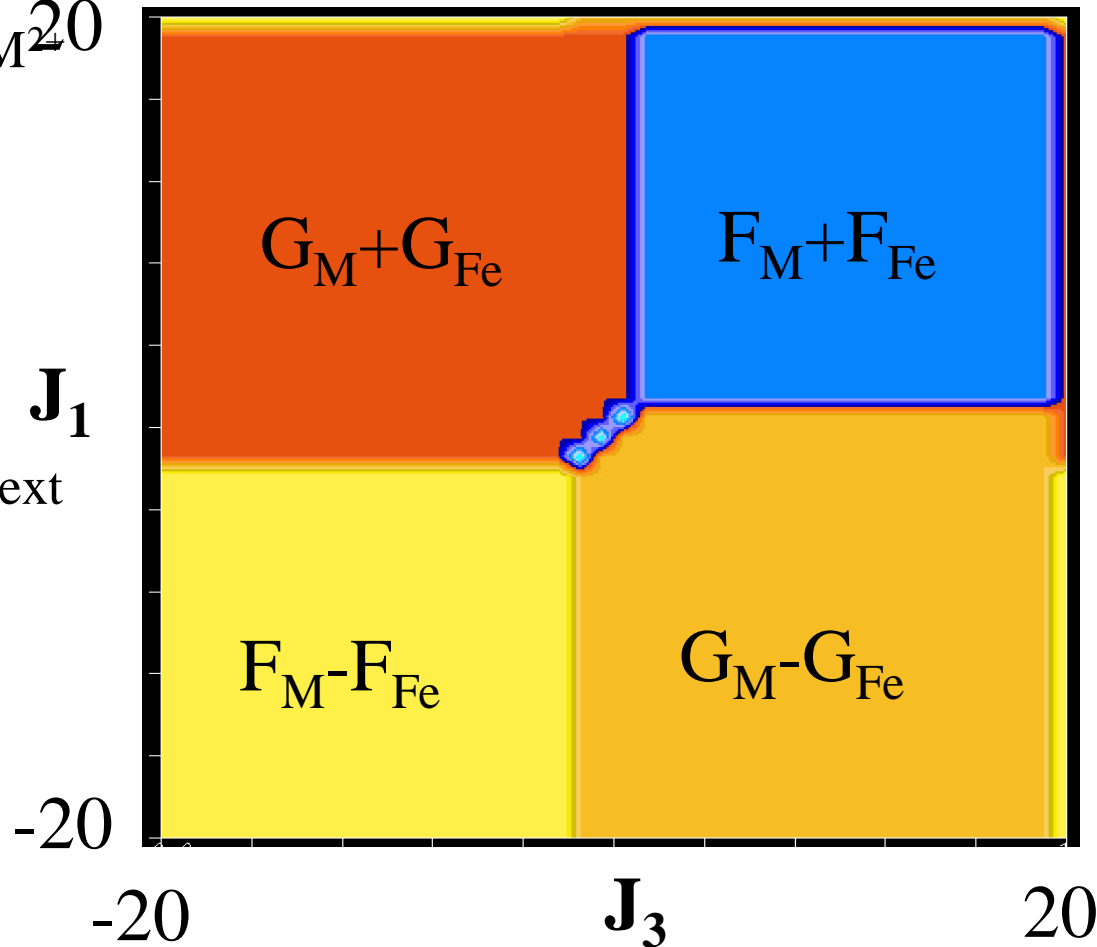
```
=> Density = Log(Frequency) (f) :
Density = Code (c) :
Density = Order (o) :
Density = User defined (u) (<cr>=u)? : o
```

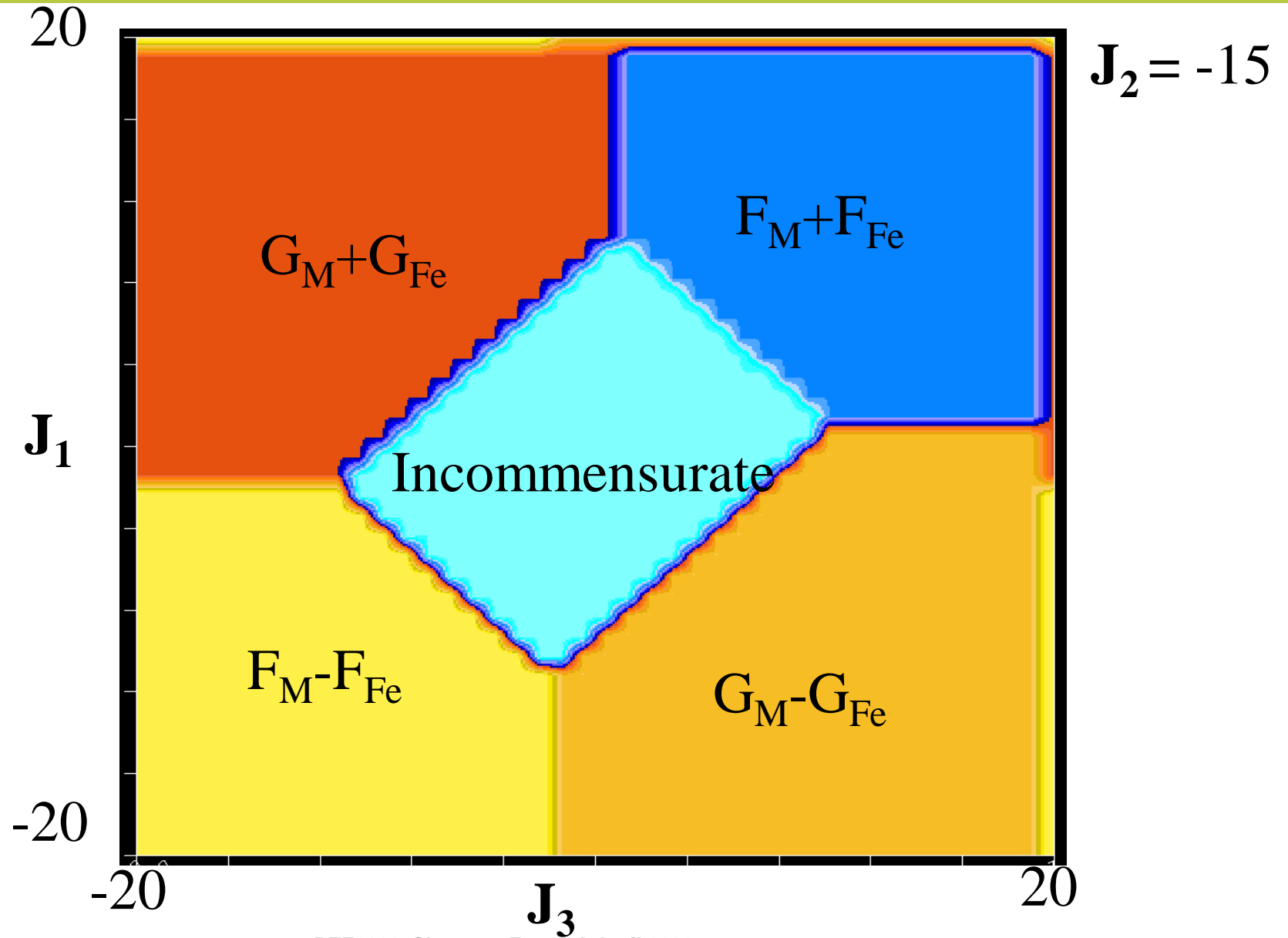
```
=> Binary file : mfepo5.bin
=> Summary file : mfepo5.ana
```

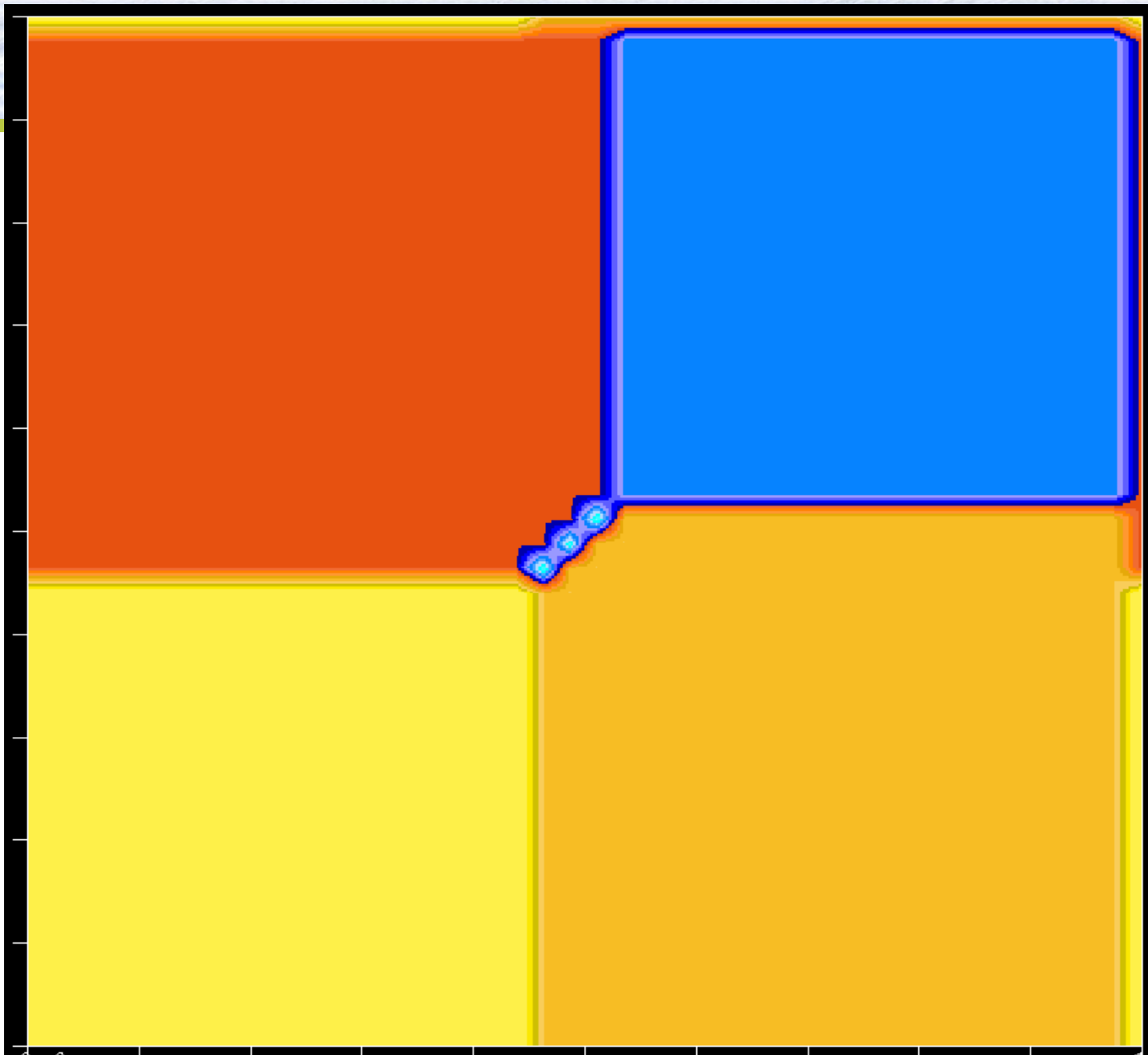

The compounds of formula $MFePO_5$ can be modelled with four exchange interactions:

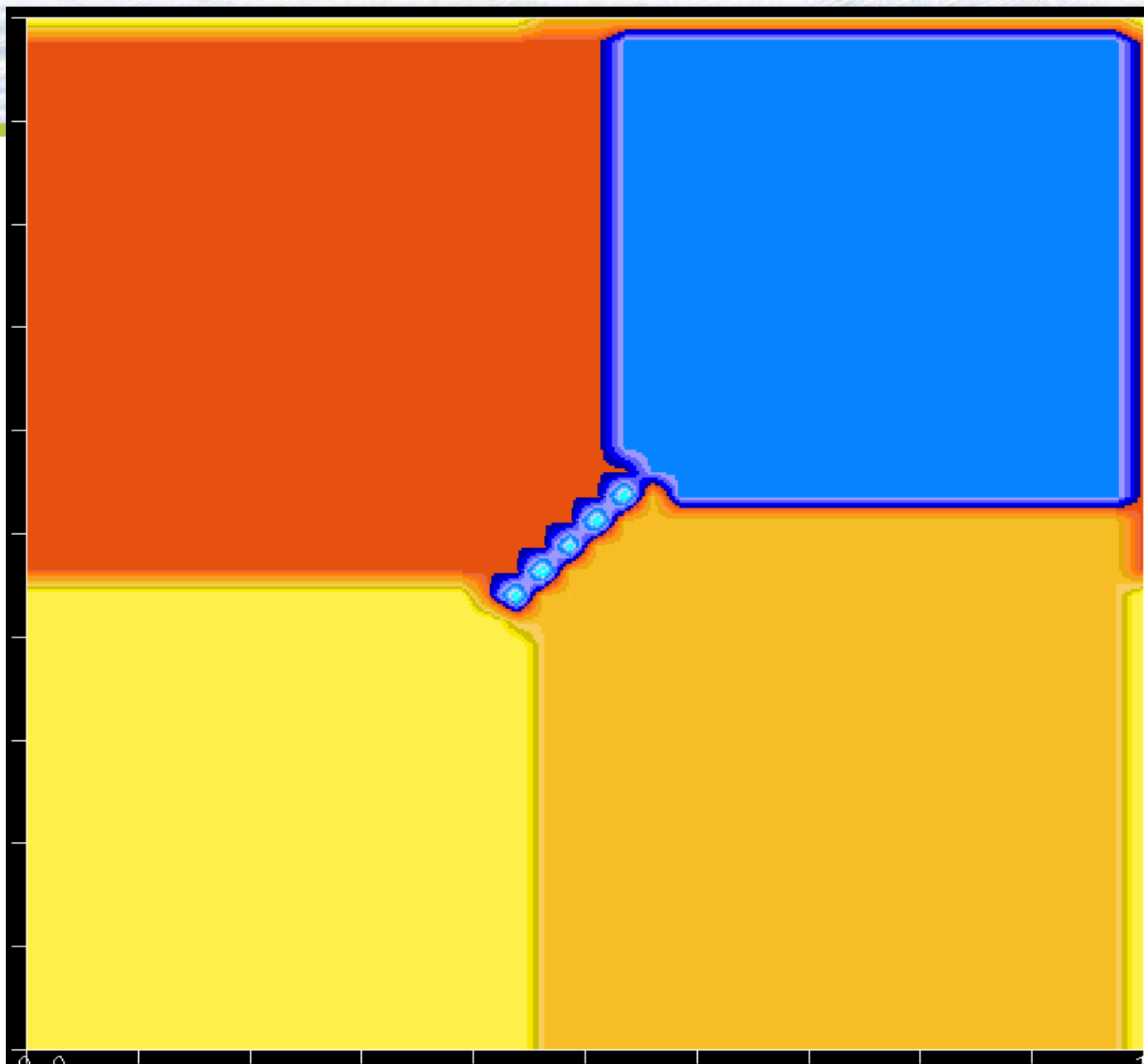
$$J_2 = -6.7$$

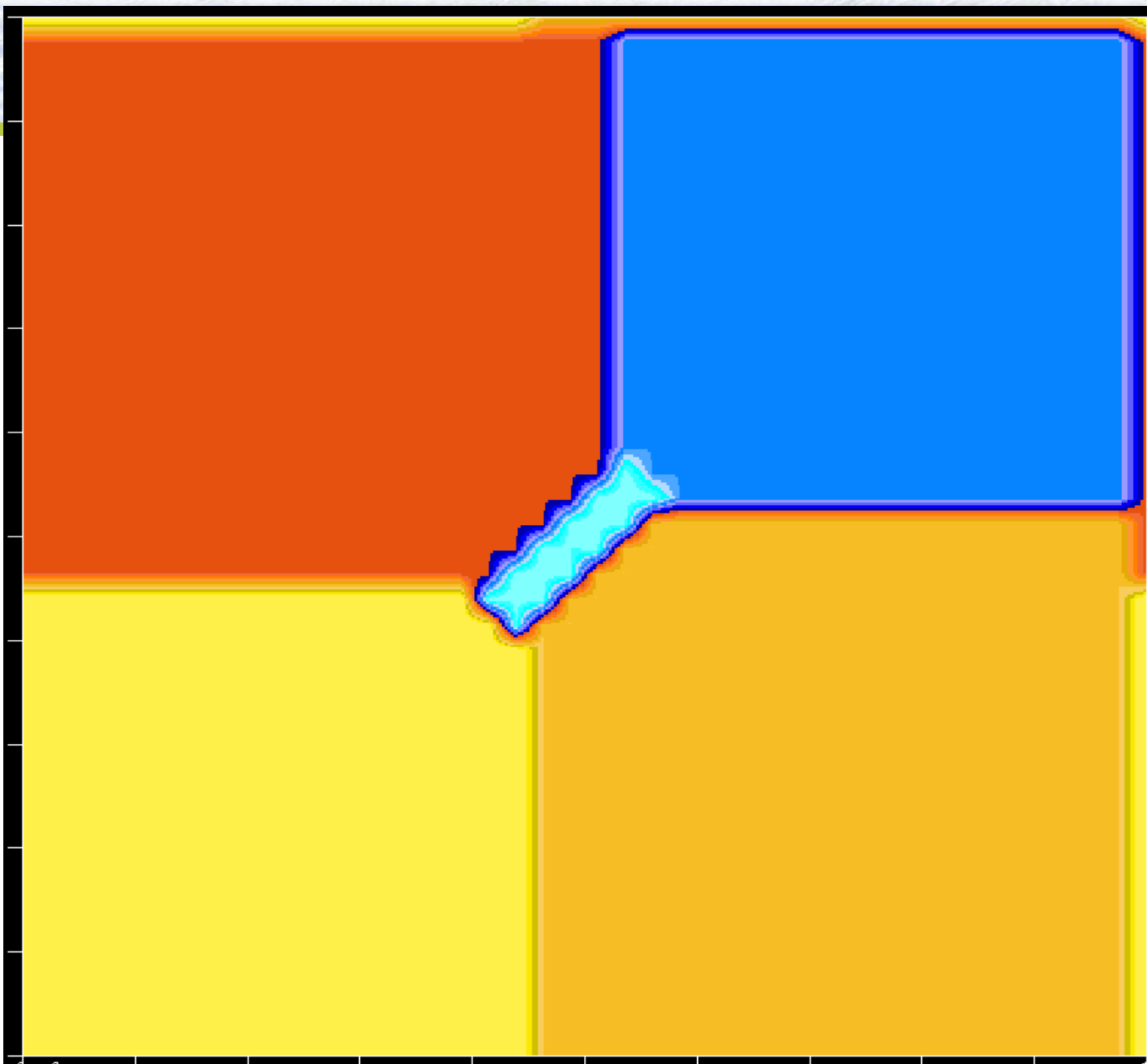
- J_1 corresponds to the exchange between M^{2+} and Fe^{3+} nearest neighbours.
- J_2 corresponds to the exchange between two M^{2+} cations (double oxygen bridge).
- J_3 corresponds to the exchange between next nearest neighbours M^{2+} and Fe^{3+} cations (single oxygen bridge).
- J_4 exchange between nearest neighbours Fe^{3+} cations (single oxygen bridge), taken here as $J_4 = -1$

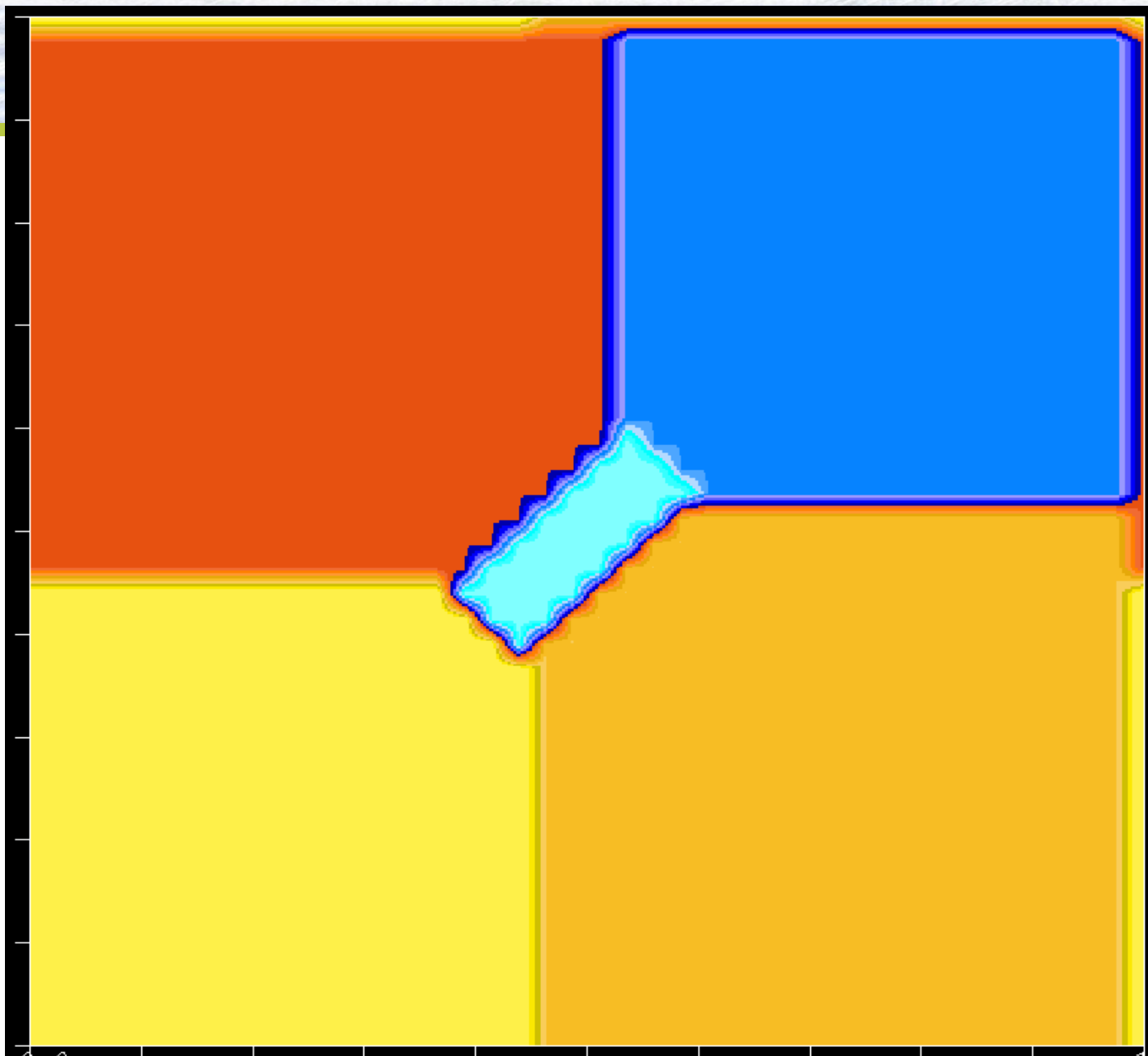


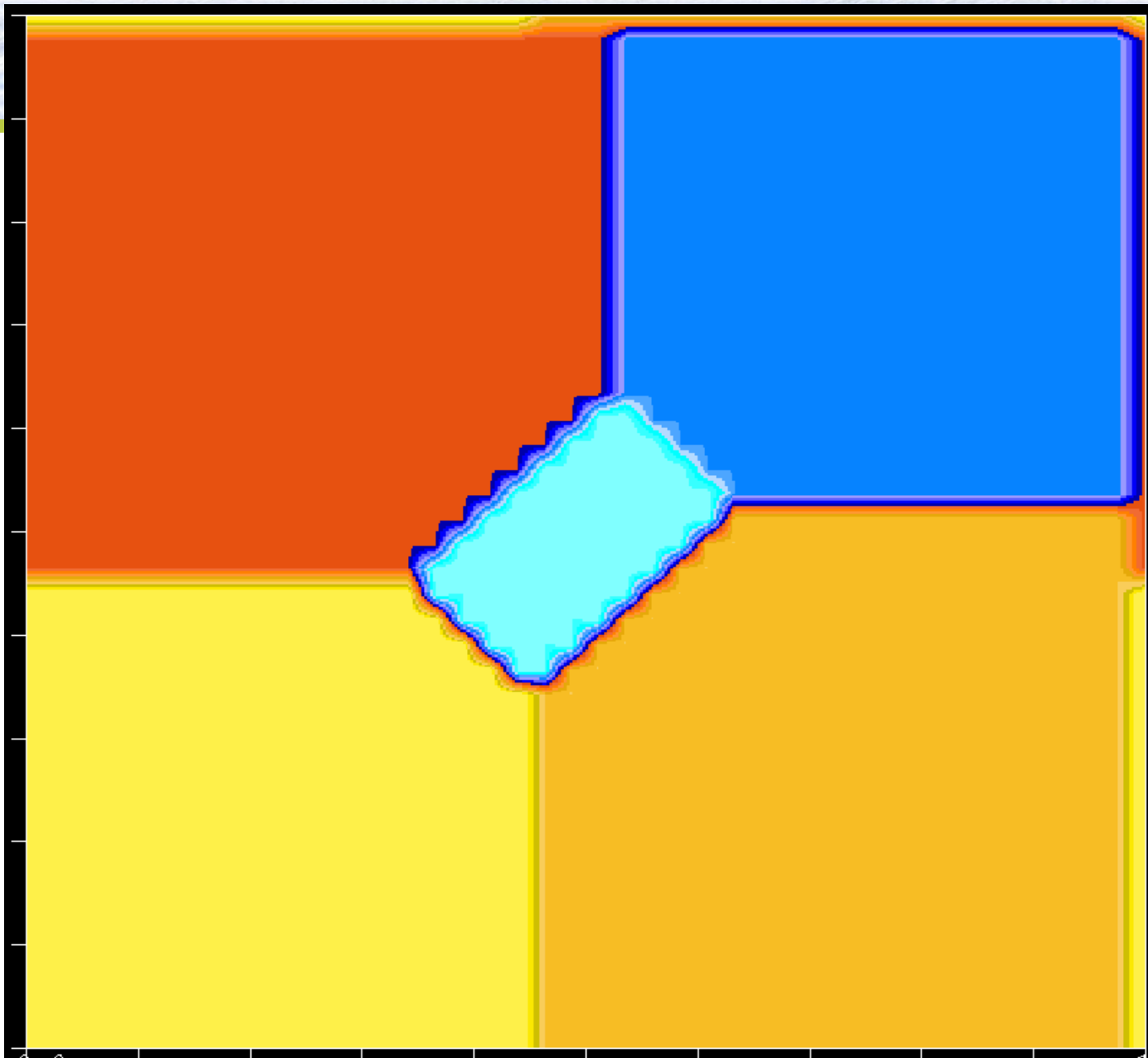


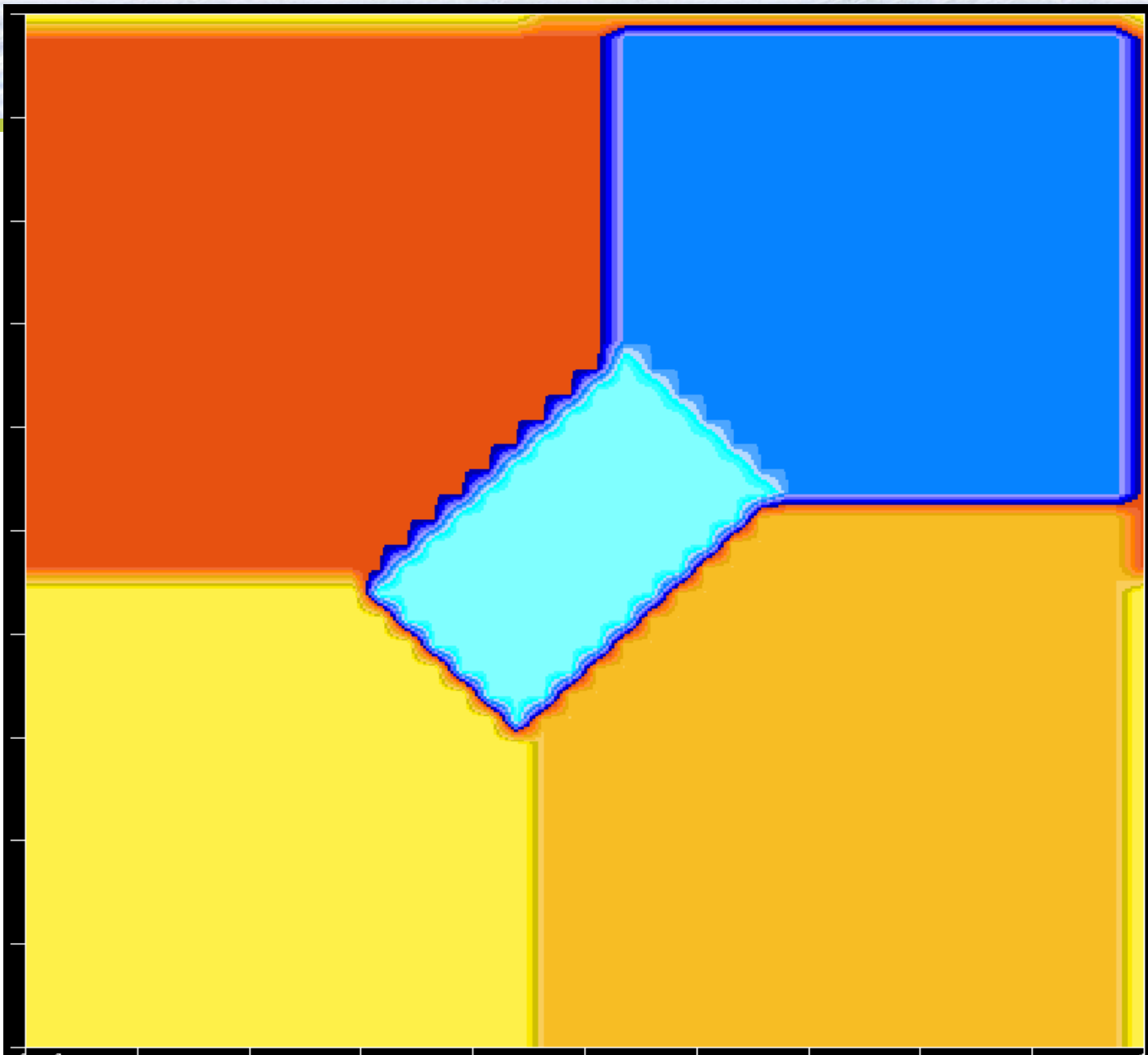


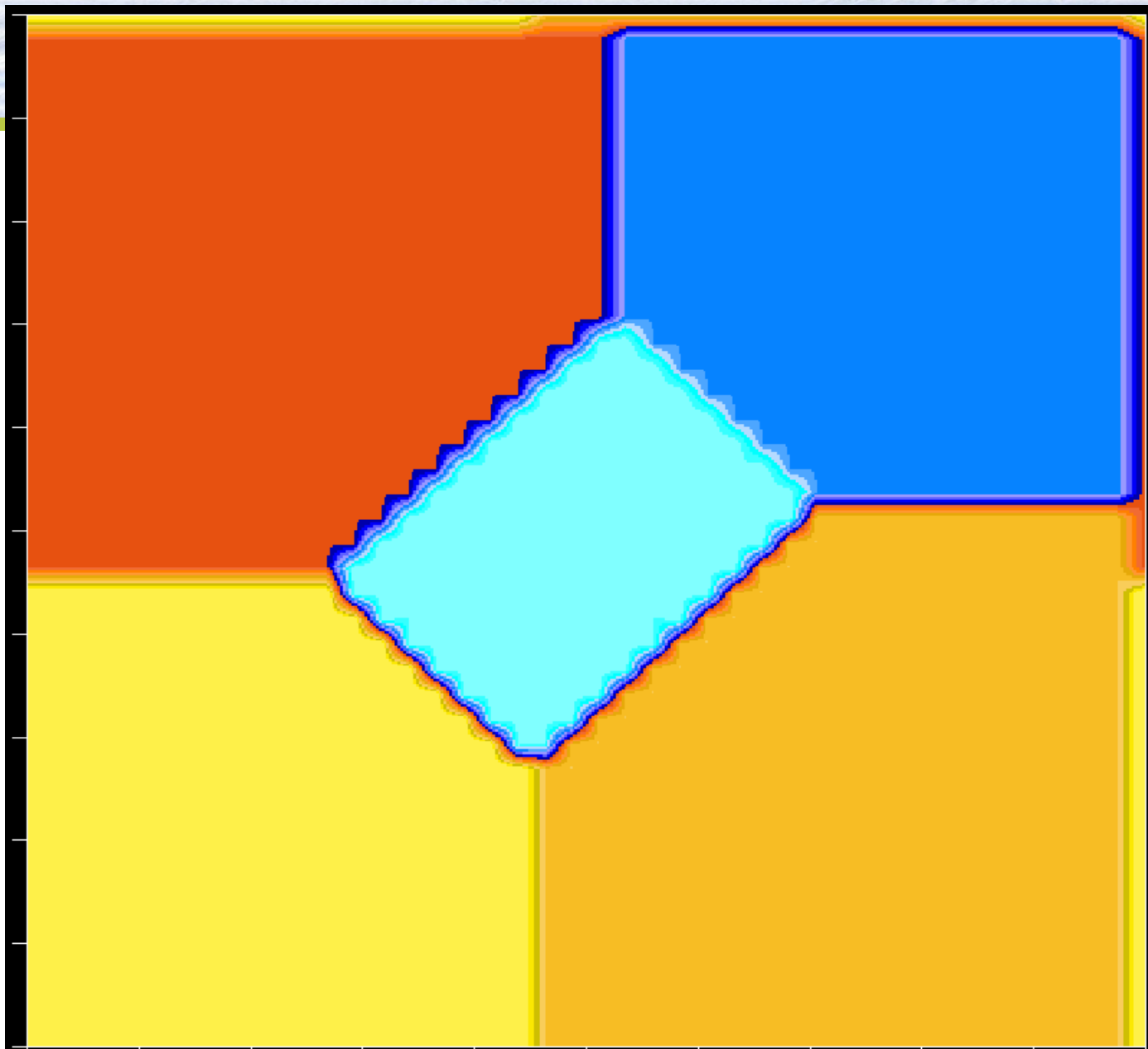


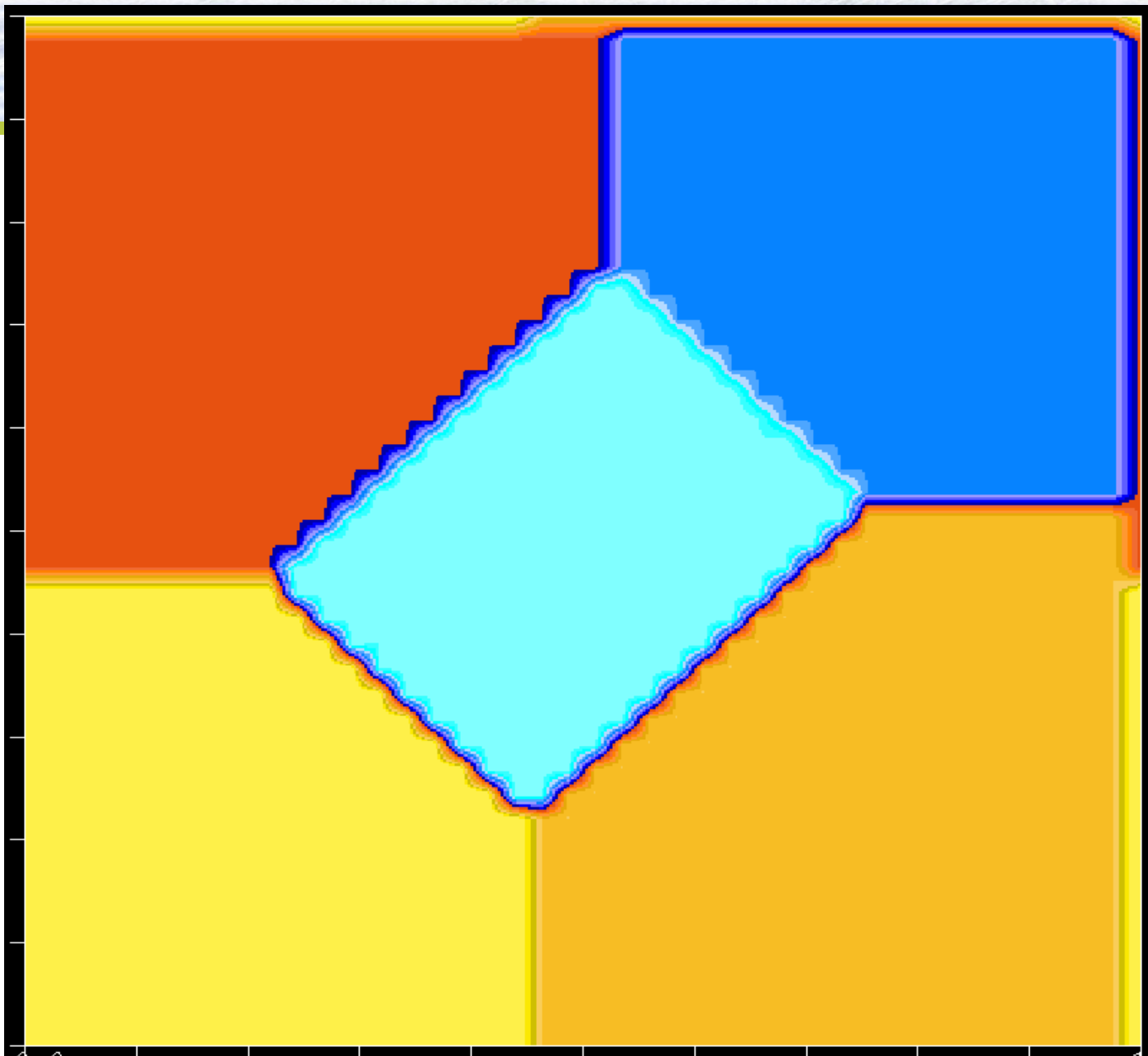












Paramelaconite Cu_4O_3

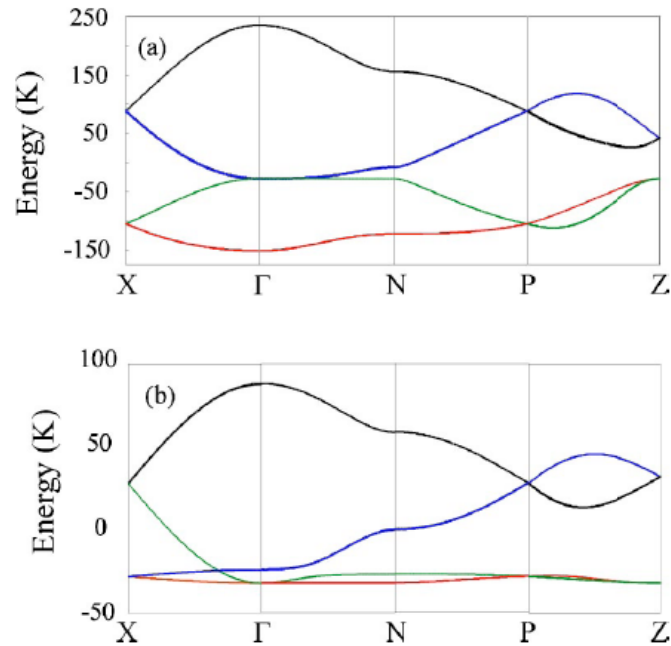


FIG. 6. (Color online) Dispersion relations $E = -\lambda_{\max}(\mathbf{k}_0, \mathbf{J})$ corresponding to some high symmetry directions in the Brillouin Zone for the values of the exchange parameters of WK (a) and TR (b). The symmetry points $\Gamma(0,0,0)$, $N(1/2, 0, 1/2)$, $X(1/2, 1/2, 0)$, $Z(1, 1, 1)$, $P(1/2, 1/2, 1/2)$; are labeled using the notation of Bradley and Cracknell (Ref. 32) but the coordinates are given with respect to the conventional crystallographic reciprocal basis.

$$\xi(\mathbf{k}, \mathbf{J}) = \begin{pmatrix} A & J_2 \alpha_y (\alpha_y + \alpha_x \alpha_z) & 2J_1 \alpha_x \alpha_z^* \cos \pi y & J_2 (1 + \alpha_x \alpha_y \alpha_z^*) \\ cc_{12} & B & J_2 \alpha_y^* \alpha_z^* (\alpha_x + \alpha_y^* \alpha_z^*) & 2J_1 \alpha_y^* \alpha_z^* \cos \pi x \\ cc_{13} & cc_{23} & A & J_2 (1 + \alpha_x^* \alpha_y \alpha_z) \\ cc_{14} & cc_{24} & cc_{34} & B \end{pmatrix}$$

$$A = 2J_3 \cos 2\pi y, \quad B = 2J_3 \cos 2\pi x$$

$$\alpha_b = \exp(\pi i b), \quad \alpha_b^* = \exp(-\pi i b), \quad \text{with } b = x, y \text{ or } z$$

cc_{ij} = complex conjugate of element ij

$$\mathbf{k} = (x, y, z)$$

Magnetic properties of paramelaconite Cu_4O_3 : A pyrochlore lattice with $S=1/2$, L Pinsard-Gaudart, J. Rodríguez-Carvajal, A. Gukasov, P. Monod. *Physical Review B* **69**, 104408 (2004).

Multiferroics RMn_2O_5

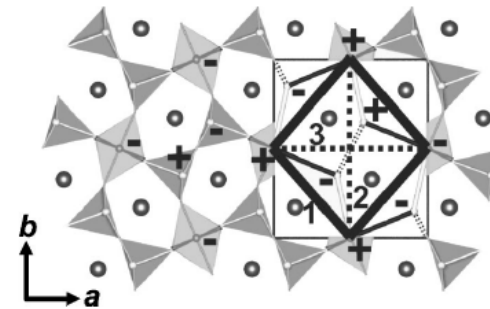
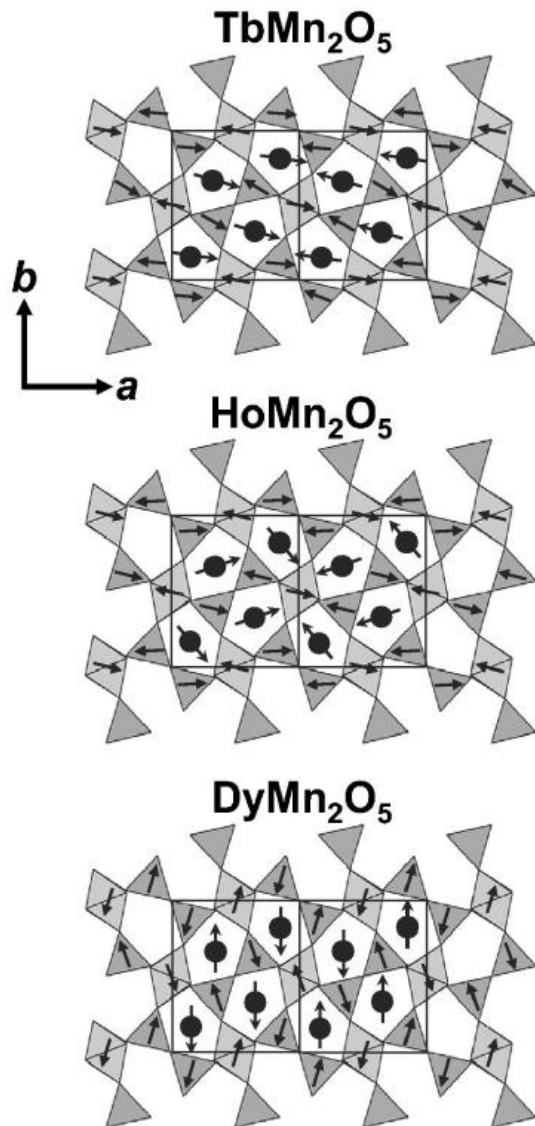


FIG. 7. Next-nearest-neighbor (NNN) magnetic exchange interactions in the ab plane. Spin directions are indicated by “+” and “-”. Exchange interaction 3 is stronger than interaction 2, resulting in a square lattice of Mn^{4+} with asymmetric NNN exchange and the stabilization of AFM zigzag chains parallel to the a axis.

Spin structure and magnetic frustration in multiferroic RMn_2O_5 ($\text{R}=\text{Tb}, \text{Ho}, \text{Dy}$), G.R. Blake, L.C. Chapon, P.G. Radaelli, S. Park, N. Hur, S.W. Cheong, J. Rodríguez-Carvajal. *Physical Review B* **71**, 214402 (2005).

Multiferroics RMn_2O_5

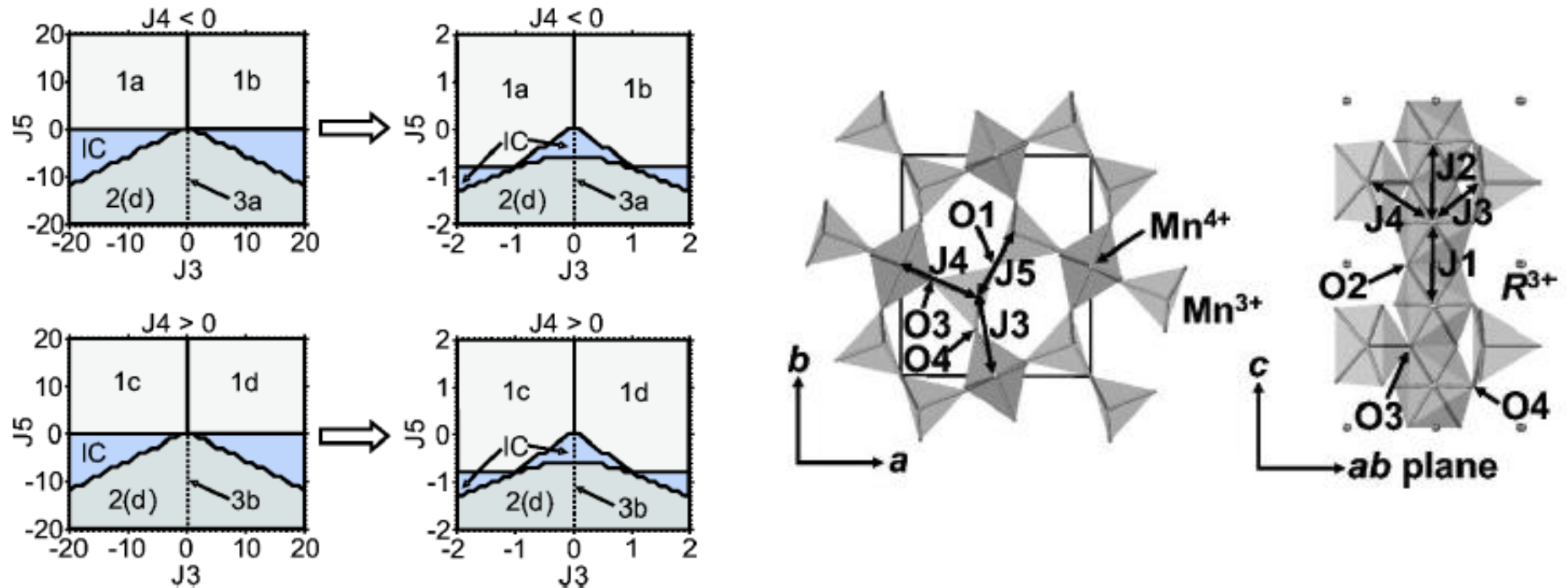
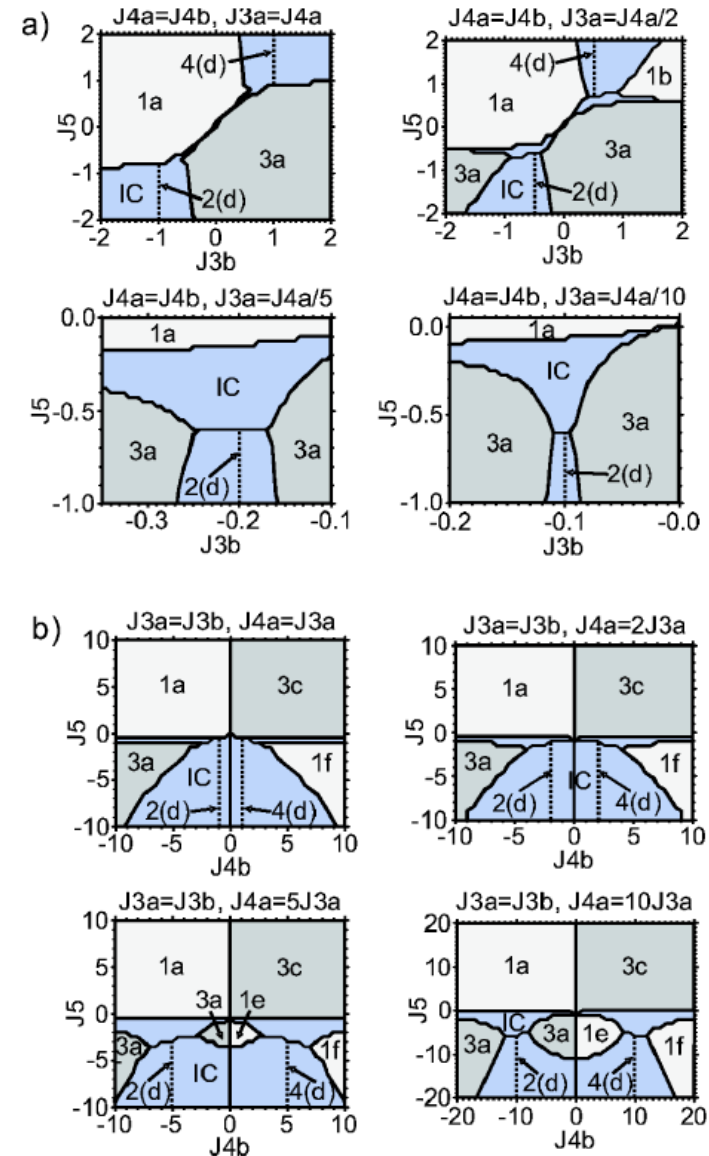


FIG. 8. Schematic magnetic phase diagrams calculated using ENERMAG, in space group $Pbam$. Exchange interactions J_3 and J_5 (see Fig. 1) are expressed in units of J_4 . Labels are as follows: structures 1a–1d have $\mathbf{k}=(0,0)$ and spin configurations as listed in Table III; structures 2(d) have $\mathbf{k}=(0.5,0.5)$ and degenerate spin configurations; structures 3a and 3b have $\mathbf{k}=(0.5,0)$ and configurations as in Table III; structures IC are incommensurate.

Multiferroics RMn_2O_5

FIG. 9. Schematic magnetic phase diagrams calculated using ENERMAG, in space group $Pb2_1m$. Labels are as follows: structures 1a–1f have $\mathbf{k}=(0,0)$ and spin configurations as listed in Table III; structures 2(d) have $\mathbf{k}=(0.5,0.5)$ and degenerate spin configurations; structures 3a and 3c have $\mathbf{k}=(0.5,0)$ and configurations as in Table III; structures 4(d) have $\mathbf{k}=(0,0.5)$ and degenerate spin configurations; structures IC are incommensurate. (a) The pair of exchange interactions $J4a$ and $J4b$ are equal and fixed. $J3b$ and $J5$ are expressed in units of $J4a$ ($J4b$). (b) The pair of exchange interactions $J3a$ and $J3b$ are equal and fixed. $J4b$ and $J5$ are expressed in units of $J3a$ ($J3b$).



Conclusions

- In many cases neutron diffraction is not able to provide a unique solution for a magnetic structure. It is very important to have a good knowledge of the possible exchange interaction in order to be able to select one of the solutions.
- The analysis of the exchange paths and the magnetic topology is crucial for understanding the observed magnetic structures.
- The use of the programs SIMBO and ENERMAG can help considerably to this task.
- If you want to get more detail contact me during the meeting or send me an e-mail to jrc@ill.fr

Some references using SIMBO and ENERMAG



Crystal and magnetic structures of the oxyphosphates MFePO_5 ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). Analysis of the magnetic ground state in terms of superexchange interactions, N. El Khayati, R. Cherkaoui El Moursli, J. Rodríguez-Carvajal, G. André, N. Blanchard, F. Bourée, G. Collin, and T. Roisnel. *The European Physical Journal B* **22**, 429-442 (2001).

Neutron diffraction study of the magnetic ordering in the series R_2BaNiO_5 ($\text{R}=\text{Rare Earth}$), E. García-Matres, J.L. Martínez, and J. Rodríguez-Carvajal. *The European Physical Journal B* **24**, 59 (2001).

Magnetic Structural Studies of the Two Polymorphs of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$: Analysis of the Magnetic Ground State from Super-Super Exchange Interactions, G. Rousse, J. Rodríguez-Carvajal, C. Wurm, and C. Masquelier. *Chemistry of Materials* **13**, 4527 (2001).

A neutron diffraction study of the antiferromagnetic diphosphate LiFeP_2O_7 , Gwenaëlle Rousse, Juan Rodríguez-Carvajal, Calin Wurm and Christian Masquelier. *Solid State Sciences* **4**, 973 (2002).

Magnetic structure and exchange interactions in $\text{CuFe}_2(\text{P}_2\text{O}_7)_2$, N. El Khayati, J. Rodríguez-Carvajal, F. Bourée, T. Roisnel, R. Cherkaoui, A. Bouffessi, A. Boukhari, *Solid State Sciences* **4**, 1273 (2002).

Magnetic properties of paramelaconite Cu_4O_3 : A pyrochlore lattice with $S=1/2$, L Pinsard-Gaudart, J. Rodríguez-Carvajal, A. Gukasov, P. Monod. *Physical Review B* **69**, 104408 (2004).

Spin structure and magnetic frustration in multiferroic RMn_2O_5 ($\text{R}=\text{Tb}, \text{Ho}, \text{Dy}$), G.R. Blake, L.C. Chapon, P.G. Radaelli, S. Park, N. Hur, S.W. Cheong, J. Rodríguez-Carvajal. *Physical Review B* **71**, 214402 (2005).