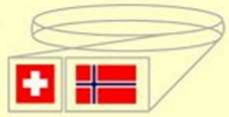
The Swiss-Norwegian Beam Lines at ESRF



Структурные аспекты киральности и абсолютная структура.

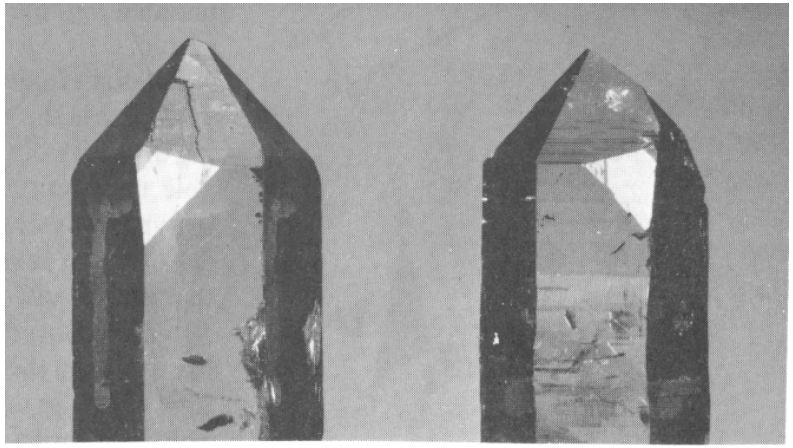
Д. Ю. Чернышов

SNBL at ESRF, Grenoble, France

Кафедра кристаллографии, СПбГУ

Chirality (Greek, from *χειρ* "hand")

Hans Erni's drawing

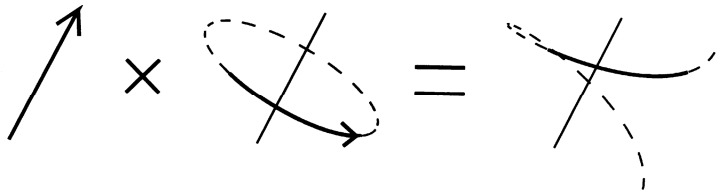


Часть I

1. [illegible], обсолютная структура, обсолютная конструкция....
2. [illegible]? [illegible] кристаллическая структура?
3. [illegible] определяется [illegible] дефекты

Часть II

1. 2,3 MnS – кристаллическая структура
2. MnS – обсолютная структура
3. Симметрия подрешеток MnS
4. Смена [illegible] следствие фазового перехода.

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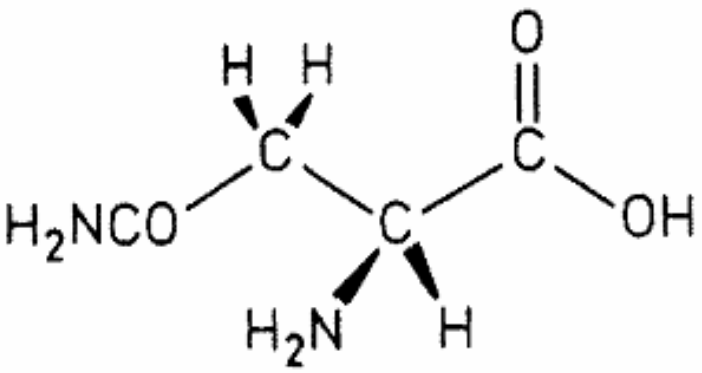
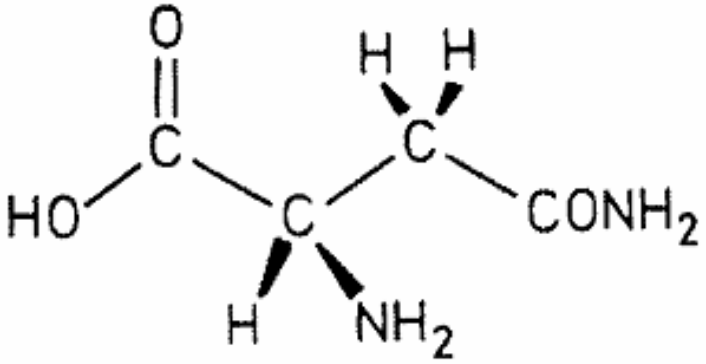
21st International Symposium on Chirality
If the following topics are important to you,
you can't afford to miss Chirality 2009!
Separation of enantiomers/measurement of ee
Supermolecular and materials chirality
Chiroptics
Enantioselective reactions/synthesis
Founded in 1988, the annual International Symposium on Chirality (ISCD) is the premier scientific conference series focusing on molecular and supramolecular dissymmetry in the natural and life sciences. Don't miss ISCD-21, covering the impact of chirality on fundamental and practical issues in science and technology in multiple disciplines.
Join scientists and engineers from around the world who will focus on some of the most cutting-edge areas of scientific research related to molecular and supramolecular dissymmetry in the natural and life sciences.
Topics range from fascinating and important fundamental questions in the natural and life sciences through the impact of chirality on fundamental, practical and economic issues in science and technology in multiple disciplines.
Explore new developments and applications to solve today's practical problems.
See how the latest products and technologies are driving the pace of innovation in scientific research.
Participate in educational training opportunities through short courses and seminars.
Course 1: Supermolecular Stereochemistry in Liquid Crystals, presented by David
July 12-15, 2009
Breckenridge, Colorado,
USA
FEATURED ATTRACTION
Sessions on Nonbiological Enantioenrichment and the Origins of Life, moderated by Professor Kurt Mislow, promises to be controversial and entertaining!
CHIRALITY MEDAL
And the winner is... Professor Ben Feringa, from the University of Groningen, The Netherlands. Professor Feringa's Chirality Medal Award Lecture will take place on Sunday Evening, July 12.
MESSAGE FROM CHAIR
David M. Walba is serving as chair for this year's program. Please view his message by clicking here.
IMPORTANT DATES
:: December 1, 2008
Deadline for nominations for Chirality Medal 2009
:: March 1, 2009
REGISTER NOW!



bitter



sweet

Bitter/sweet structural formulas for asparagin

Этамбутол: один энантиомер используется при лечении туберкулёза, другой вызывает слепоту.

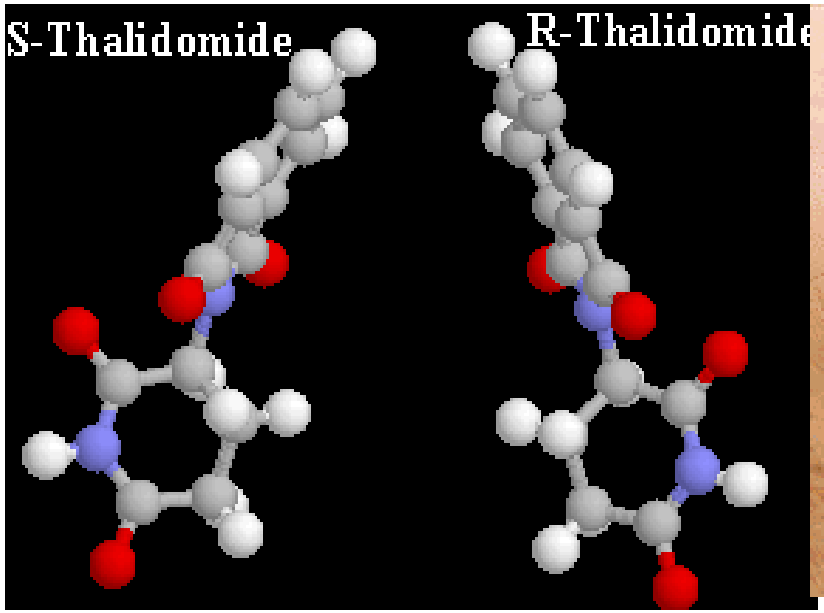
Напроксен: один энантиомер лечит артрит, но другой вызывает отравление печени

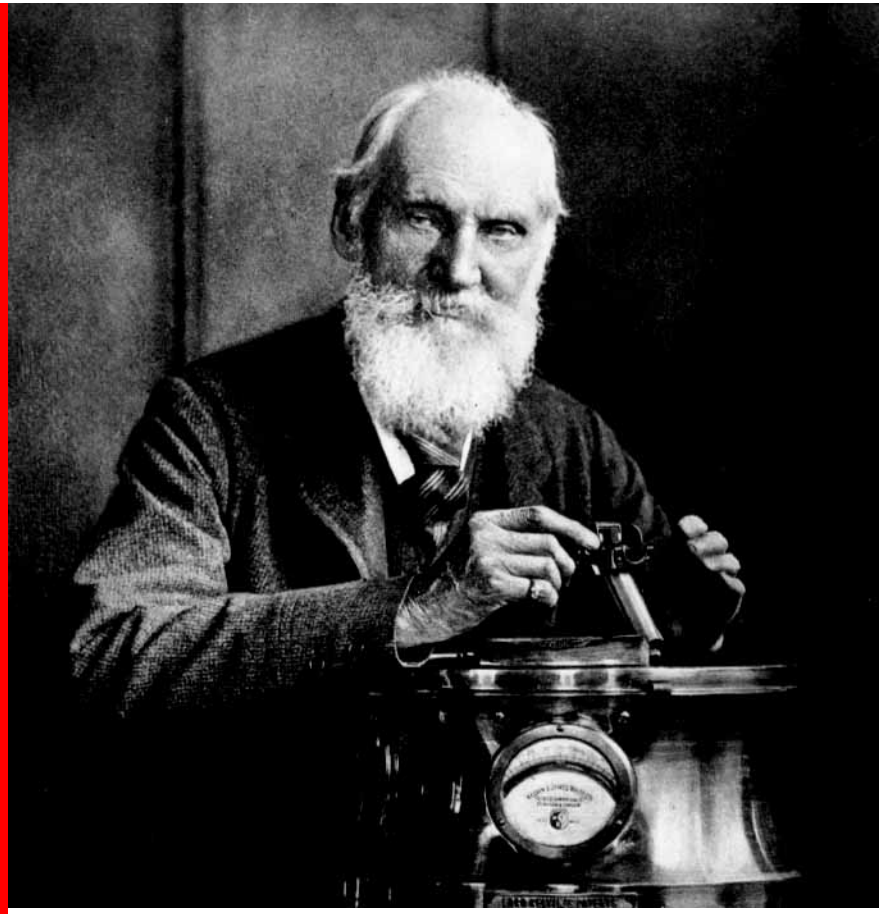
Wikipedia.org

“Perhaps Looking-glass milk isn’t good to drink” (Alice), Lewis Carroll

Талидомид — седативное снотворное лекарственное средство, получившее широкую известность из-за своей тератогенности, после того, как было установлено, что в период с 1956 по 1962 годы в ряде стран мира родилось по разным подсчётам от 8000 до 12 000 детей с врождёнными уродствами.

Wikipedia.org





BALTIMORE LECTURES

ON

MOLECULAR DYNAMICS

AND

THE WAVE THEORY OF LIGHT

FOUNDED ON MR A. S. HATHAWAY'S STENOGRAPHIC REPORT OF TWENTY LECTURES DELIVERED IN JOHNS HOPKINS UNIVERSITY, BALTIMORE, IN OCTOBER 1884: FOLLOWED BY TWELVE APPENDICES ON ALLIED SUBJECTS

BY

LORD KELVIN, O.M., G.C.V.O., P.C., F.R.S., &c.

PRESIDENT OF THE ROYAL SOCIETY OF EDINBURGH,
FELLOW OF ST PETER'S COLLEGE, CAMBRIDGE,
AND EMERITUS PROFESSOR OF NATURAL PHILOSOPHY IN THE UNIVERSITY OF GLASGOW.

* I call any geometrical figure, or group of points, *chiral*, and say that it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself. Two equal and similar right hands are homochirally similar. Equal and similar right and left hands are heterochirally similar or 'allochirally' similar (but heterochirally is better). These are also called 'enantiomorphs,' after a usage introduced, I believe, by German writers. Any chiral object and its image in a plane mirror are heterochirally similar.

Modern definition of *Chirality*

•The geometric property of a rigid object (or spatial arrangement of point or atoms) of being non-superposable by pure rotation and translation on its image formed by inversion through a point; the symmetry group of such an object contains no symmetry operations of the second kind ($\bar{1}$, m, $\bar{3}$, $\bar{4}$, $\bar{6}$). When the object is superposable by pure rotation and translation on its inverted image, the object is described as being achiral; the symmetry group of such an object contains symmetry operations of the second kind.

Symmetry elements of 1st and 2nd kind

1, 2, 3, 4, 6

$\bar{1}$, *m*, $\bar{3}$, $\bar{4}$, $\bar{6}$

$$\bar{1} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Mirror (Lord Kelvin) vs. Inversion (IUPAC)

$$\overline{X} = \bar{1}X$$

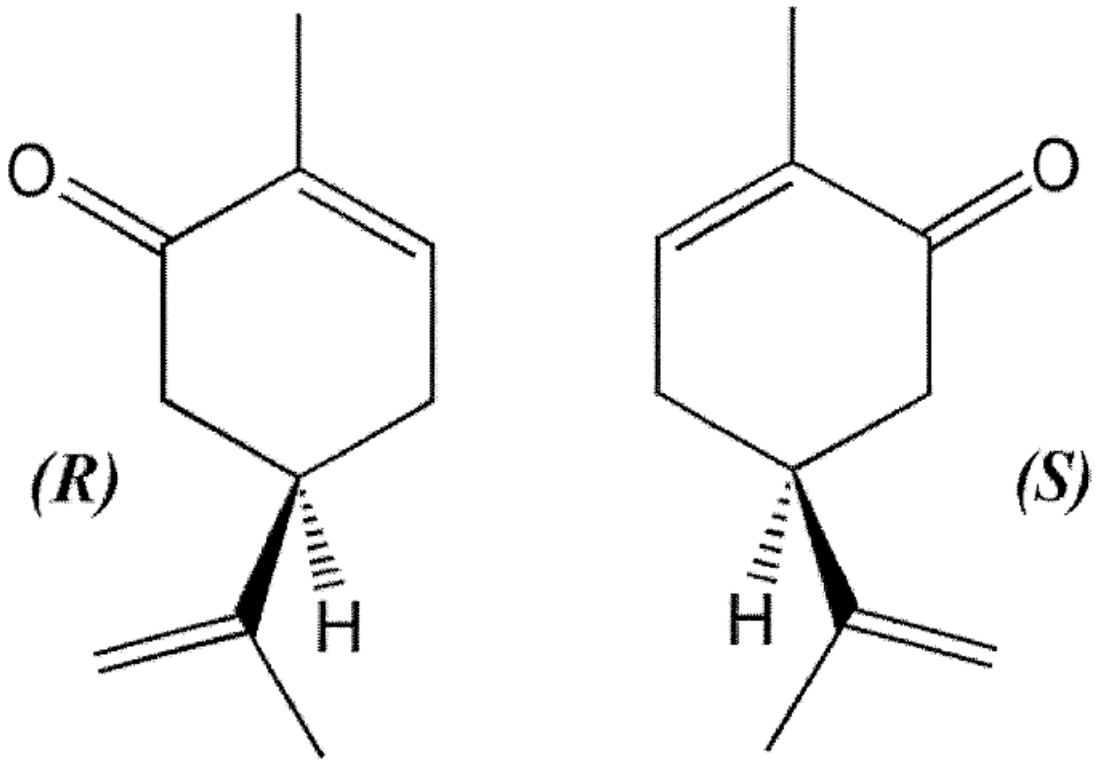
$$m = 2 \cdot \bar{1}$$

$$R \cdot m = R \cdot 2 \cdot \bar{1} = S \cdot \bar{1}$$

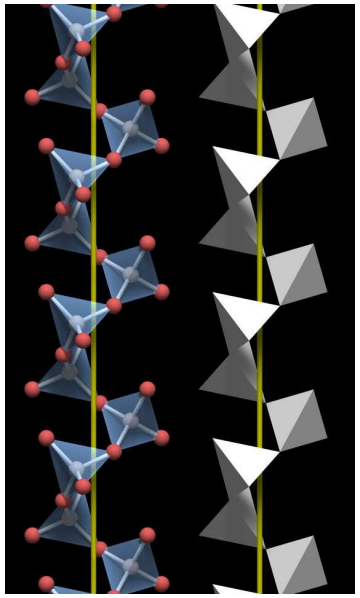
Терминология

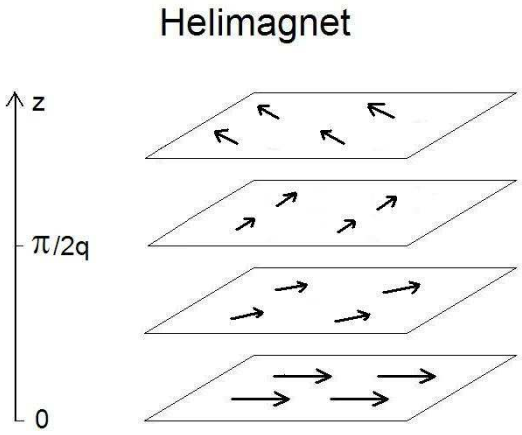
- Absolute configuration
- Absolute structure
- Enantiomer
- Enantiomerically pure
- Racemat / Racemic compound
- Racemic conglomerate
- Enantiomorph

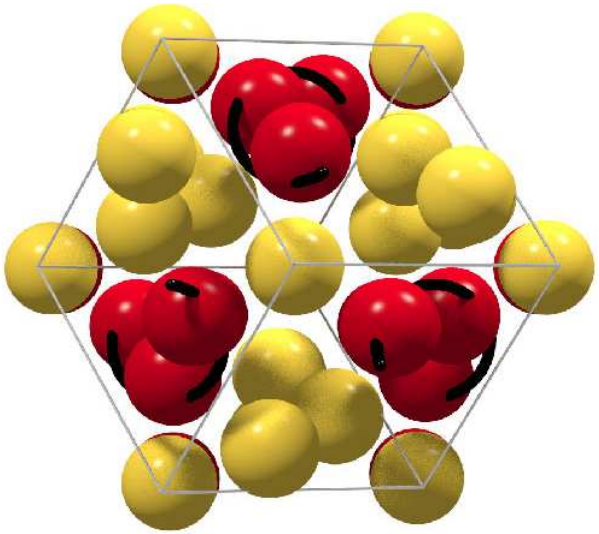
Absolute configuration

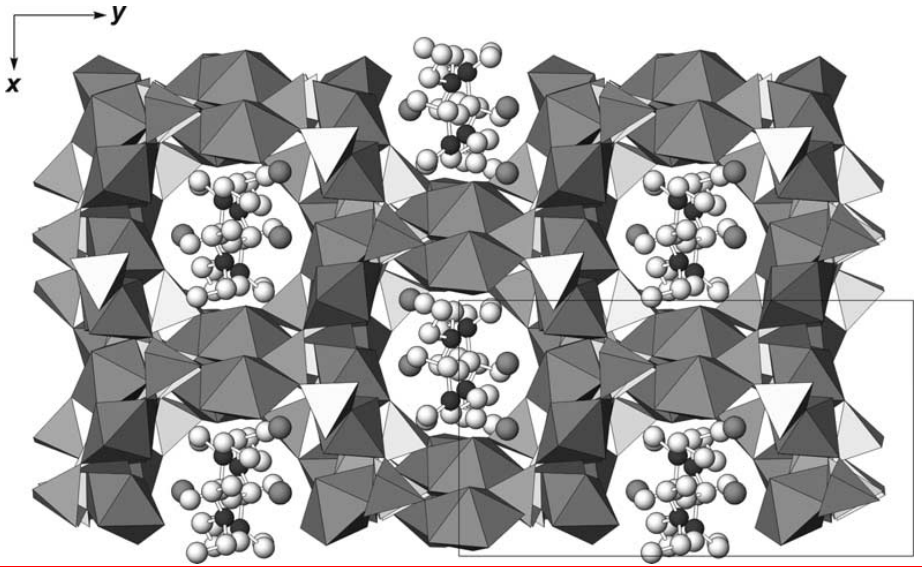


Absolute structure

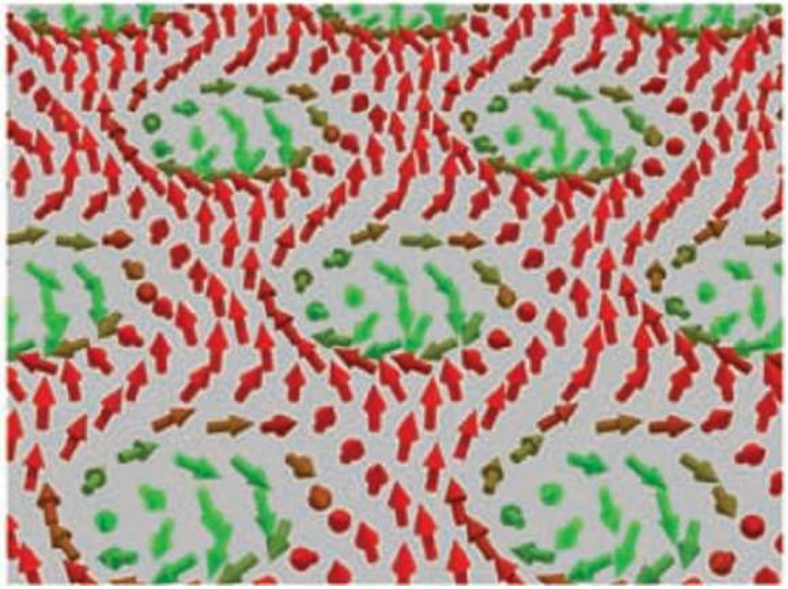




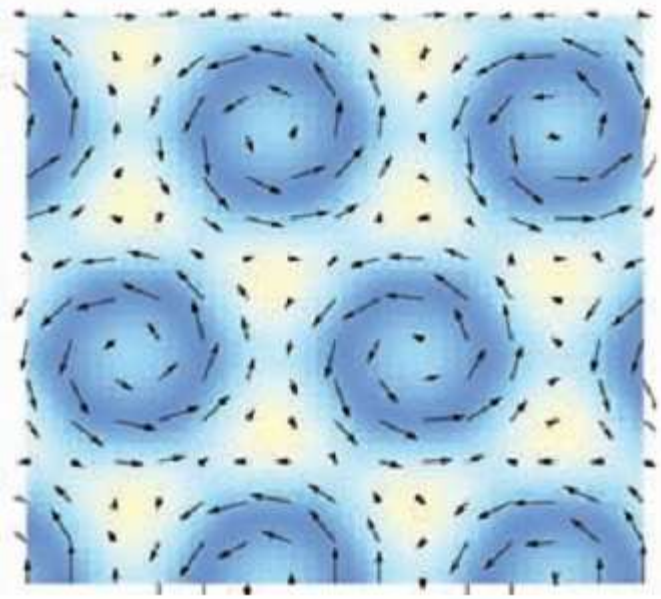




Scyrmions: absolute structure or absolute configuration?

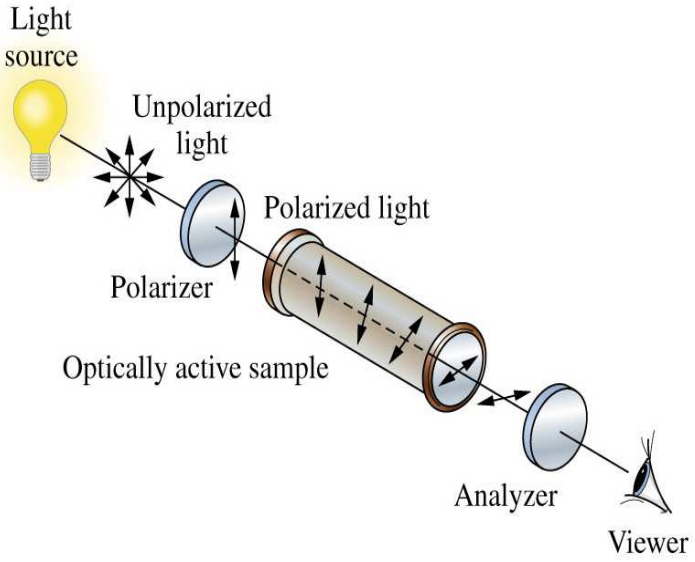


"real space depiction of spin arrangement"



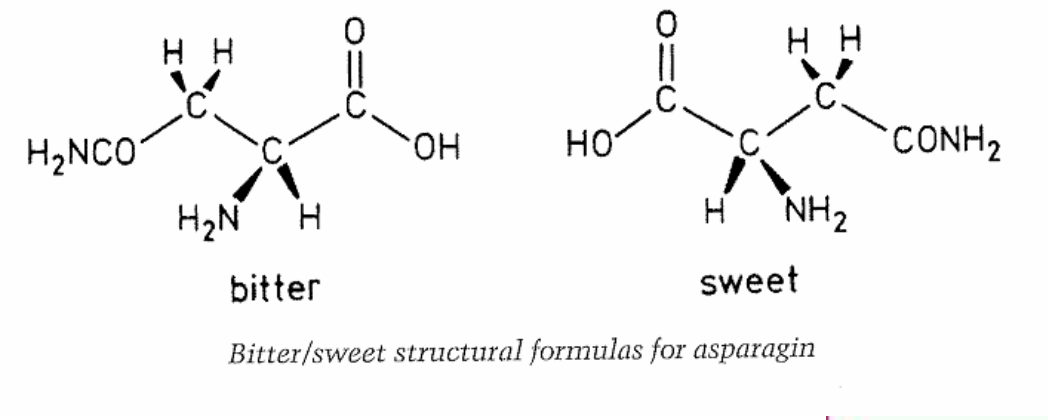
Scyrmion density

Skyrmion Lattice in a Chiral Magnet
S. Mühlbauer, *et al.*
Science **323**, 915 (2009);

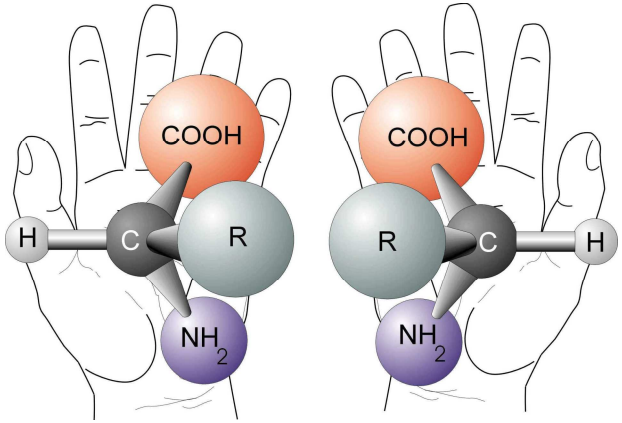

Light
source
Unpolarized
light
Polarized light
Polarizer
Optically active sample
Analyzer
Viewer

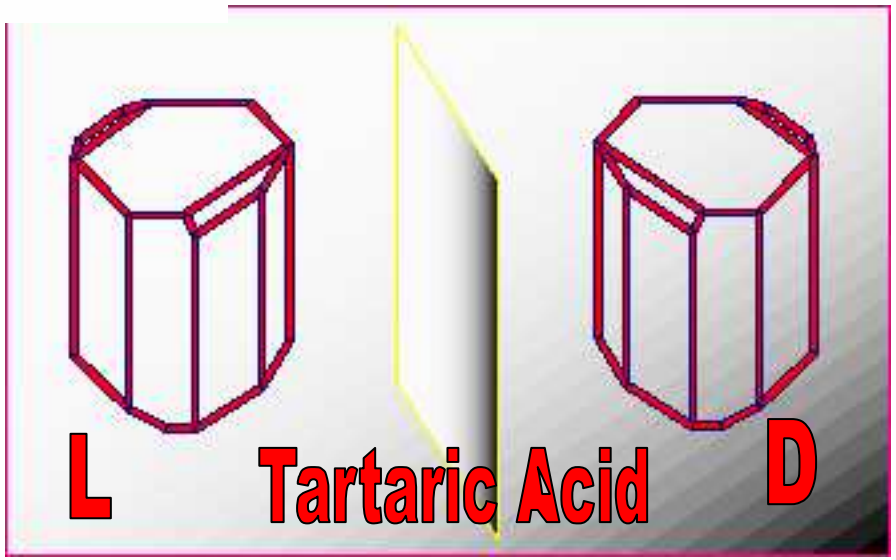

C. Viedma

Enantiomer // Enantiomerically pure // Racemat / Racemic compound // Racemic conglomerate

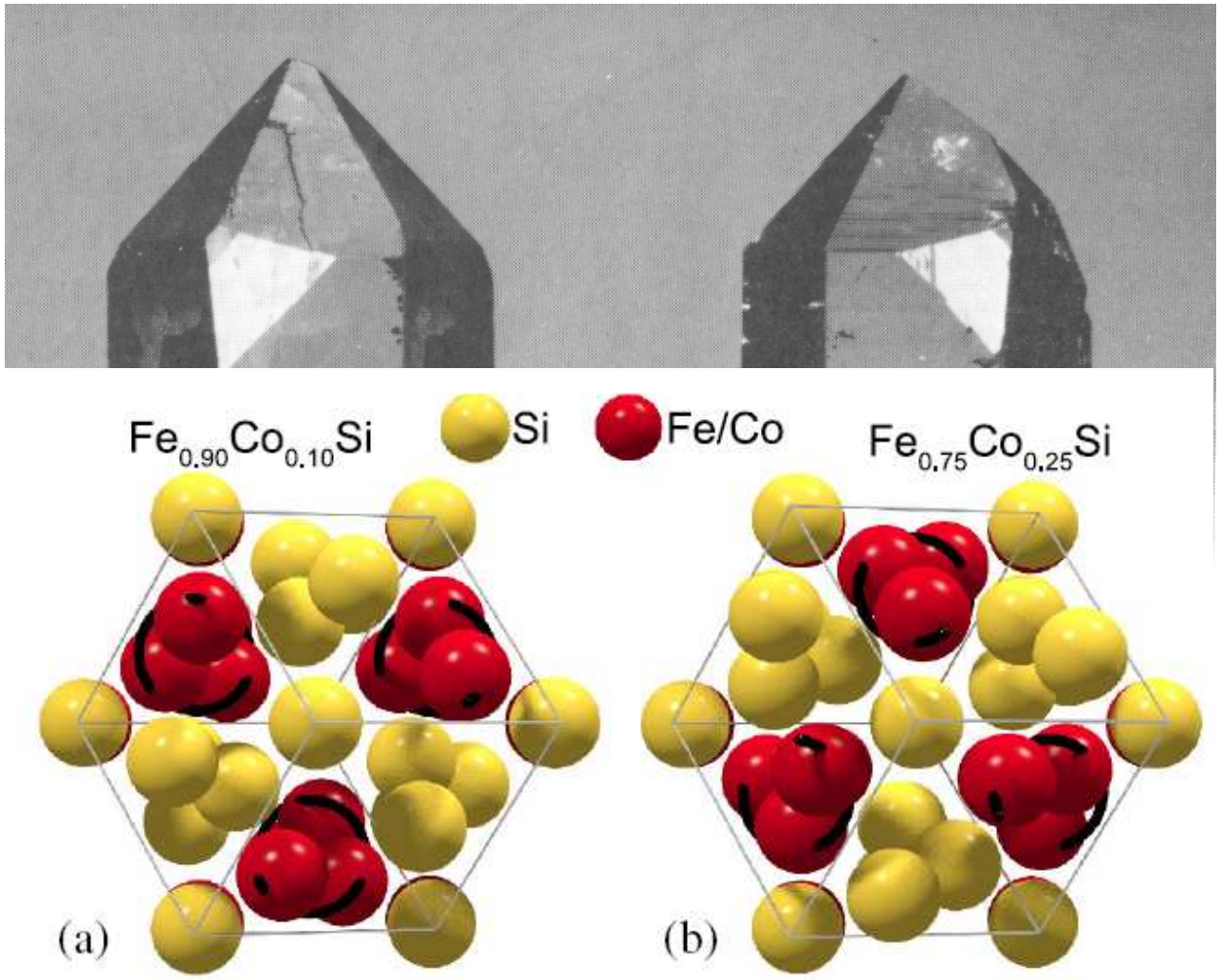


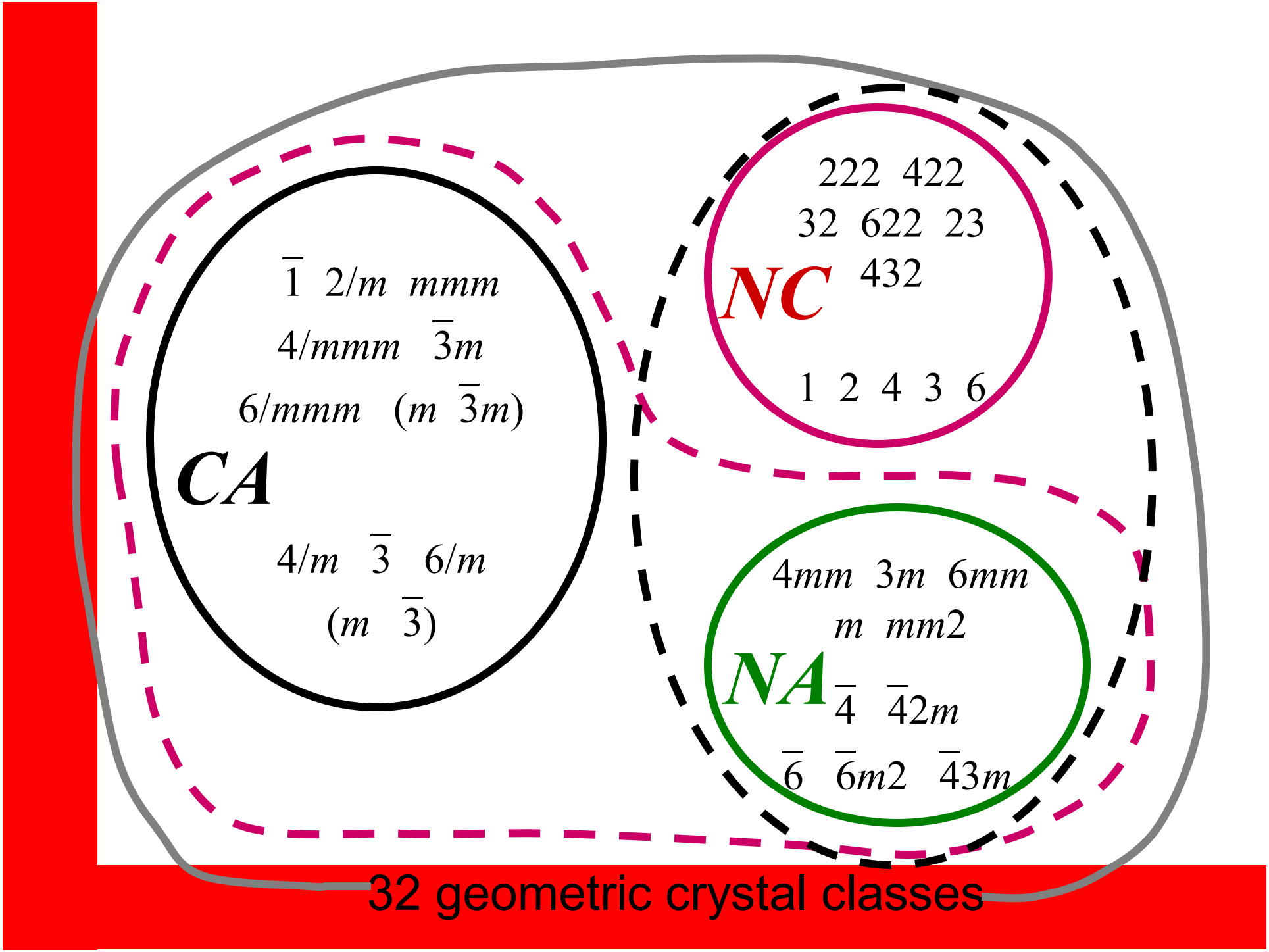
Bitter/sweet structural formulas for asparagin





Enantiomorphs




$\bar{1}$ 2/m mmm
4/mmm $\bar{3}$m
6/mmm (m $\bar{3}$m)
CA
4/m $\bar{3}$ 6/m
(m $\bar{3}$)
222 422
32 622 23
NC 432
1 2 4 3 6
4mm 3m 6mm
m mm2
NA $\bar{4}$ $\bar{4}$2m
$\bar{6}$ $\bar{6}$m2 $\bar{4}$3m
32 geometric crystal classes

Chiral crystal structure vs. chiral space group

International Tables for Crystallography (2006). Vol. A, Space group 198, pp. 610–611.

$P2_13$ T^4 23 Cubic

No. 198 $P2_13$ Patterson symmetry $Pm\bar{3}$

A crystal structure with $P2_13$ symmetry is non-centrosymmetric and chiral.

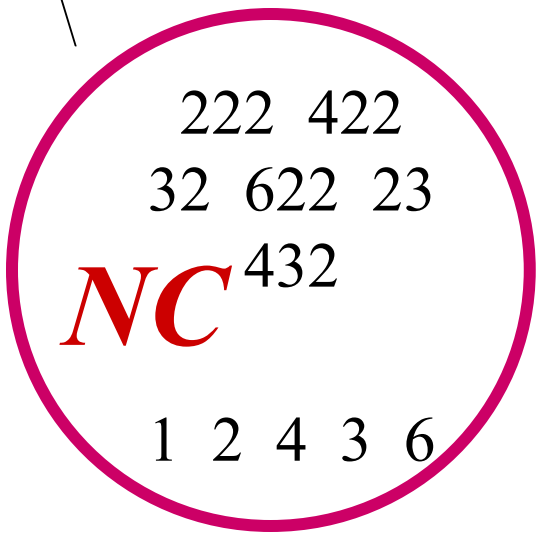
BUT

$P2_13$ space group is non-chiral.

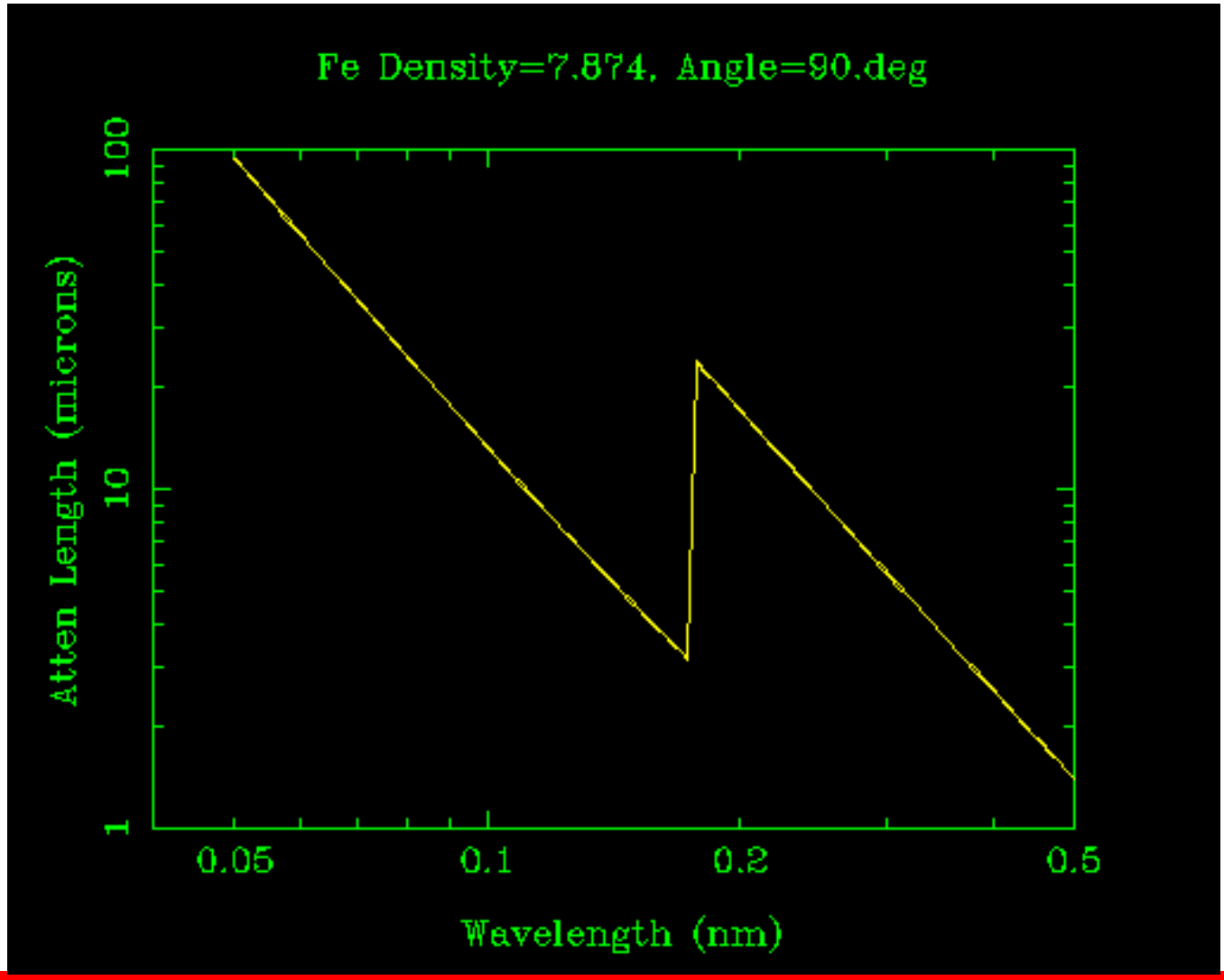
There are only 11 enantiomorphic pairs of chiral space groups.

$$\bar{1}[P2_13] = [P2_13]$$

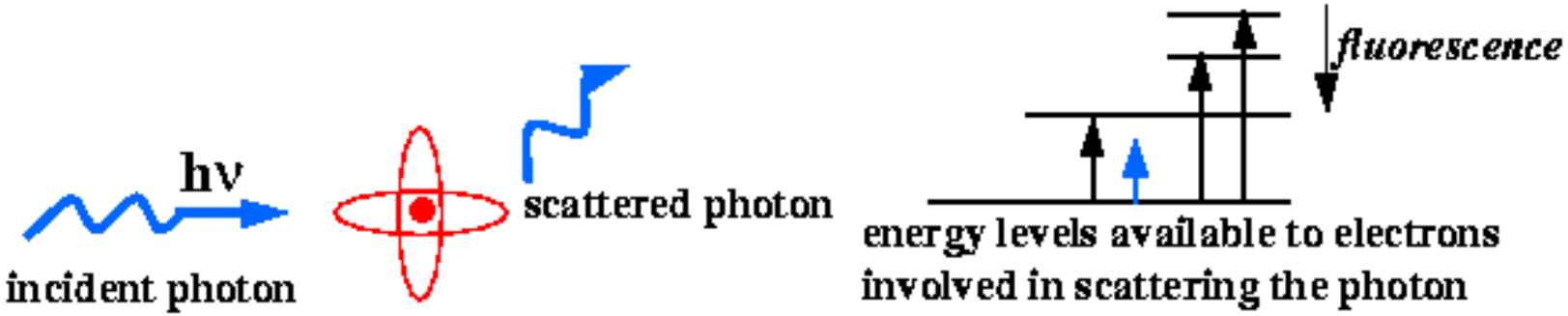
$$\bar{1}[P6_1] = [P6_5] \neq [P6_1]$$

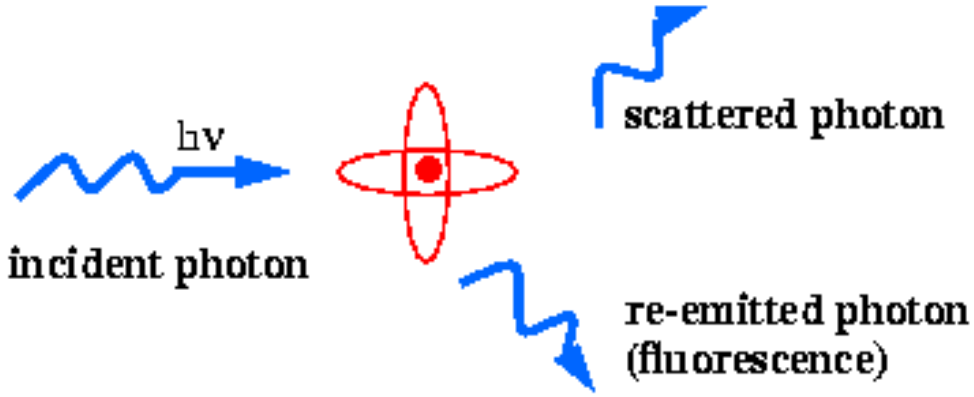


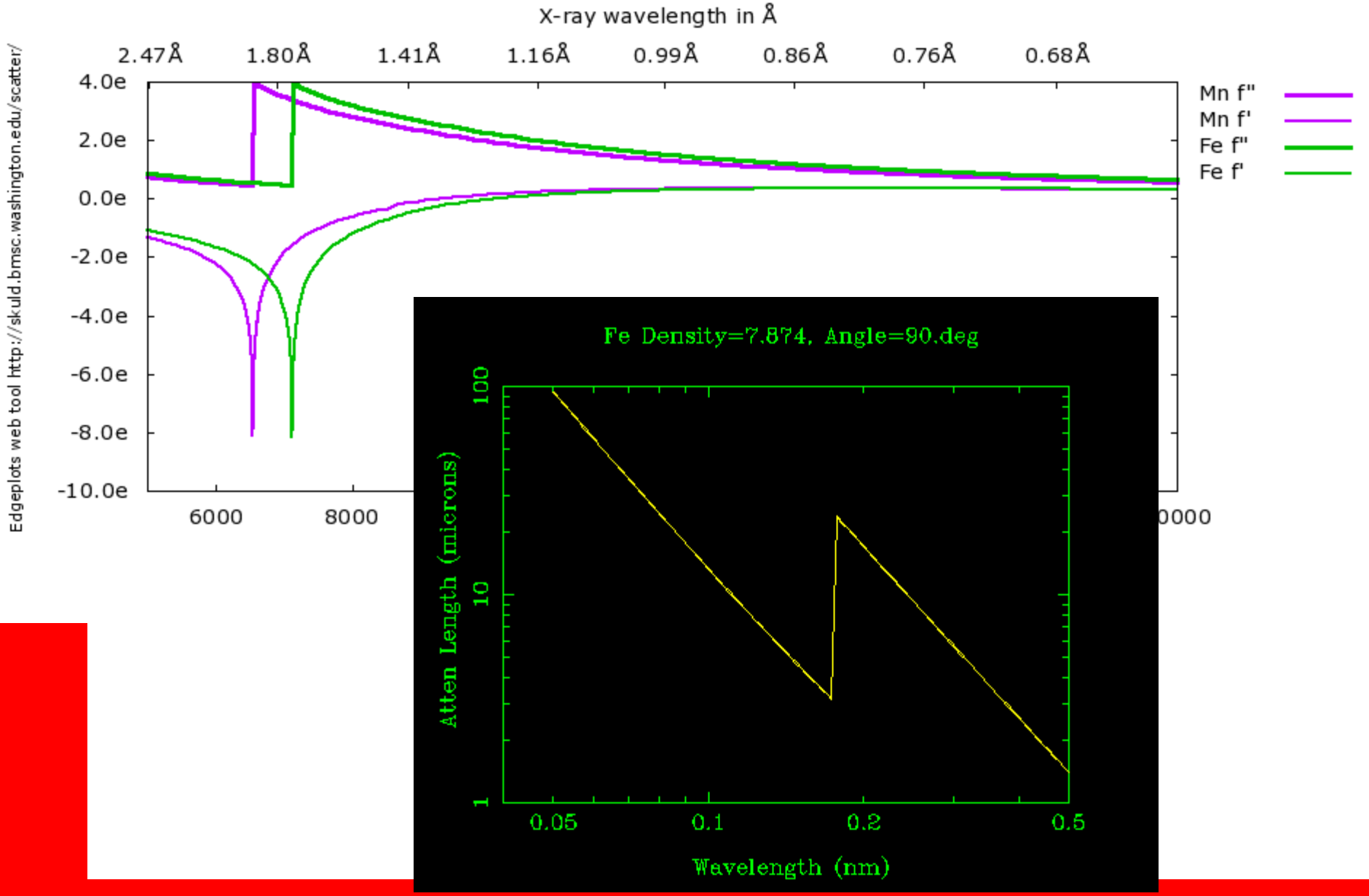
How to distinguish enantiomorphs with X-ray diffraction?



Resonant scattering (anomalous dispersion)






X-ray wavelength in Å
2.47Å
1.80Å
1.41Å
1.16Å
0.99Å
0.86Å
0.76Å
0.68Å
4.0e
2.0e
0.0e
-2.0e
-4.0e
-6.0e
-8.0e
-10.0e
6000
8000
Mn f"
Mn f'
Fe f"
Fe f'
Edgeplots web tool http://skuld.bmsc.washington.edu/scatter/
Fe Density=7.874, Angle=90.deg
Atten Length (microns)
100
10
1
0.05
0.1
0.2
0.5
Wavelength (nm)

$$F(\mathbf{Q}) = \sum_j \left(f_j + if_j''\right)\exp\left(i\mathbf{Q}\mathbf{r}_j\right) = \sum_j \left(f_j + if_j''\right)\left(\cos\left(\mathbf{Q}\mathbf{r}_j\right) + i\sin\left(\mathbf{Q}\mathbf{r}_j\right)\right) =$$

$$= \sum_j \left(f_j + if_j''\right)\left(A_j + iB_j\right) = \sum f_j A_j + i\sum f_j'' A_j + i\sum f_j B_j - \sum f_j'' B_j$$

$$F(\mathbf{Q}) = \sigma + i\sigma'' + i\xi - \xi''$$

$$F(-\mathbf{Q}) = \sigma + i\sigma'' - i\xi + \xi''$$

$$\Sigma = \frac{1}{2}\left(\left|F(\mathbf{Q})\right|^2 + \left|F(-\mathbf{Q})\right|^2\right) = \sigma^2 + \sigma''^2 + \xi^2 + \xi''^2$$

$$D = \frac{1}{2}\left(\left|F(\mathbf{Q})\right|^2 - \left|F(-\mathbf{Q})\right|^2\right) = 4\left(\sigma''\xi - \sigma\xi''\right)$$

1951

-272

(Reprinted from Nature, Vol. 168, p. 271, August 18, 1951)

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF OPTICALLY ACTIVE COMPOUNDS BY MEANS OF X-RAYS

By Prof. J. M. BIJVOET, A. F. PEERDEMAN
AND
A. J. van BOMMEL
van 't Hoff Laboratory, University of Utrecht

J. H. VAN 'T HOFF extended the structural formulæ of organic chemistry to include spatial configuration ("La chimie dans l'espace" (1874), the aliphatic carbon atom with hydrogen or other atoms at the corners of a tetrahedron surrounding it). X-ray analysis has determined the exact configurations and the interatomic distances accurately to within a hundredth of an angstrom unit.

Optically active compounds are not superimposable and are the inverted image of each other. Now it is a remarkable fact that while all details of such configurations can be determined, it yet remained unsolved, whether model or inversion corresponds with a given—say the dextrorotatory—compound. Our present investigation was concerned with this question.

It is impossible to determine absolute configurations by chemical means, which show only the relationship between different structures. These relationships would not alter in any respect if every optically active compound should possess its inverted configuration. Absolute configurations—introduced for the sake of expressing relationship—were based on mere convention. Emil Fischer attributed the configuration of Fig. 2*b* to natural, dextrorotatory, tartaric acid—with an even chance that this choice would fit the real situation.

Of the physical methods of determining absolute configuration, the theoretical calculation of the rotatory power is the most obvious and that most studied; hitherto, the results, however, have lacked conclusiveness. Recently, a discussion of the relation between crystal structure and face development has

Bijvoet used Anomalous Dispersion (Resonant Scattering)
to Solve the Absolute Structure Problem around 1950

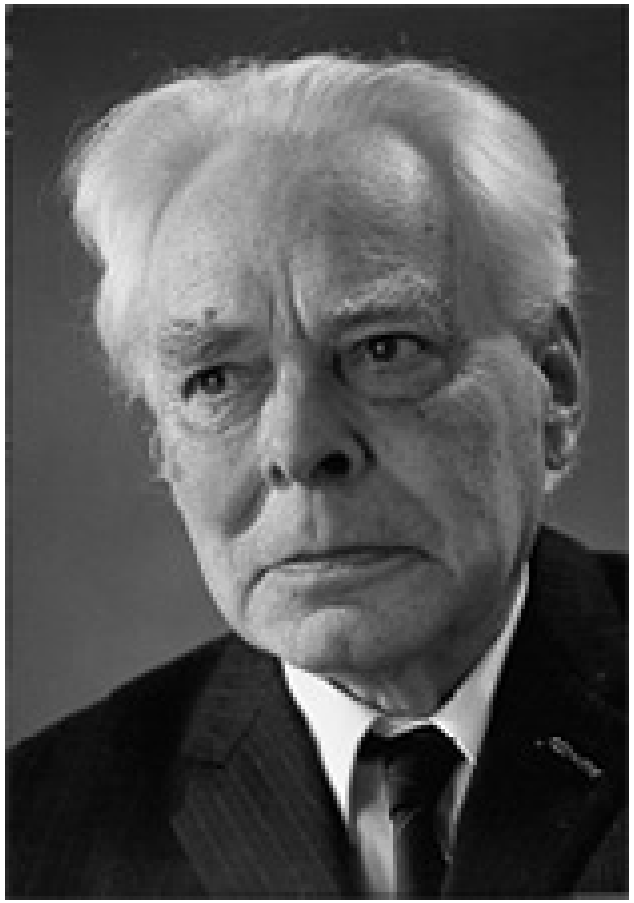
$$A(hkl) = \tfrac{1}{2}[I(hkl) + I(\bar{h}\bar{k}\bar{l})],$$
$$D(hkl) = I(hkl) - I(\bar{h}\bar{k}\bar{l})$$

and the Bijvoet intensity ratio is defined as

$$\chi = \sqrt{\langle D^2 \rangle} / \langle A \rangle .$$

More information on the modern use of Bijvoet intensity ratio:

www.absolutestructure.com



J.M. Bijvoet (1892-1980)

Flack (1983) *parameter*. The parameter x in the structure-amplitude equation

$$G^2(h, k, l, x) = (1 - x)|F(h, k, l)|^2 + x|F(\bar{h}, \bar{k}, \bar{l})|^2$$

(Flack, 1983).

Howard Flack proposed to refine the fractional contribution of "inversion twins"

Twins – non-merohedral, merohedral, partially meroderdal – are crystals of the same structure related by certain symmetry operation (twin operation)/

Reporting and evaluating absolute-structure and absolute-configuration determinations

H. D. Flack* and G. Bernardinelli

J. Appl. Cryst. (2000). **33**, 1143–1148

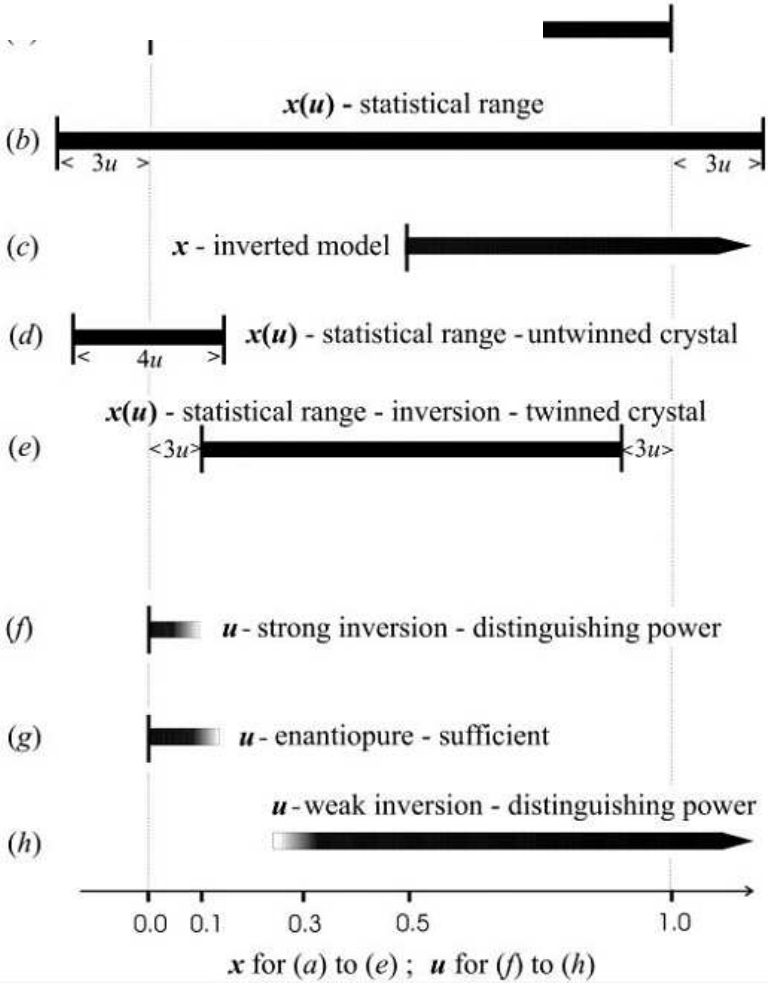


Figure 1
Domains of values of x, its u and the inversion-distinguishing power: (a) the physical domain of x; (b) the statistical domain of x; (c) the domain of x where the crystal and the model are inverted one with respect to the other; (d) the statistical domain of a crystal untwinned by inversion; (e) the statistical domain of a crystal twinned by inversion; (f) the domain of strong inversion-distinguishing power; (g) the domain of enantiopure-sufficient inversion-distinguishing power; (h) the domain of weak inversion-distinguishing power. For (f), (g) and (h), the horizontal lines are of varying intensity. In the part of the line which is black, the inversion-distinguishing power may be deduced from the value of u alone. In the part of the line which is grey, the inversion-distinguishing power may *not* be deduced from the value of u alone. In (b), (d) and (e), arbitrary values of u have been drawn and in practical applications the value of u yielded by the experiment must be used.

Fe(Co)Si story.

S.G. says:

- We have opposite magnetic chirality for $Fe_{0.9}Co_{0.1}Si$ and $Fe_{0.75}Co_{0.25}Si$. Is their structural chirality the same or different?
- We can easily distinguish left and right magnetic structures with neutrons. Can one do the same for crystal structures?

n

Microsoft Excel - Friedif.xls

File Edit View Insert Format Tools Data Window Help Adobe PDF

C48 fx 0

	A	B	C	D	E	F	G	H	I	J	K	L
4	Version: 8th August 2007.											
5												
6	Method of	Use:										
7		Click the button ZERO COMP										
8		Set the values in columns 'Composition All' to the elemental composition of the compound.										
9		Set the values in columns 'Composition Centro' to the elemental composition of the centrosymmetric substructure.										
10		Move the cursor to a zero value in column 'Composition'.										
11		Read the values of molecular mass, Friedif and Friedif centro in the lines just below.										
12												
13	**Molecular**			**Friedif**	**Friedif-centro**							
14	**Mass**		**Cr Ka**	**237**	**237**							
15	**83.93**		**Cu Ka**	**1160**	**1160**							
16			**Mo Ka**	**324**	**324**							
17												
18		ZERO COMP										
19												
20	**Element**	**Composition**		Cu f"	Mo f"	Cr f"	Z	Cu N*f"**2	Mo N*f"**2	Cr N*f"**2	N*Z**2	AtomMass
21		**All**	**Centro**									
22												
23	H	0	0	0	0	0	1	0	0			

1. ***Can we resolve absolute structure?***
2. ***How to collect data?***
3. ***How to compare two absolute structures?***

u=m/Friedif

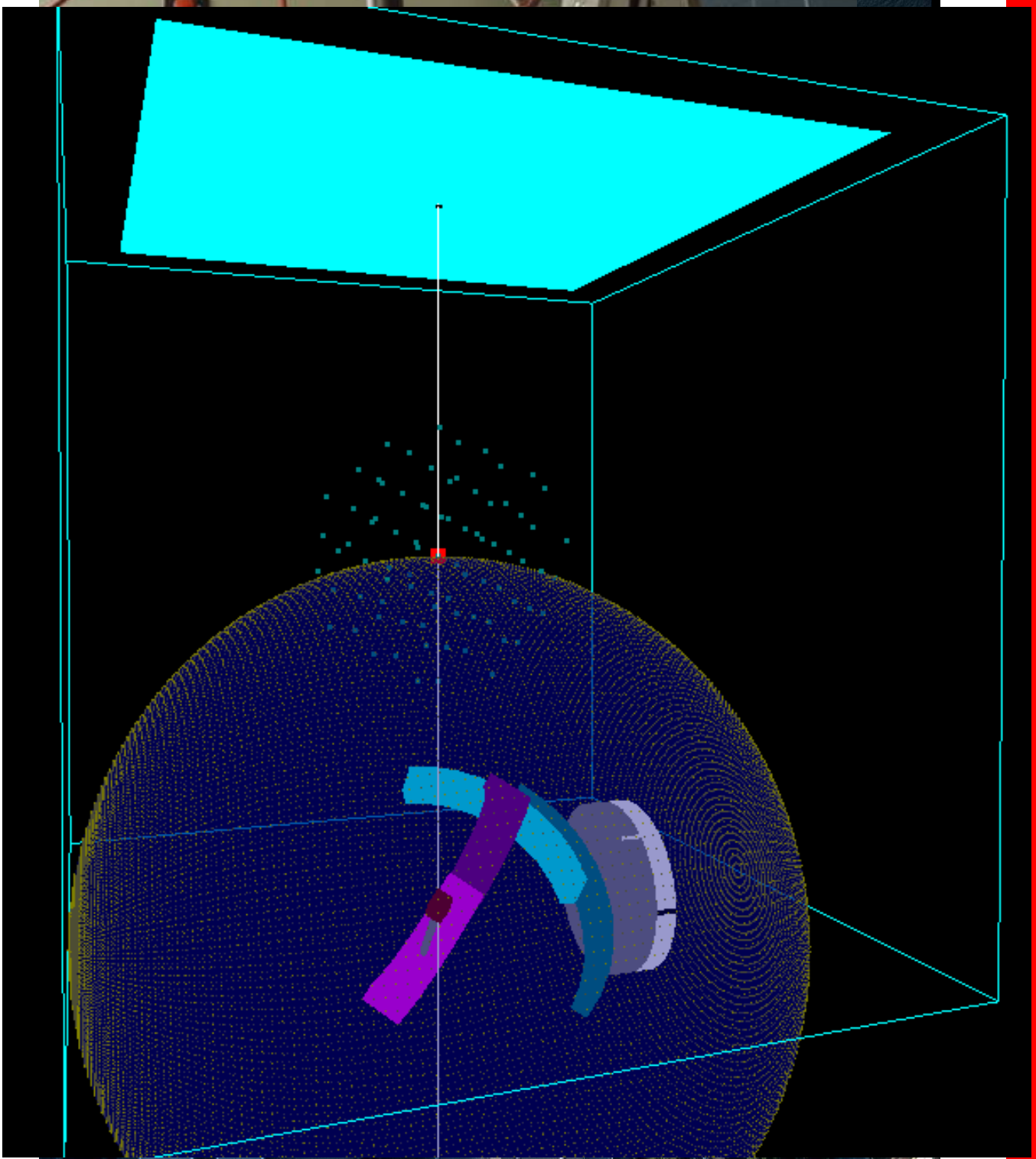
m=8-12

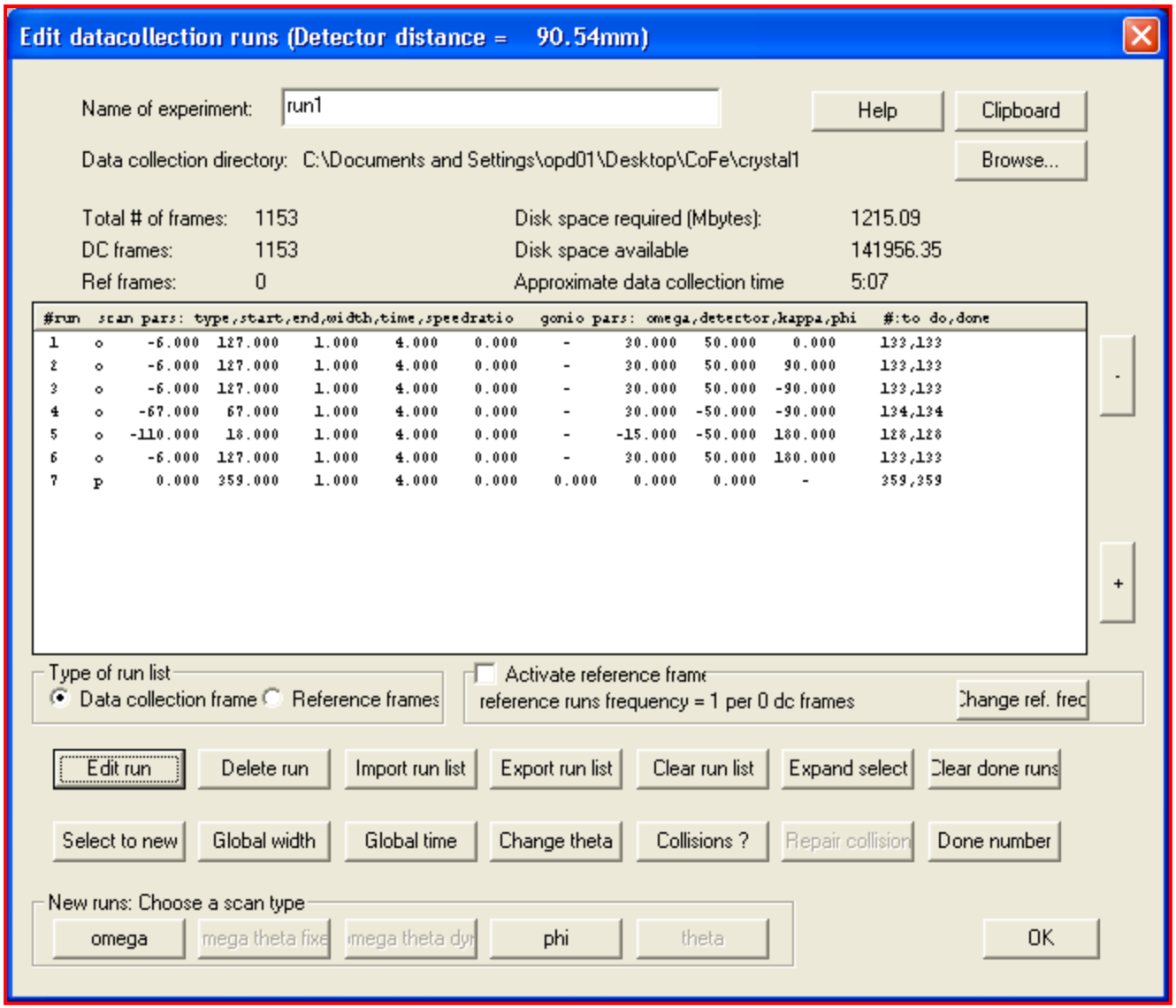
Mo Ka:

u=8/324=0.025

0.01- ideal for AS

0.1 - good enough for enantiopure

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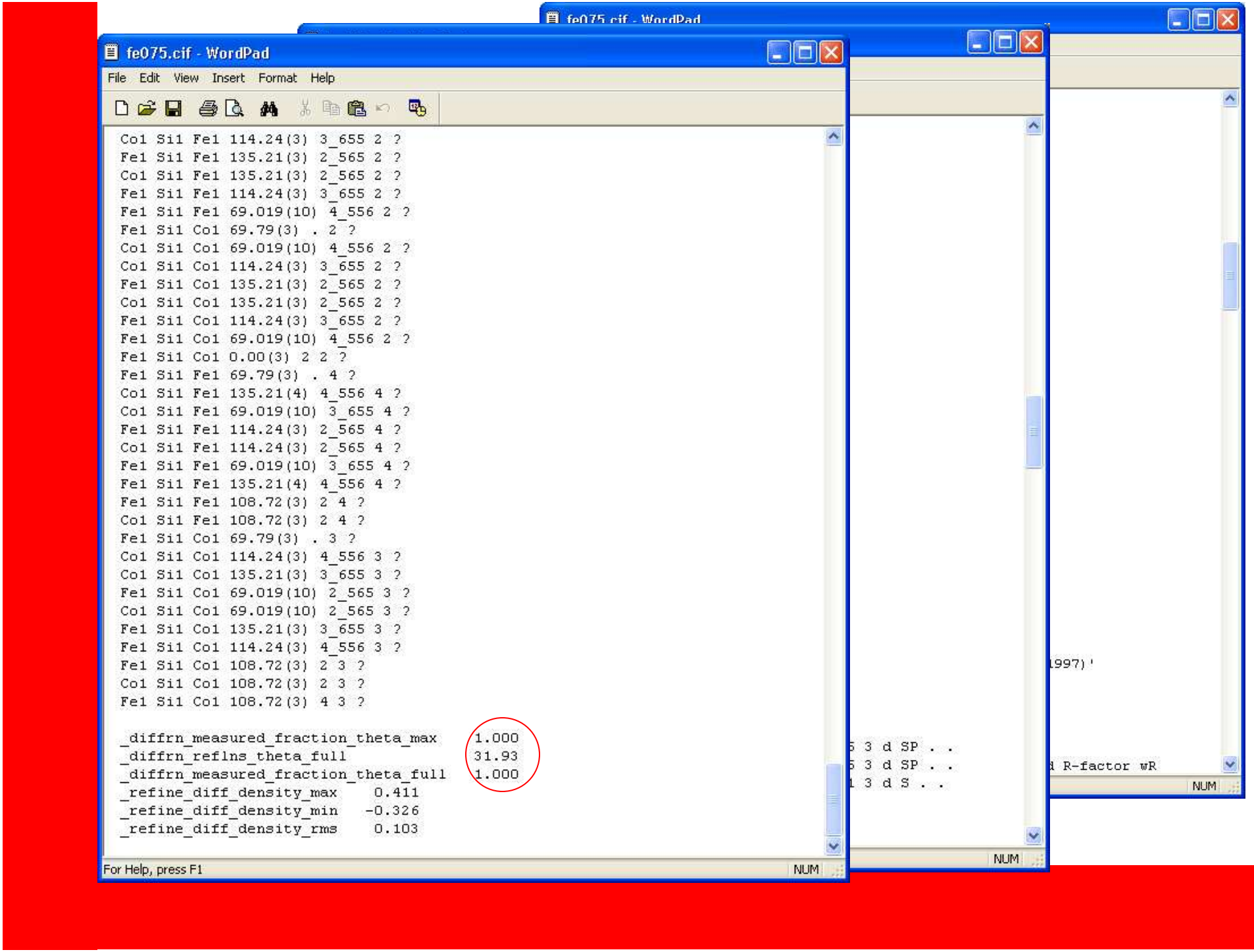
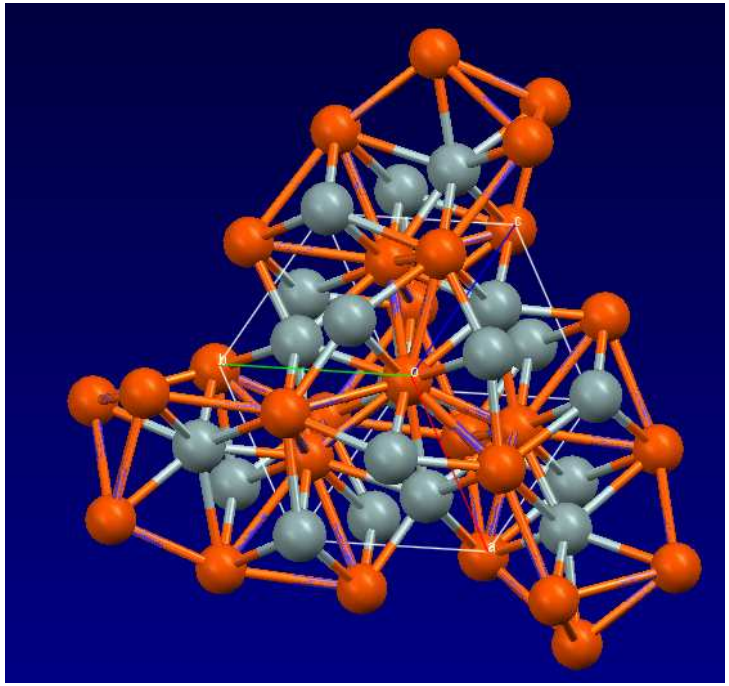
Name of experiment: run1
Help
Clipboard
Data collection directory: C:\Documents and Settings\opd01\Desktop\CoFe\crystal1
Browse...
Total # of frames: 1153
DC frames: 1153
Ref frames: 0
Disk space required (Mbytes): 1215.09
Disk space available 141956.35
Approximate data collection time 5:07
#run scan pars: type,start,end,width,time,speedratio goniо pars: omega,detector,kappa,phi #:to do,done
1 o -6.000 127.000 1.000 4.000 0.000 - 30.000 50.000 0.000 133,133
2 o -6.000 127.000 1.000 4.000 0.000 - 30.000 50.000 90.000 133,133
3 o -6.000 127.000 1.000 4.000 0.000 - 30.000 50.000 -90.000 133,133
4 o -67.000 67.000 1.000 4.000 0.000 - 30.000 -50.000 -90.000 134,134
5 o -110.000 18.000 1.000 4.000 0.000 - -15.000 -50.000 180.000 128,128
6 o -6.000 127.000 1.000 4.000 0.000 - 30.000 50.000 180.000 133,133
7 p 0.000 359.000 1.000 4.000 0.000 0.000 0.000 0.000 - 359,359
-
+
Type of run list
Data collection frame
Reference frames
Activate reference frame
reference runs frequency = 1 per 0 dc frames
Change ref. freq
Edit run
Delete run
Import run list
Export run list
Clear run list
Expand select
Clear done runs
Select to new
Global width
Global time
Change theta
Collisions ?
Repair collision
Done number
New runs: Choose a scan type
omega
mega theta fixe
mega theta dyn
phi
theta
OK

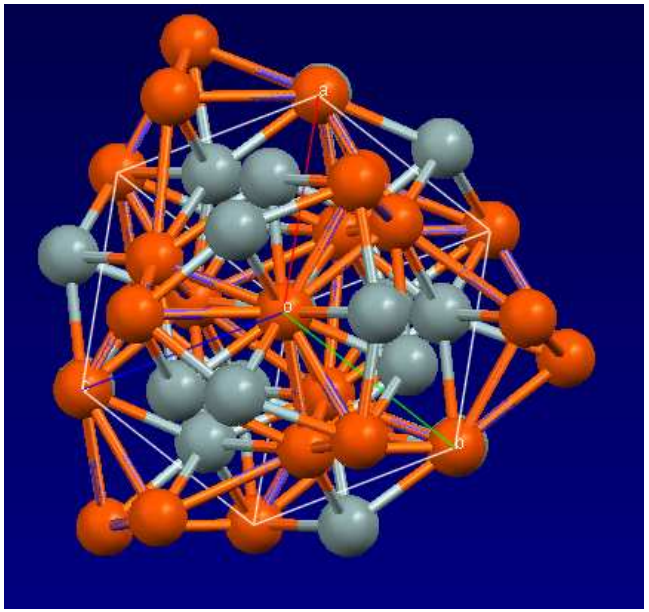

fe075.cif - WordPad
File Edit View Insert Format Help
Co1 Si1 Fe1 114.24(3) 3_655 2 ?
Fe1 Si1 Fe1 135.21(3) 2_565 2 ?
Co1 Si1 Fe1 135.21(3) 2_565 2 ?
Fe1 Si1 Fe1 114.24(3) 3_655 2 ?
Fe1 Si1 Fe1 69.019(10) 4_556 2 ?
Fe1 Si1 Co1 69.79(3) . 2 ?
Co1 Si1 Co1 69.019(10) 4_556 2 ?
Co1 Si1 Co1 114.24(3) 3_655 2 ?
Fe1 Si1 Co1 135.21(3) 2_565 2 ?
Co1 Si1 Co1 135.21(3) 2_565 2 ?
Fe1 Si1 Co1 114.24(3) 3_655 2 ?
Fe1 Si1 Co1 69.019(10) 4_556 2 ?
Fe1 Si1 Co1 0.00(3) 2 2 ?
Fe1 Si1 Fe1 69.79(3) . 4 ?
Co1 Si1 Fe1 135.21(4) 4_556 4 ?
Co1 Si1 Fe1 69.019(10) 3_655 4 ?
Fe1 Si1 Fe1 114.24(3) 2_565 4 ?
Co1 Si1 Fe1 114.24(3) 2_565 4 ?
Fe1 Si1 Fe1 69.019(10) 3_655 4 ?
Fe1 Si1 Fe1 135.21(4) 4_556 4 ?
Fe1 Si1 Fe1 108.72(3) 2 4 ?
Co1 Si1 Fe1 108.72(3) 2 4 ?
Fe1 Si1 Co1 69.79(3) . 3 ?
Co1 Si1 Co1 114.24(3) 4_556 3 ?
Co1 Si1 Co1 135.21(3) 3_655 3 ?
Fe1 Si1 Co1 69.019(10) 2_565 3 ?
Co1 Si1 Co1 69.019(10) 2_565 3 ?
Fe1 Si1 Co1 135.21(3) 3_655 3 ?
Fe1 Si1 Co1 114.24(3) 4_556 3 ?
Fe1 Si1 Co1 108.72(3) 2 3 ?
Co1 Si1 Co1 108.72(3) 2 3 ?
Fe1 Si1 Co1 108.72(3) 4 3 ?
_diffrn_measured_fraction_theta_max 1.000
_diffrn_reflns_theta_full 31.93
_diffrn_measured_fraction_theta_full 1.000
_refine_diff_density_max 0.411
_refine_diff_density_min -0.326
_refine_diff_density_rms 0.103
For Help, press F1
NUM
fe075.cif - WordPad
NUM
fe075.cif - WordPad
R-factor wR
NUM

How to compare two absolute structure?

$Fe_{0.9}Co_{0.1}Si$



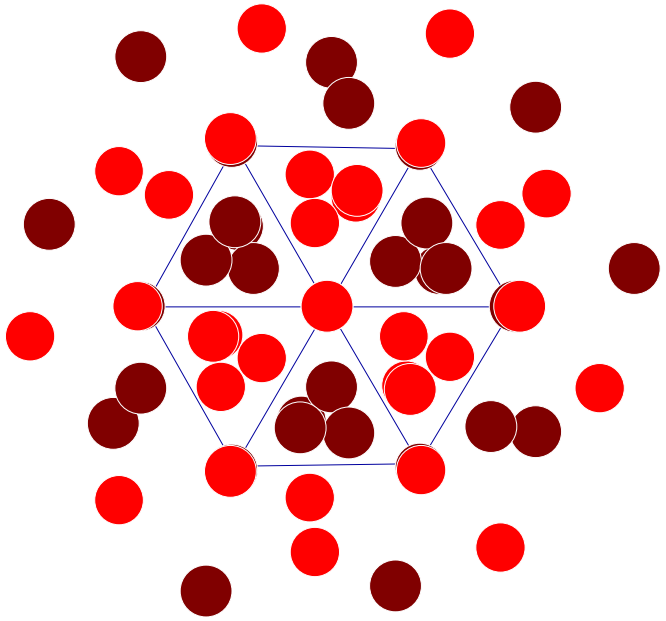
$Fe_{0.75}Co_{0.25}Si$



[111]

Opposite chirality

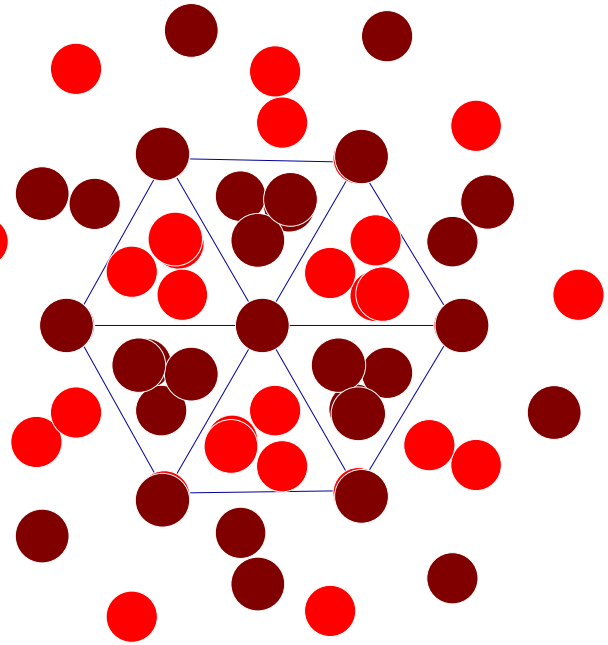
Fe0.9 Flack=0



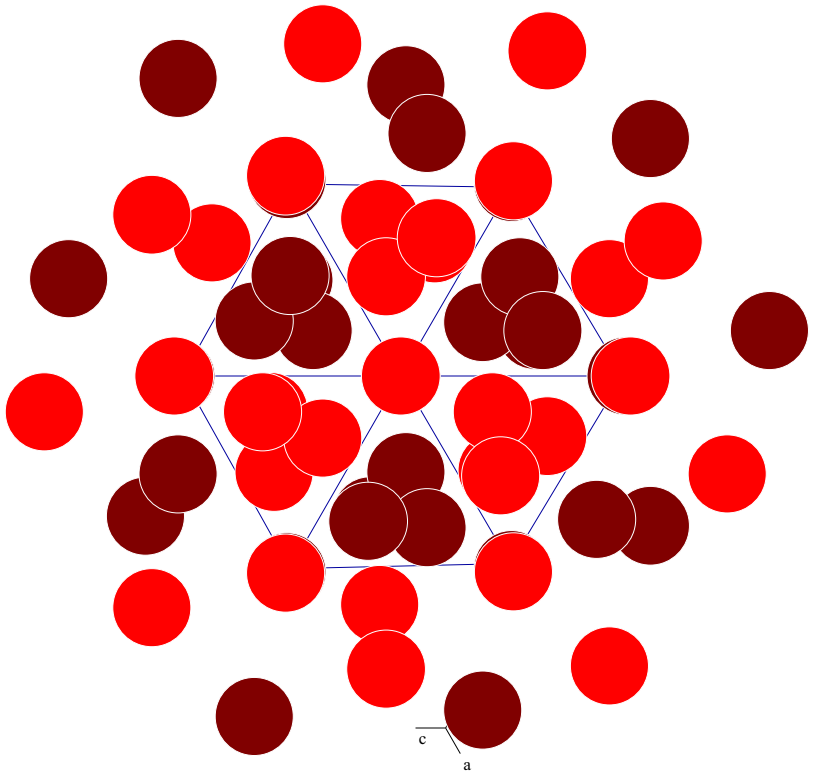
$$\bar{1} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

•MOVE 1 1 1 -1

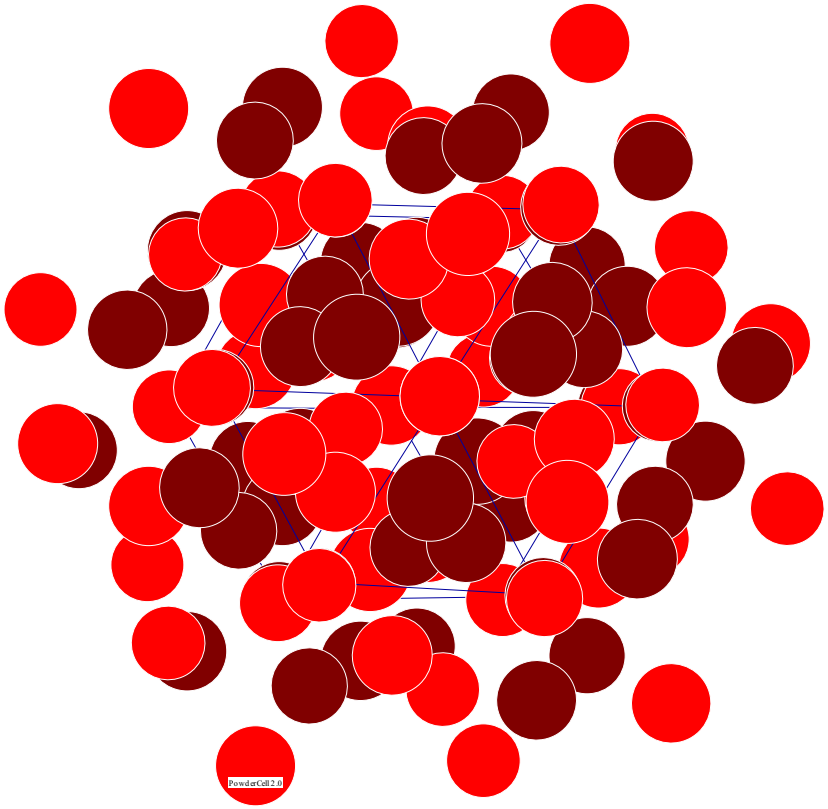
Fe0.9 Flack=1



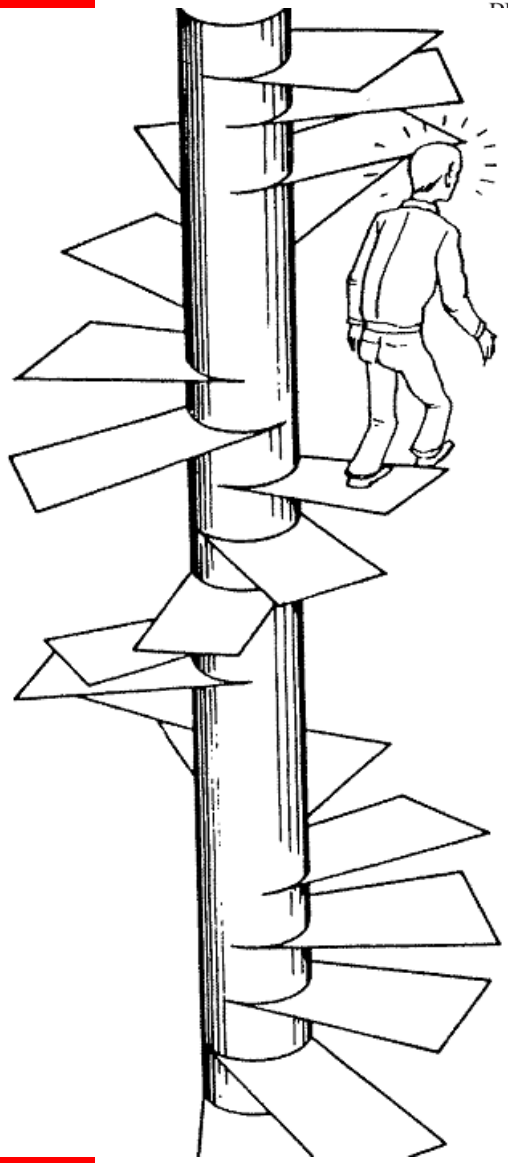
Different structures!



Fe0.9



Fe0.75



Crystal Handedness and Spin Helix Chirality in $Fe_{1-x}Co_xSi$

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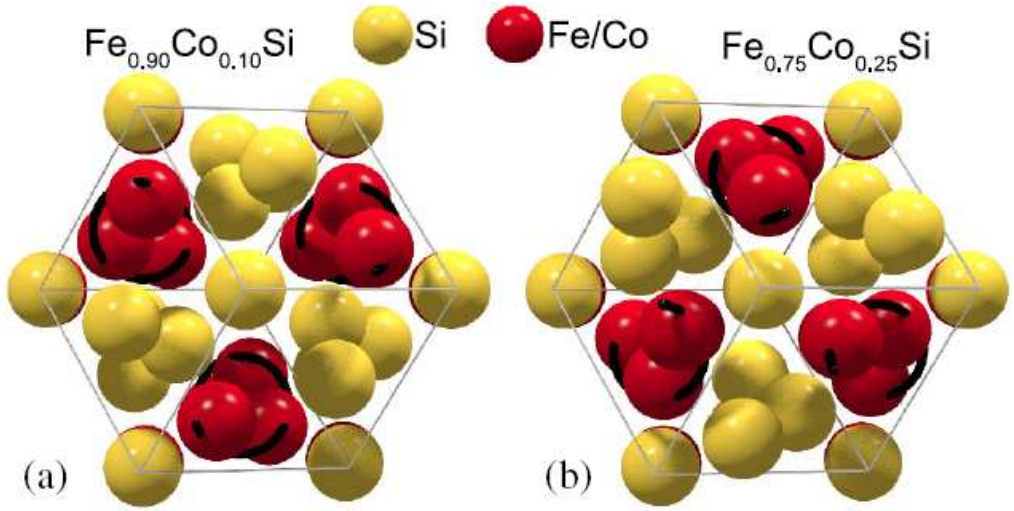


…we have it published and now it is time to think …

FeSi in $P2_13$: *how symmetry works*

International Tables for Crystallography (2006). Vol. A, Space group 198, pp. 610–611.

$P2_13$ T^4 23 Cubic

No. 198 $P2_13$ Patterson symmetry $Pm\bar{3}$

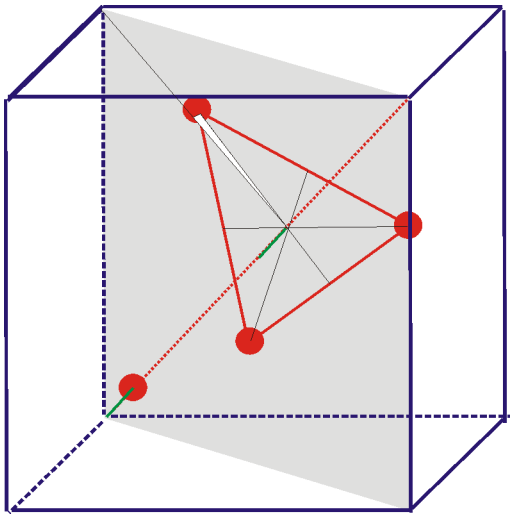
Symmetry operations

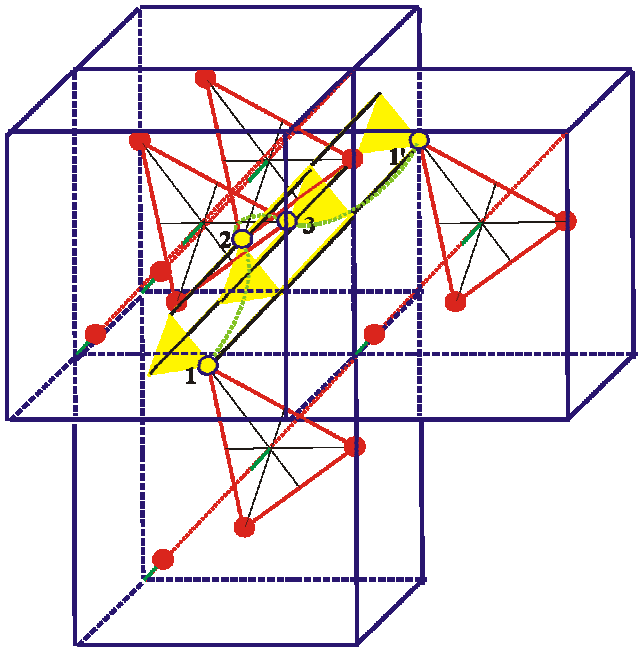
(1) 1	(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$	(3) $2(0,\frac{1}{2},0)$ $0,y,\frac{1}{4}$	(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},0$
(5) 3^+ x,x,x	(6) 3^+ $\bar{x}+\frac{1}{2},x,\bar{x}$	(7) 3^+ $x+\frac{1}{2},\bar{x}-\frac{1}{2},\bar{x}$	(8) 3^+ $\bar{x},\bar{x}+\frac{1}{2},x$
(9) 3^- x,x,x	(10) $3^-(-\frac{1}{3},\frac{1}{3},\frac{1}{3})$ $x+\frac{1}{6},\bar{x}+\frac{1}{6},\bar{x}$	(11) $3^-(\frac{1}{3},\frac{1}{3},-\frac{1}{3})$ $\bar{x}+\frac{1}{3},\bar{x}+\frac{1}{6},x$	(12) $3^-(\frac{1}{3},-\frac{1}{3},\frac{1}{3})$ $\bar{x}-\frac{1}{6},x+\frac{1}{3},\bar{x}$

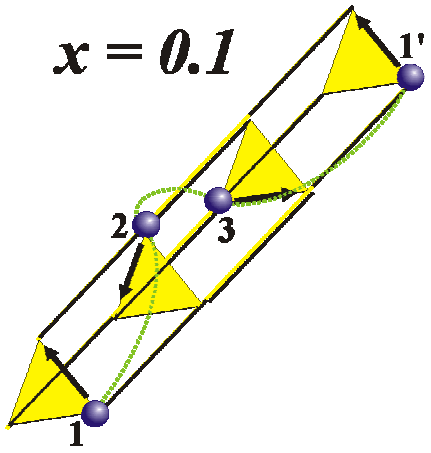
Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
						h,k,l cyclically permutable
						General:
12	b 1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	$h00:\ h=2n$
		(5) z,x,y	(6) $z+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}$	(7) $\bar{z}+\frac{1}{2},\bar{x},y+\frac{1}{2}$	(8) $\bar{z},x+\frac{1}{2},\bar{y}+\frac{1}{2}$	
		(9) y,z,x	(10) $\bar{y},z+\frac{1}{2},\bar{x}+\frac{1}{2}$	(11) $y+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{x}$	(12) $\bar{y}+\frac{1}{2},\bar{z},x+\frac{1}{2}$	
						Special: no extra conditions
4	a .3.	x,x,x	$\bar{x}+\frac{1}{2},\bar{x},x+\frac{1}{2}$	$\bar{x},x+\frac{1}{2},\bar{x}+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}$	

One sublattice.
Fe at (x,x,x)







Four equivalent Fe positions form achiral object.

To see a chirality we have to apply translations.

Fe sublattice or any part of it bigger than unit cell is chiral.

Fe vs.Si

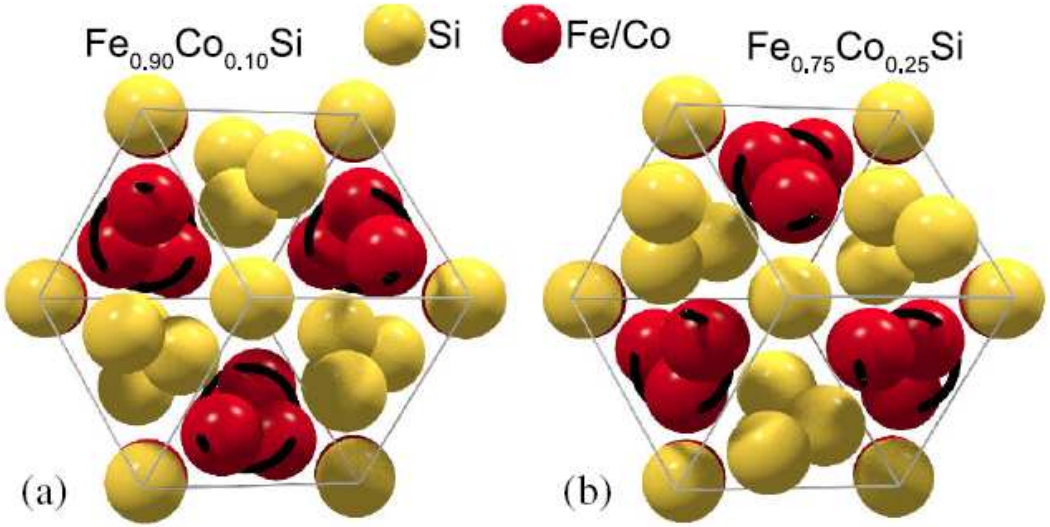
Fe [x,x,x], Si [1-x,1-x,1-x]

$$\{Fe\} \neq \bar{1}\{Fe\}$$

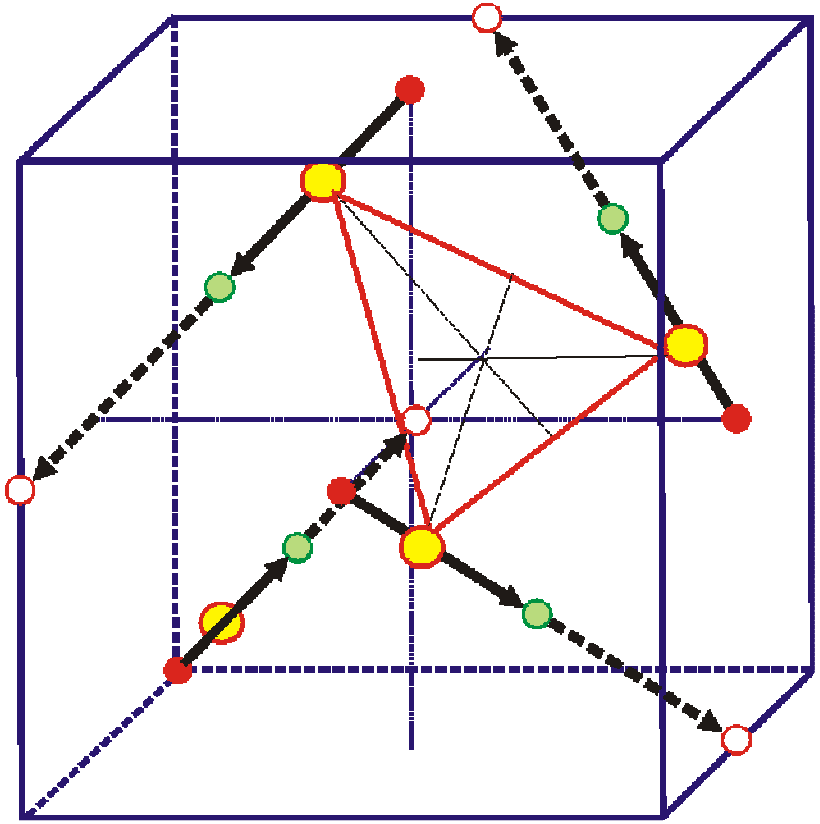
$$\{Si\} \neq \bar{1}\{Si\}$$

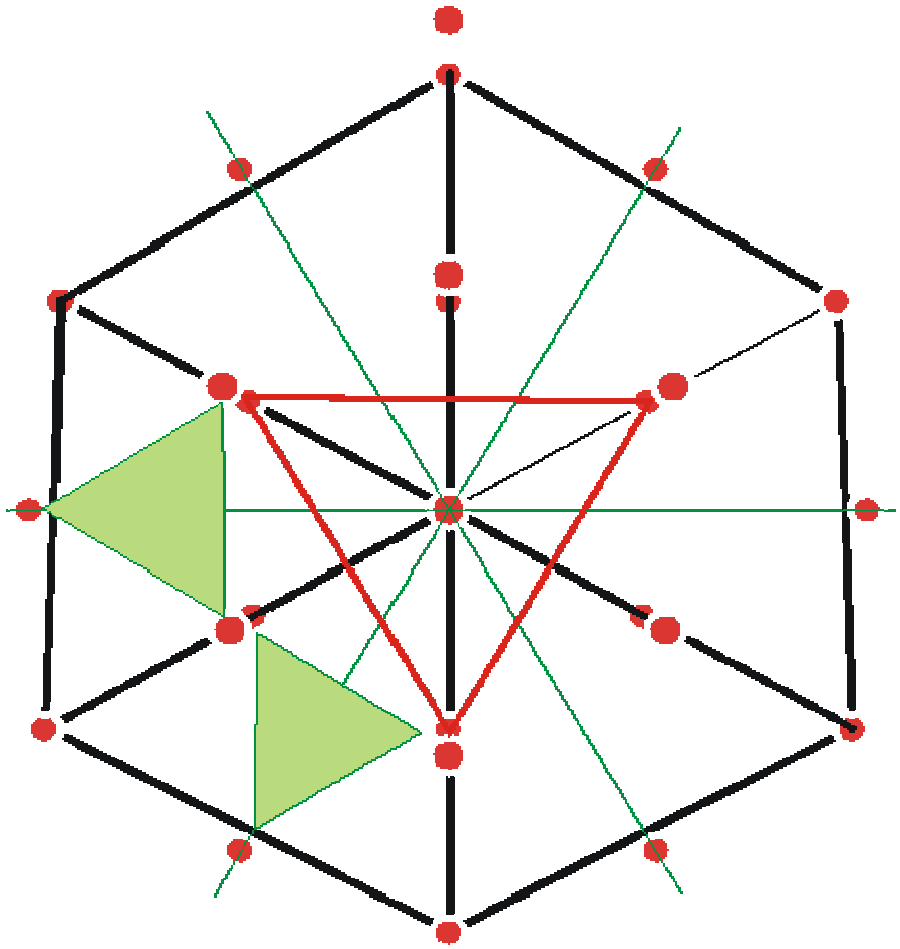
$$\{Si\} = \bar{1}\{Fe\}$$

Fe and Si sublattices have opposite chirality.



One sublattice.
Let us move Fe in [111]





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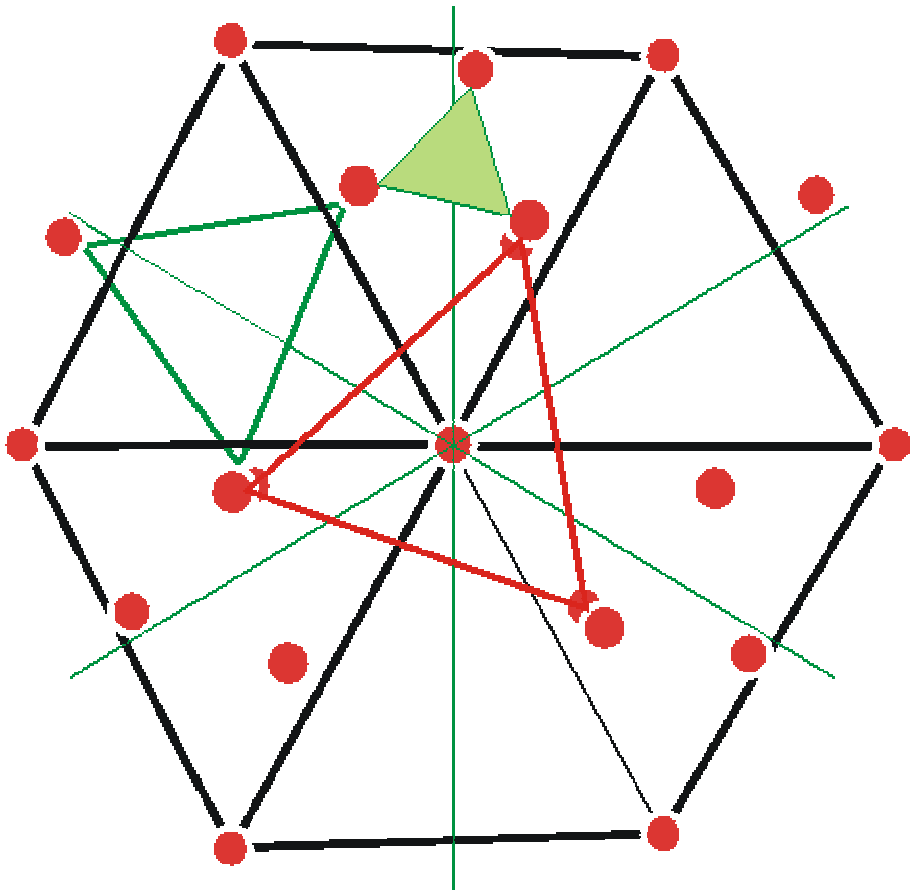

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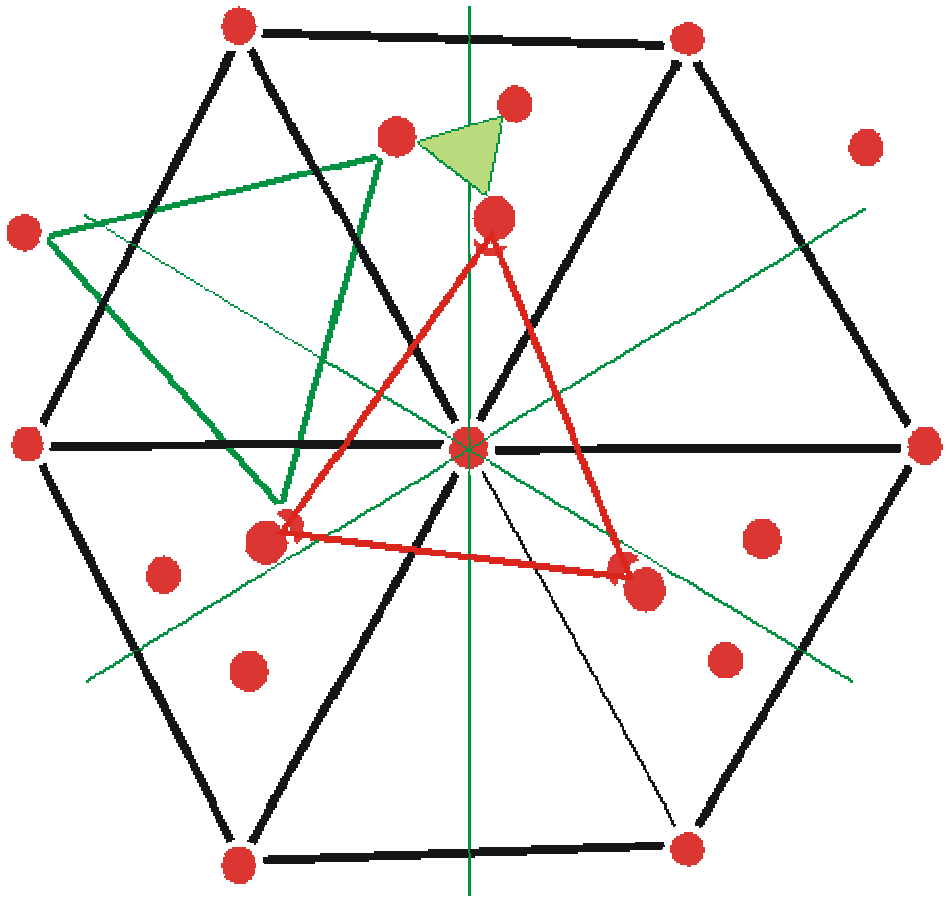

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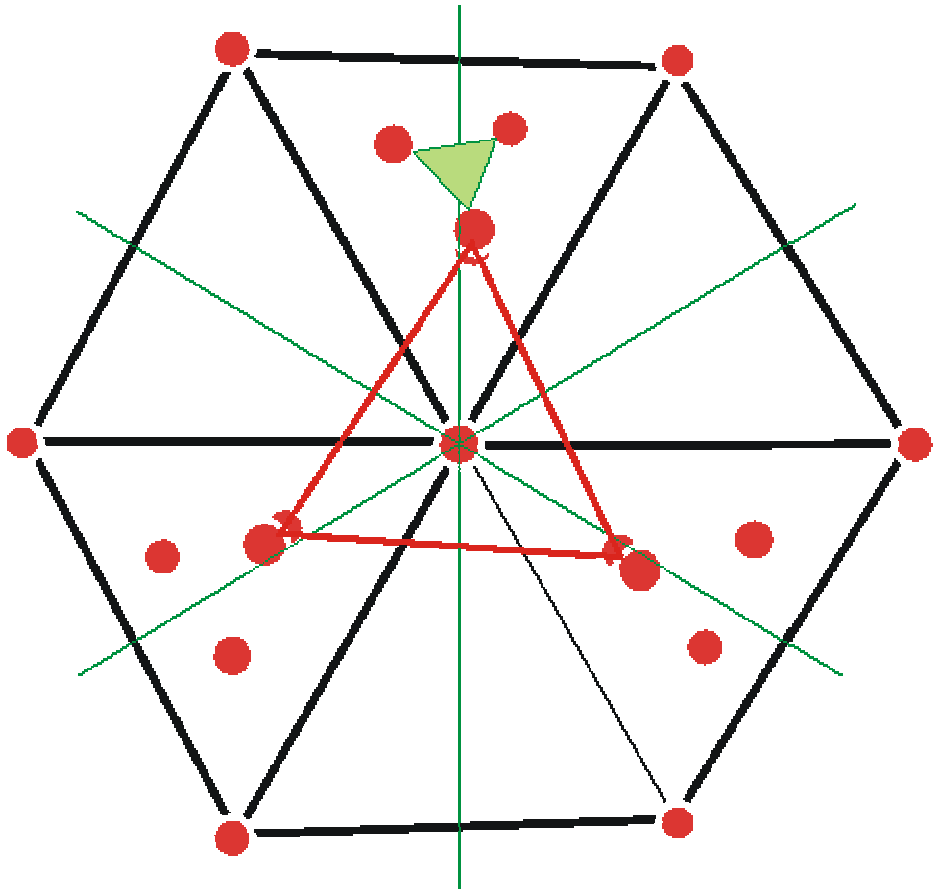

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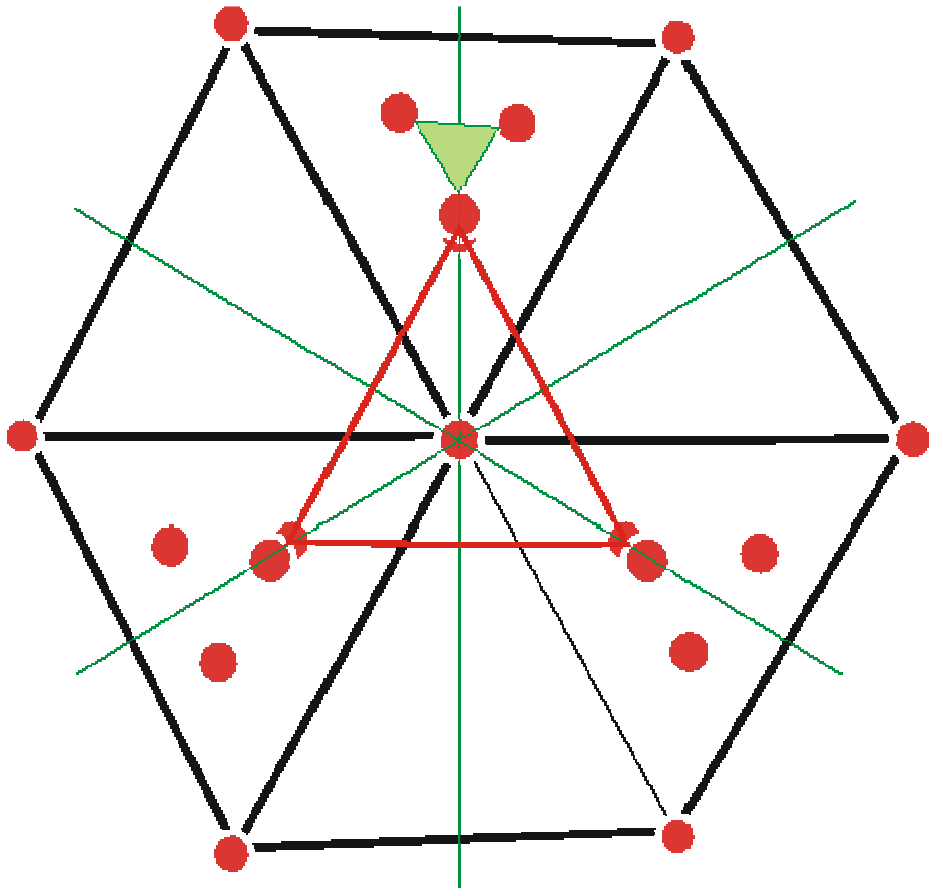

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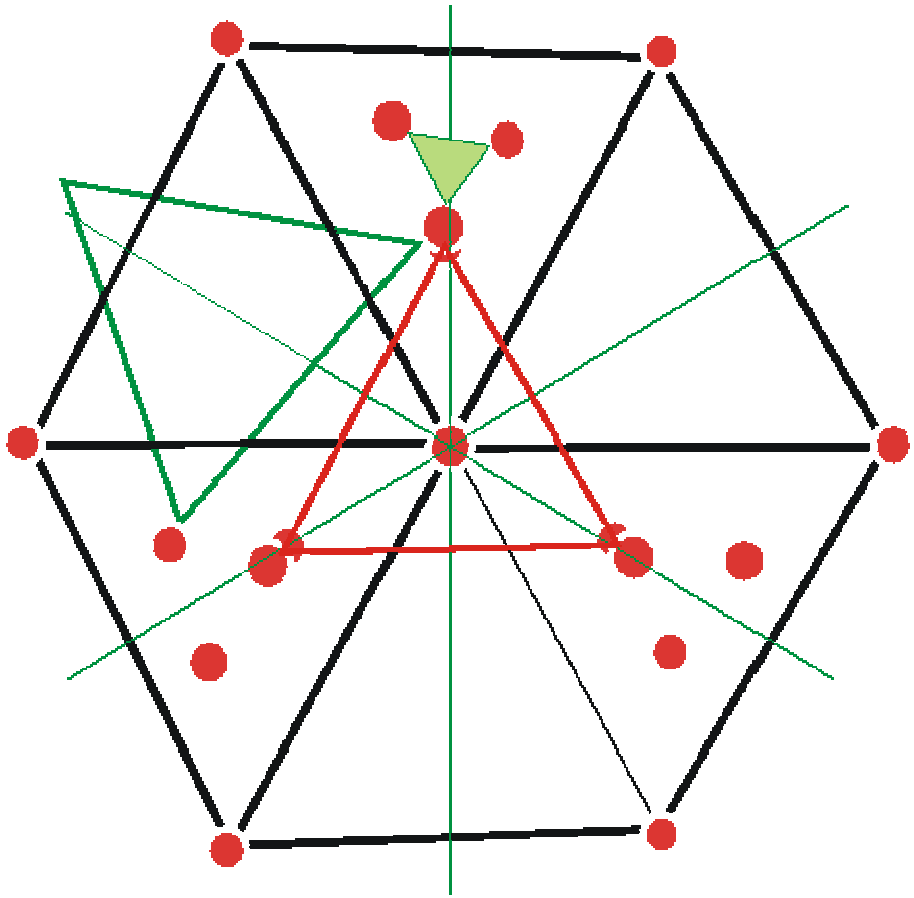

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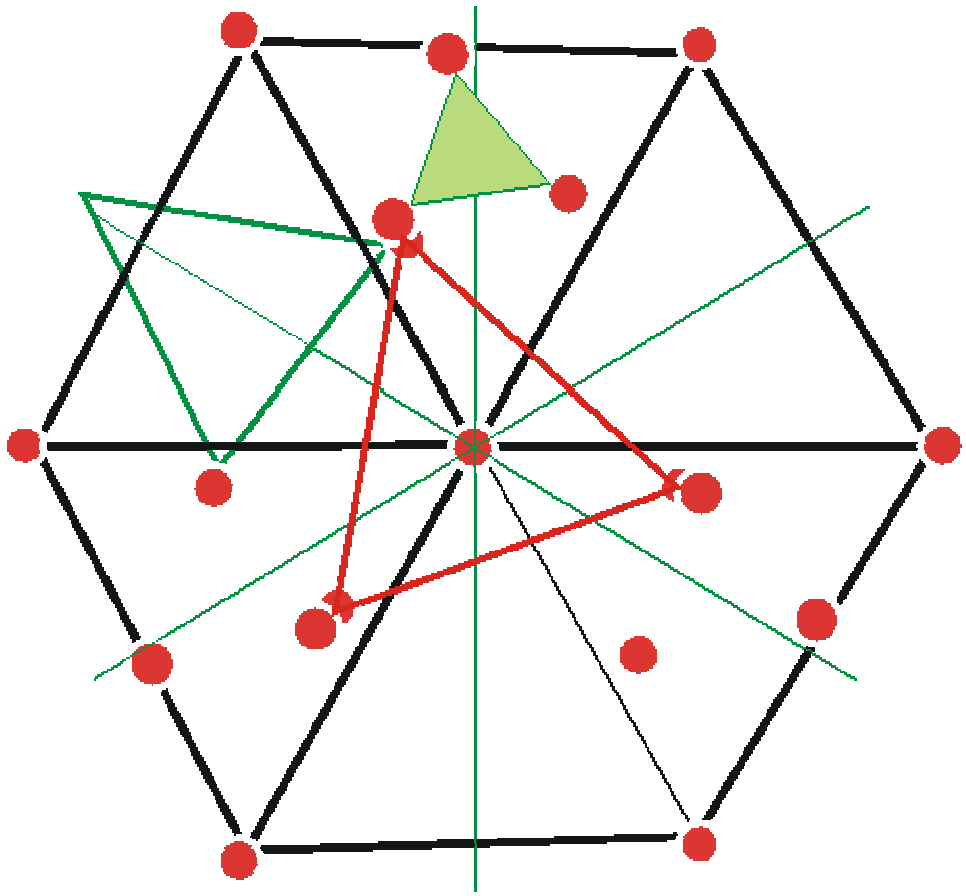

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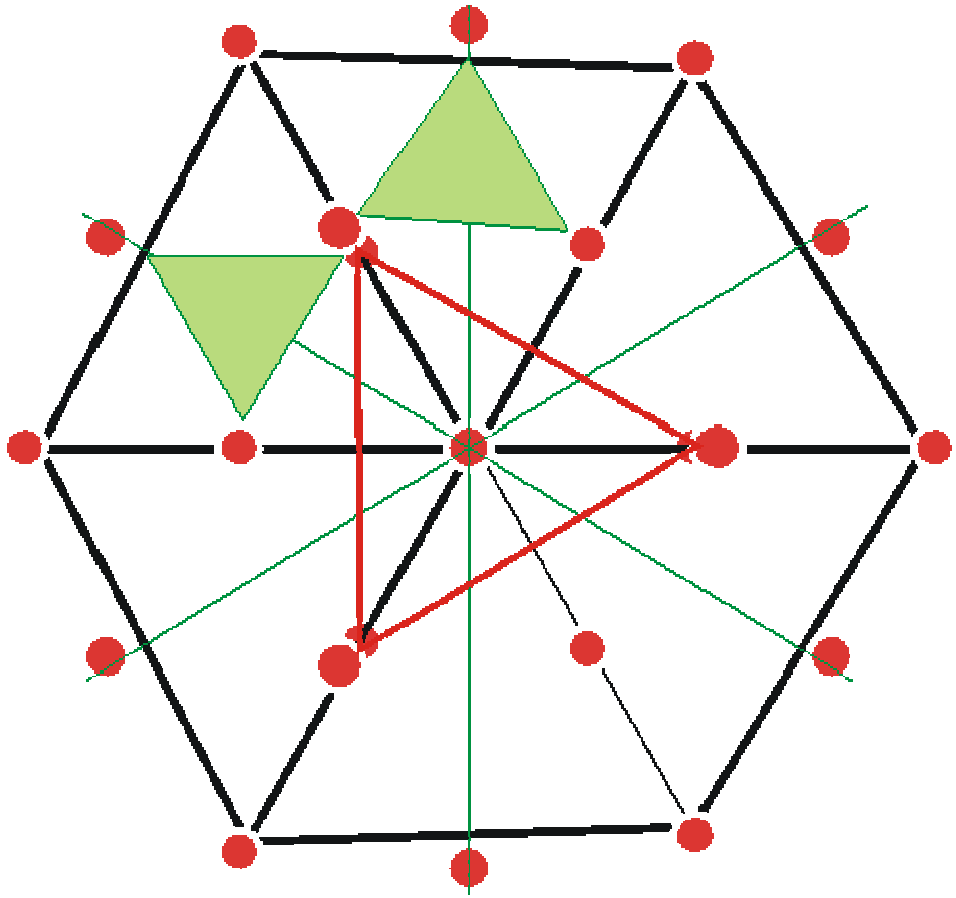

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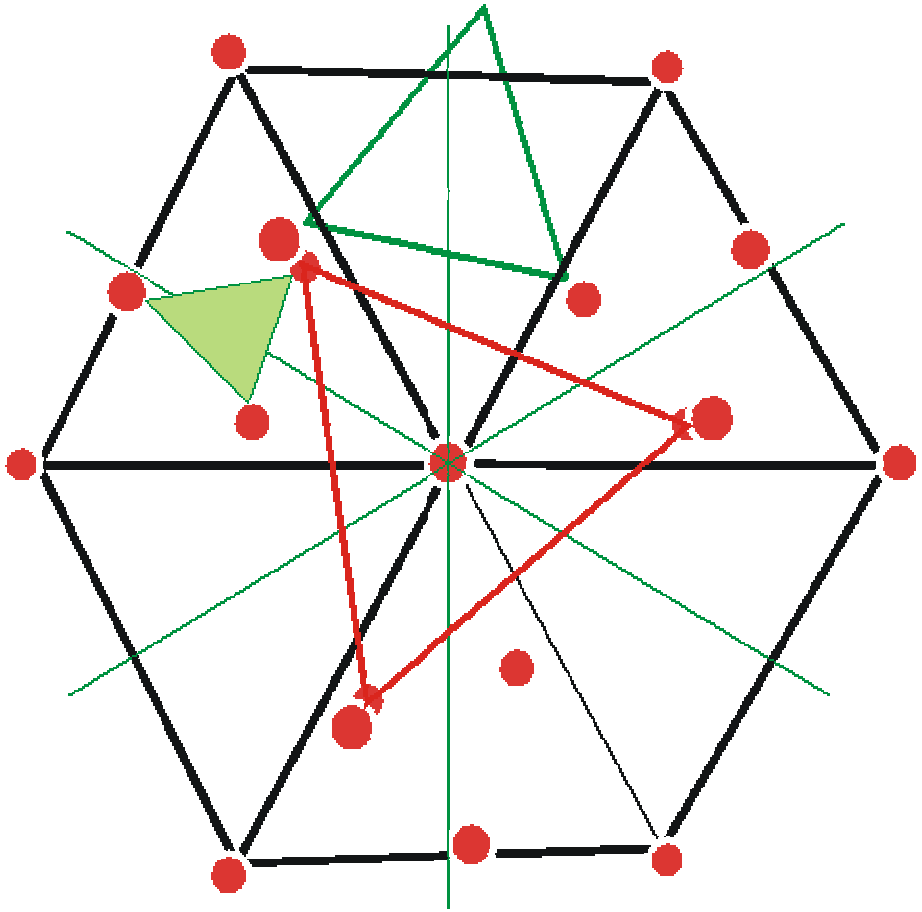

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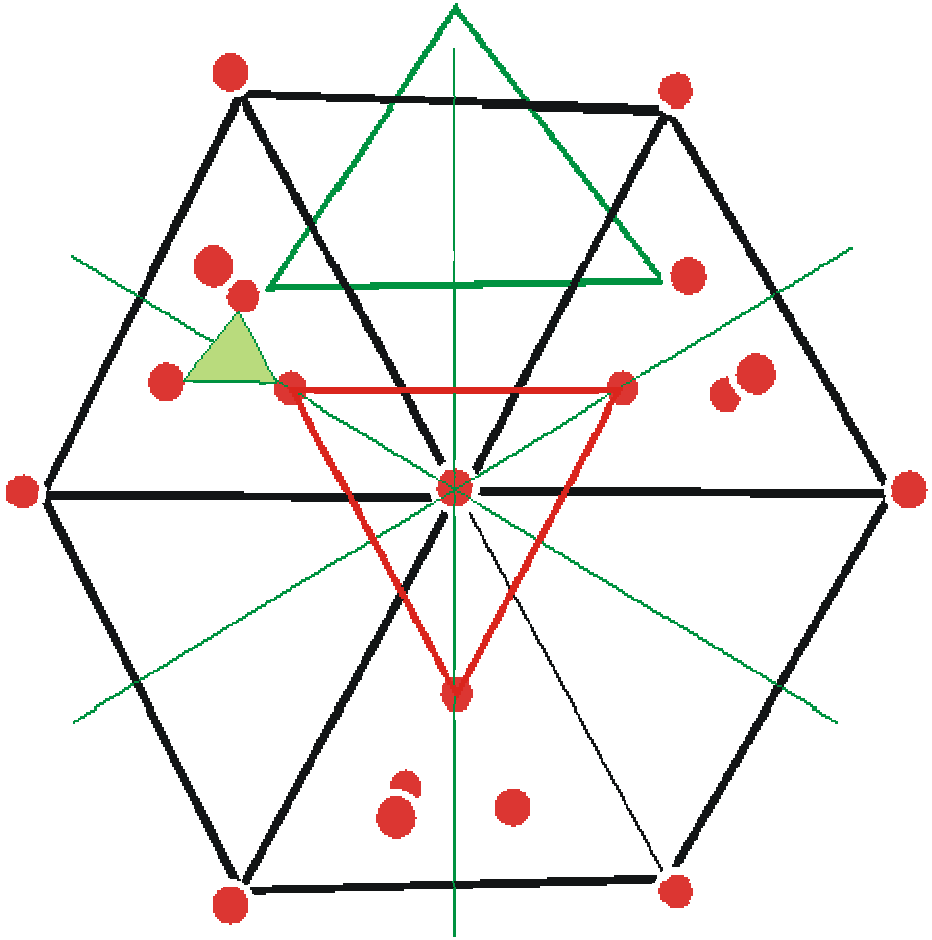

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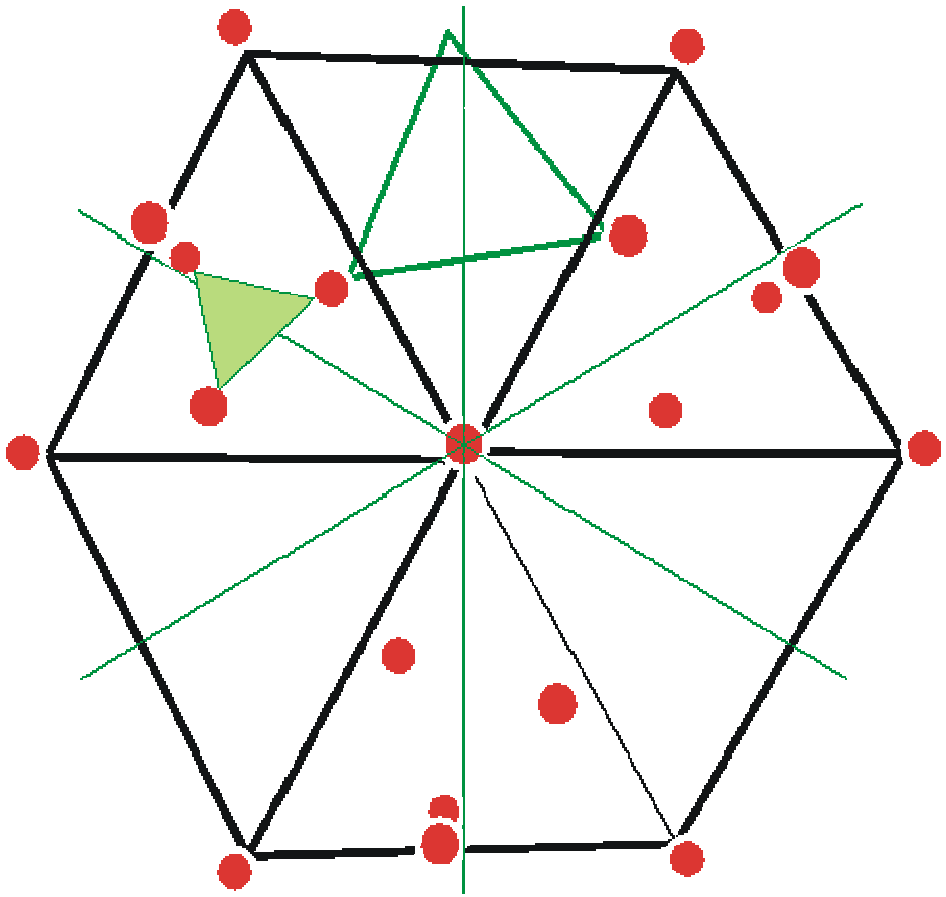

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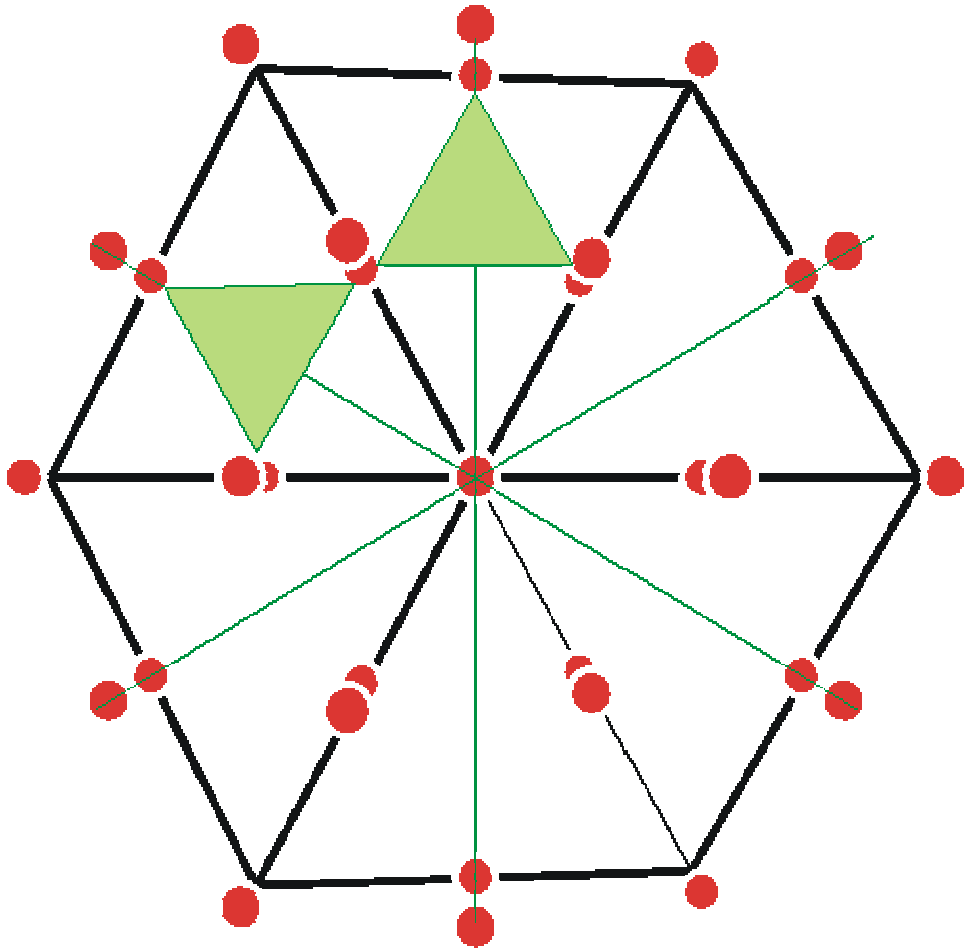

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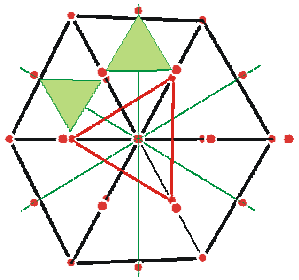

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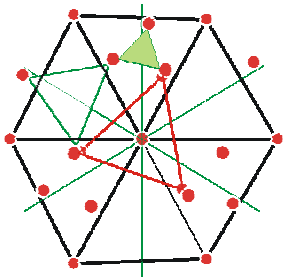

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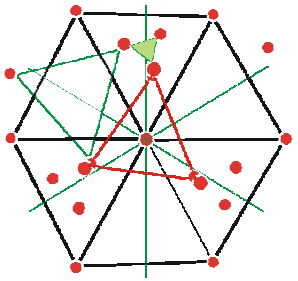

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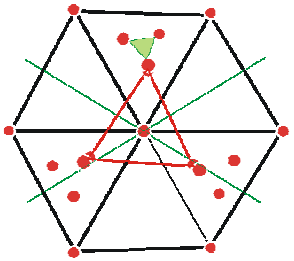

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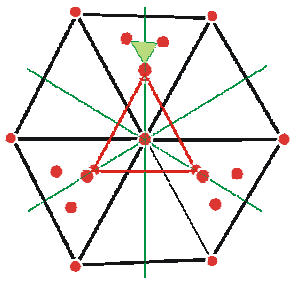

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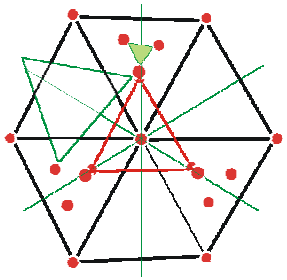

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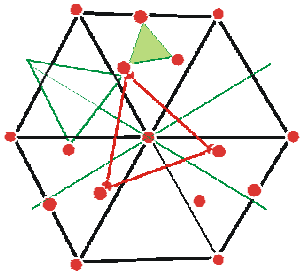

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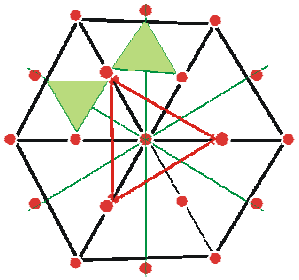

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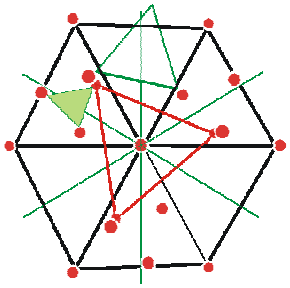

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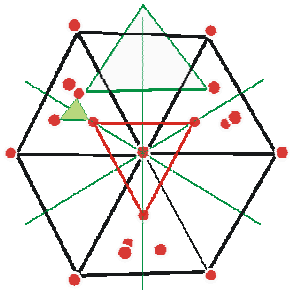

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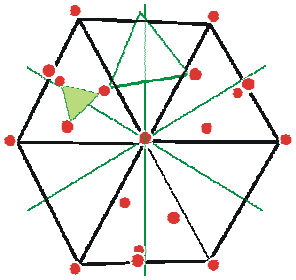

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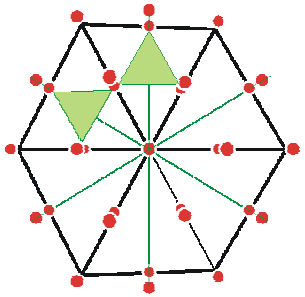

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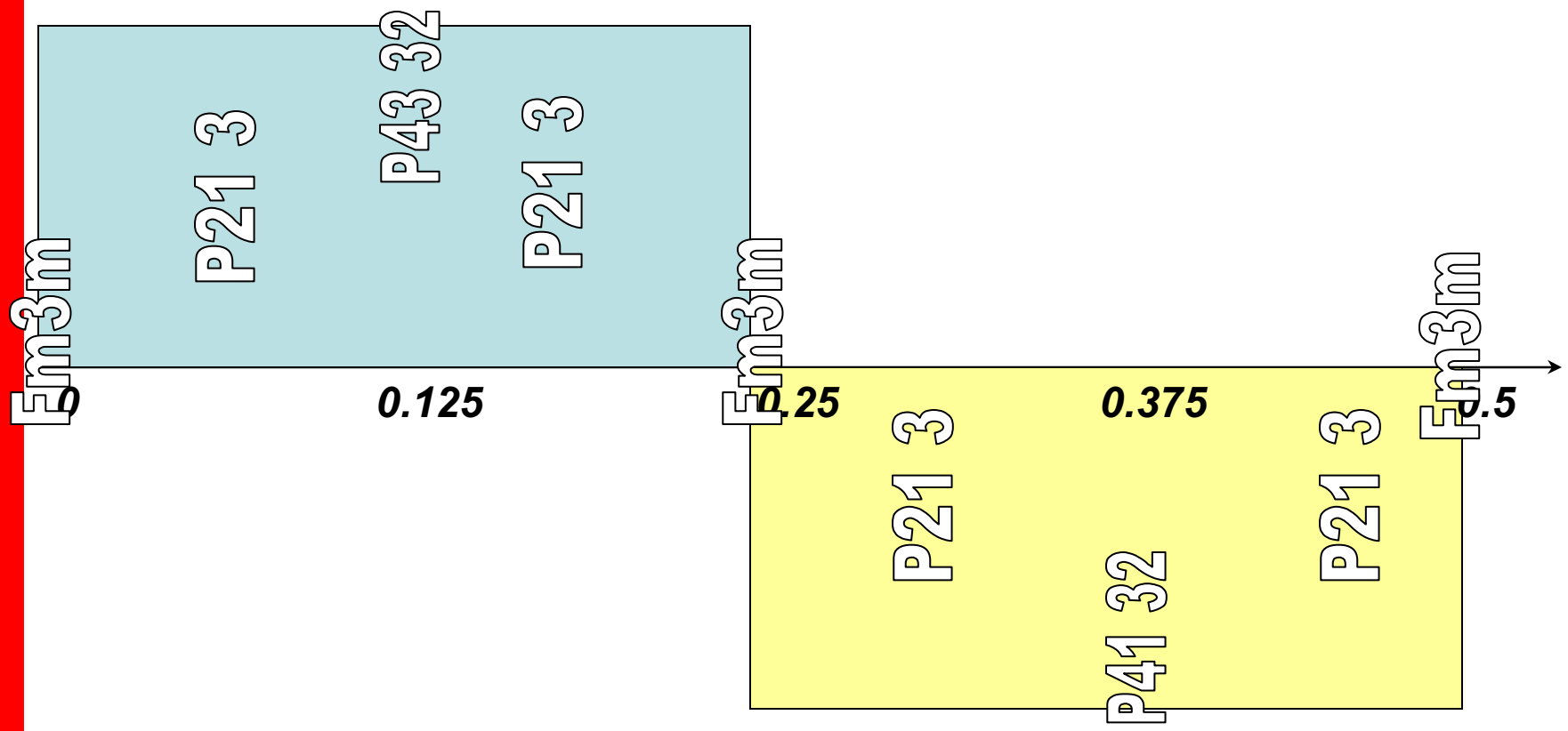
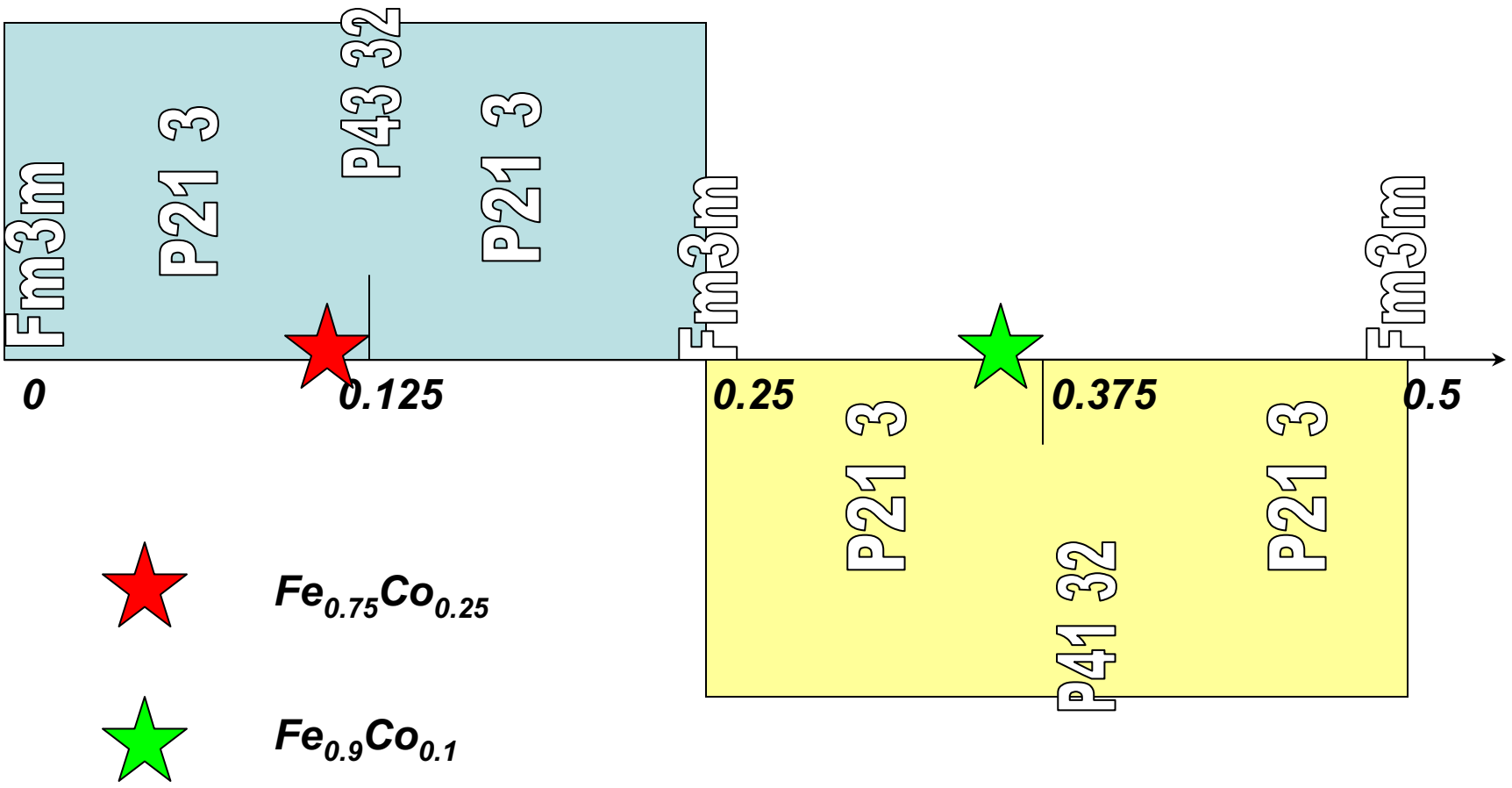
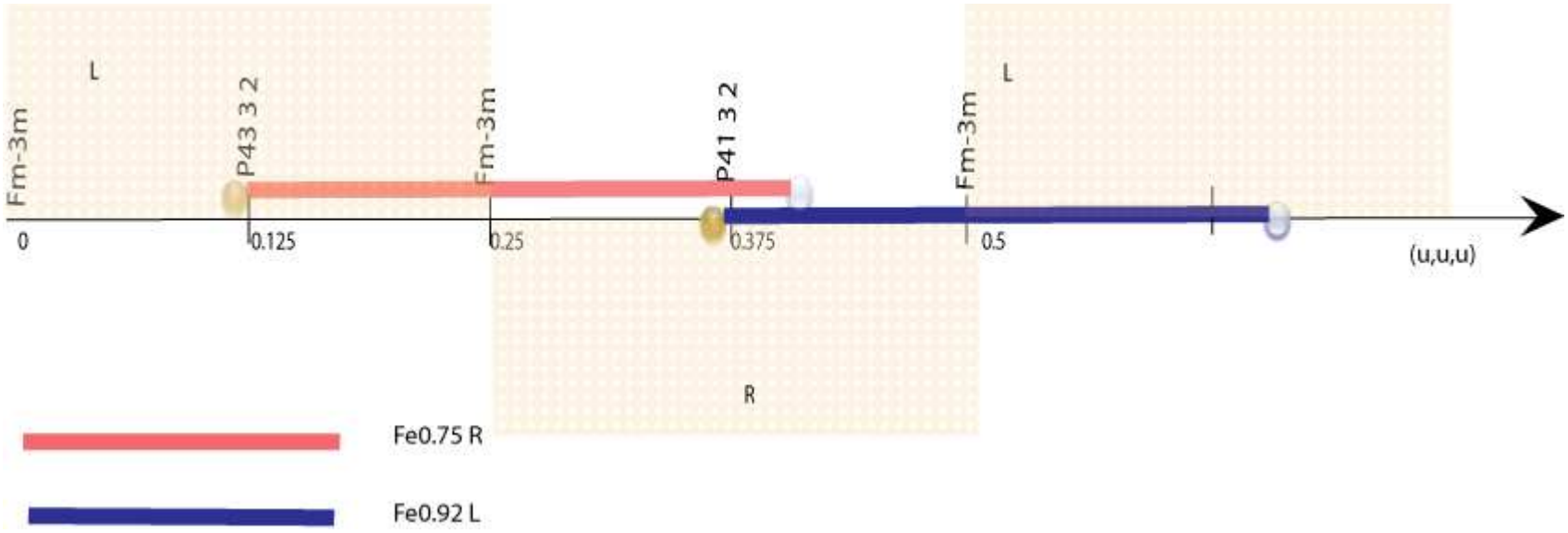
Special points with different symmetry



Special points with different symmetry



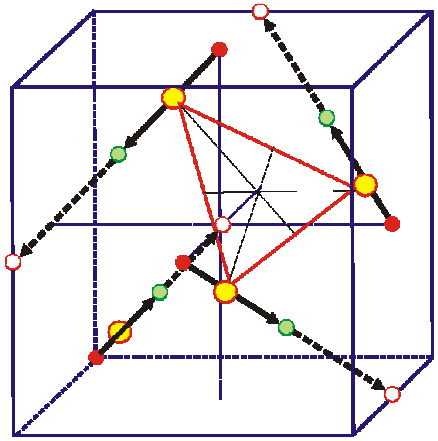
Real story:



- Chiral structures from neighboring domains that are symmetric relative to 0, ¼… are different orientation and inversion twin domains related via parent Fm3m.
- Two compounds (Fe0.92 and Fe=0.75) are not inversion twins and are not symmetric relative to ¼ . Once more, they represent two different albeit isosymmetrical structures.

Symmetry relations

$Fm3m – P2_13 – P4_332$ - $P2_13$ - $Fm3m – P2_13 – P4_332$ - $P2_13$ - $Fm3m$ …..



Space Group: 225 Fm-3m Oh-5
Point in first Brillouin zone: X, k10 (0,1,0)
Irreducible Representation: X5-, k10t10
Order Parameter: P11 (a,a,a,a,a,a) 198 P2_13 T-4
Choose one of the equivalent directions of the order parameter (distinct domains):
P11(1) (a,a,a,a,a,a) 198 P2_13 T-4

Space Group: 212 P4_332 O-6
Point in first Brillouin zone: GM, k12 (0,0,0)
Irreducible Representation: GM2, k12t2
Order Parameter: P1 (a) 198 P2_13 T-4
Order parameter is in the general direction. Continue to next step.

$Fm3m –[X_{5-}, k_{10}\ \tau_{10}] – P2_13$

$P4_332 – [\Gamma_2, k_{12}\ \tau_2] – P2_13$

$Fm3m$ - $P4_332$ – no group-subgroup relations

Phenomenology

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СКРЫТАЯ СИММЕТРИЯ СТРУКТУР И РЕКОНСТРУКТИВНЫЕ ФАЗОВЫЕ ПЕРЕХОДЫ

Ю. М. Гуфан, В. П. Дмитриев, П. Толедано [1]

На примерах конкретных структур показано, что величина компонент параметра порядка феноменологической теории является периодической функцией величин смещений атомов. Учет такой периодичности (скрытой симметрии) при смещениях на расстояния порядка межатомных логически обобщает теорию, учитывающую только малые смещения, и распространяет ее на реконструктивные переходы между фазами, не связанными соотношением «группа—подгруппа». Описан переход из структуры $A2$ в α-фазу (O_h^9—D_{4h}^1).

Free energy

$$F(T, p, u) = F\left(\eta\left(u\right)\right)$$

$$\frac{\partial F}{\partial u} = \frac{\partial F}{\partial \eta}\frac{\partial \eta}{\partial u} = 0$$

Specific:

Free energy is functional of a lattice function

Lattice function is a periodic function of atomic shift [along [111]].

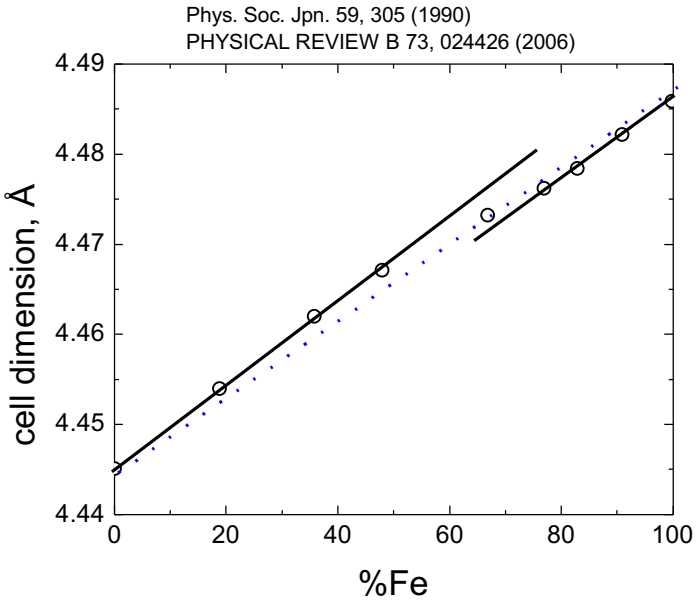
$$\frac{\partial F}{\partial \eta} = 0$$ ***Landau phases ($P2_13$)***

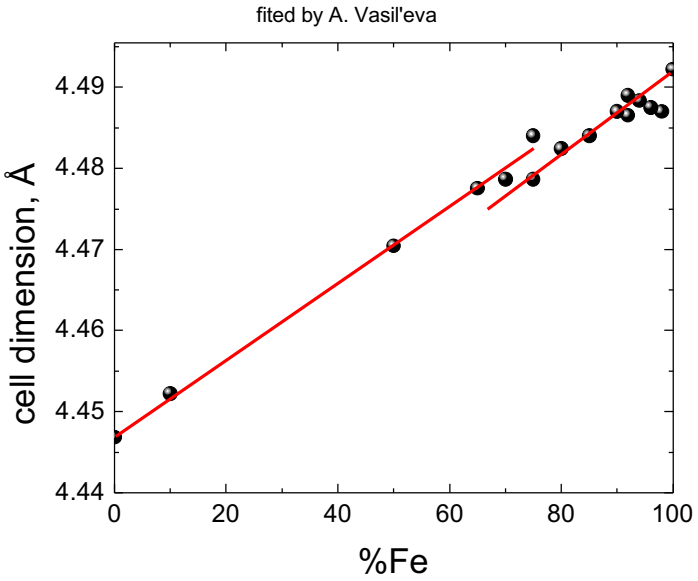
$$\frac{\partial \eta}{\partial u} = 0$$ ***limit phases ($P4_332$).***

Now with Si sublattice:

Si shifts along [111] with a phase relative to Fe. This phase difference preserves global $P2_13$ symmetry. The only phase transitions left are isostructural ones at u= 0, ¼, ½ . ***These transitions can only be of the 1st order.***

Real story: powder diffraction

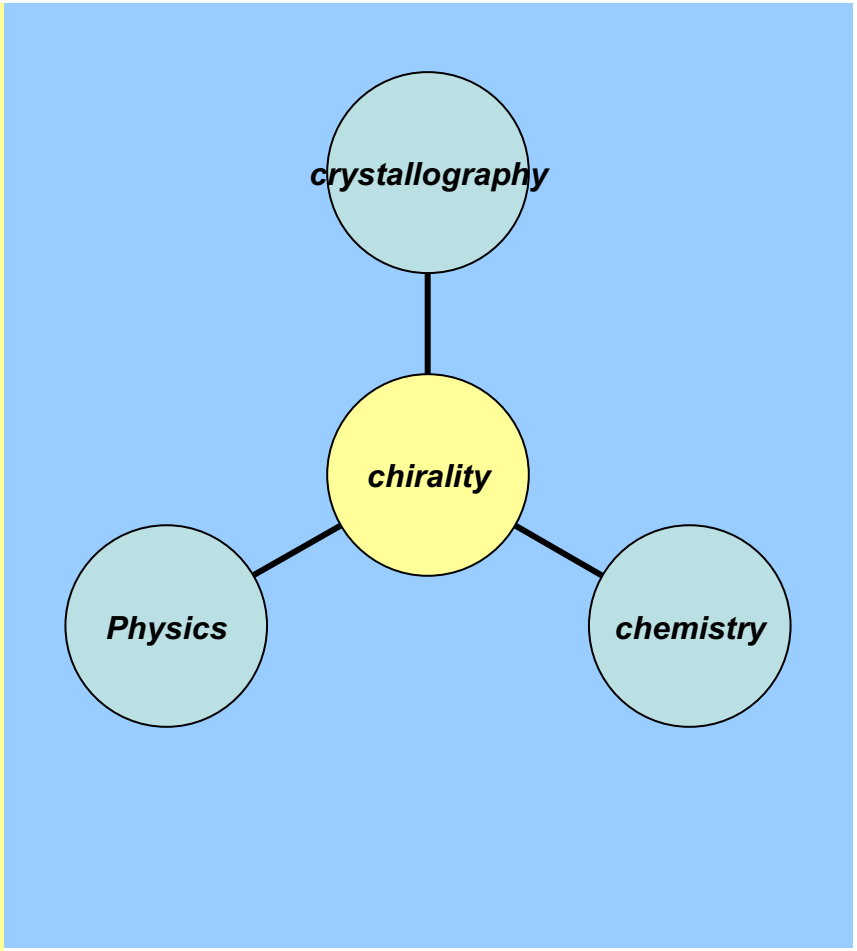




Is there a phase transition as a function of concentration?

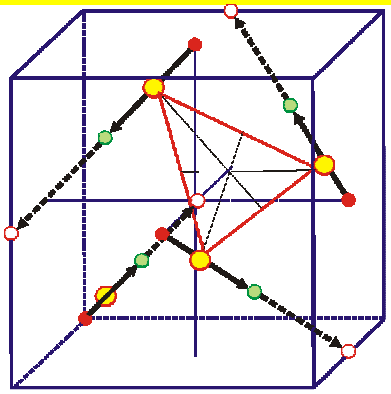
Take-home message

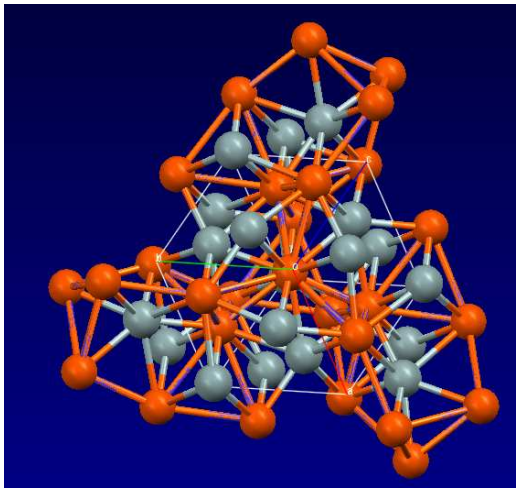
- Chirality appears as absolute structure when one deals with a crystal.
- Absolute structure is not the equivalent to absolute configuration.
- There are chiral structures and chiral space groups – they are not synonyms.
- Only an object bigger than unit cell carries chirality for a structure build from achiral molecules.



Chirality in MeSi (Me=Fe, Mn, ...)

- A periodic set of chiral structures appear as a function of atomic shift along [111] axis.
- Change of absolute structure at u=1/4, 1/2, 3/4. (change of chirality of a spiral build from Me-Me nearest neighbors)
- In the case study of Fe(Co)Si system, different absolute structures correspond to different magnetic chirality. (sign of the Dzialoshinskii-Moriya interaction is a function of atomic arrangement).
- From a crystallographer's point of view, the change of absolute structure is consequence of a phase transition between two similar isosymmetric structures.





Next things to do…

- Single crystal diffraction as a function of composition. Both metal and Si could be substituted.
- Magnetic measurements with synchrotron light – the same sample for crystal and magnetic structure.
- What could we learn after doing all that?

Thanks to:

S. V. Grigoriev

S. V. Maleev

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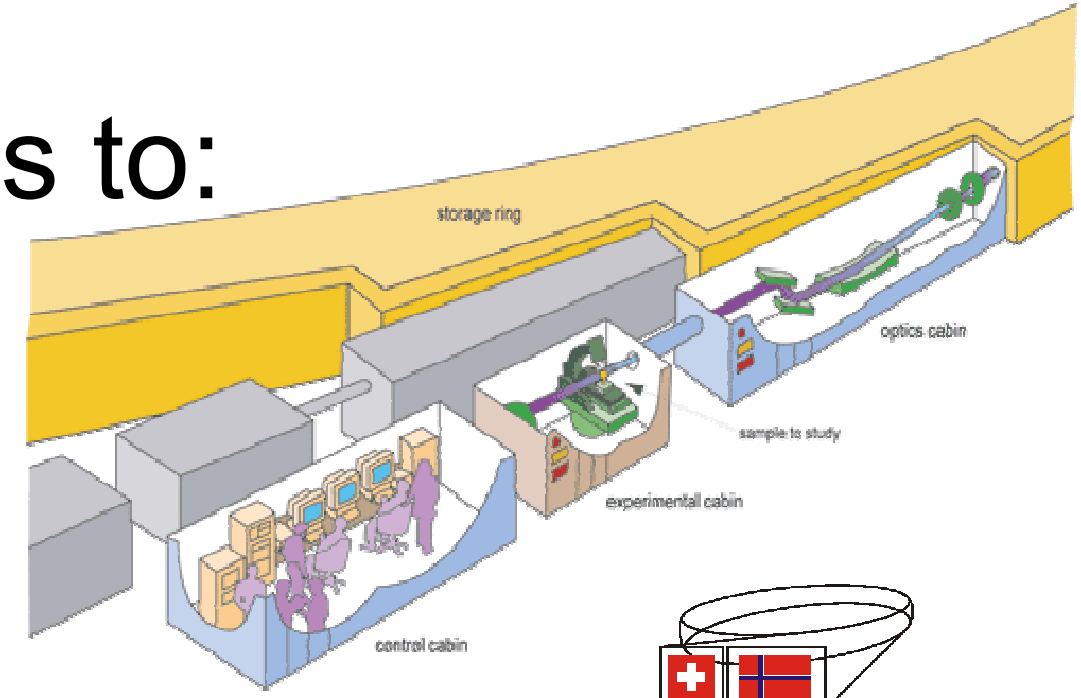
V. Dyadkin

A. Vasilieva



Swiss-Norwegian Beam Lines
at ESRF

Thank you for attending and having listened

- Jps of japan, 49, 2 1980
- Prl, 100, 145502 2008