Multi-k magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: representation approach and Shubnikov symmetry

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V. Pomjakushin, arXiv:1404.1683 (2014).

Two topics of the talk

- Multi-arm antiferromagnetic order in $Ca_3CuNi_2(PO_4)_4$ from ND: Shubnikov symmetry & representation analysis using full star *vs.* "usual" one-k propagation vector approach

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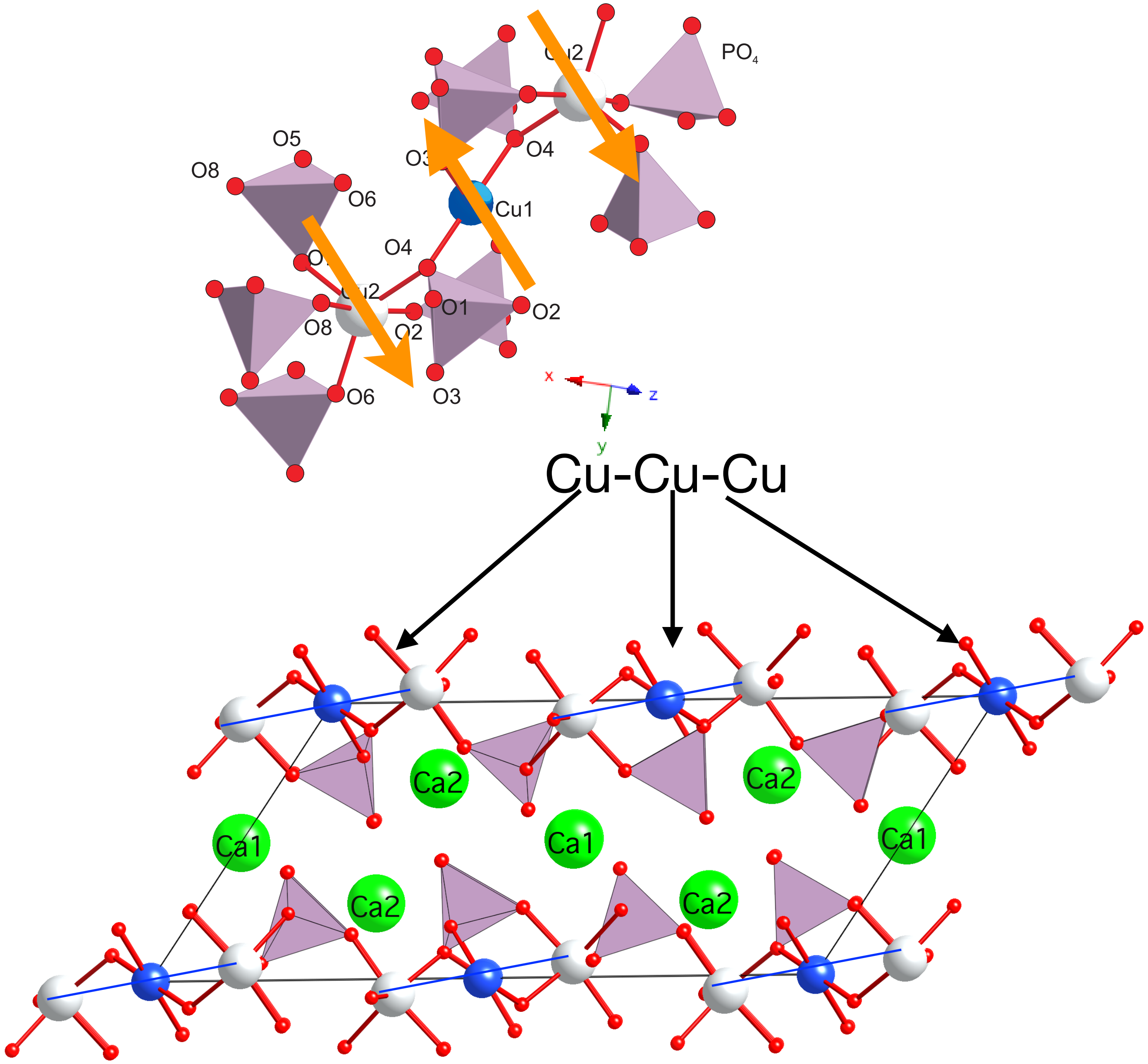
- Multi-arm antiferromagnetic order in $Ca_3CuNi_2(PO_4)_4$ from ND: Shubnikov symmetry & representation analysis using full star *vs.* "usual" one-k propagation vector approach
- Calculation of spin expectation values of $<S_{Ni}>$, $<S_{Cu}>$ in the quantum spin-trimer $CuNi_2$ using a Hamiltonian with realistic parameters taken from INS

Initial motivation to study $Ca_3Cu_xNi_{2-x}(PO_4)_4$

$Ca_3Cu_3(PO_4)_4$ is a quantum spin trimer system in which the three Cu^{2+} ($S = 1/2$) spins are antiferromagnetically coupled giving rise to a doublet ground state. By substituting a Cu^{2+} spin in the trimer by Ni^{2+} ($S = 1$) a *singlet ground state* could be in principle realised offering the observation of the *Bose-Einstein (BE) condensation* in a quantum spin trimer system.



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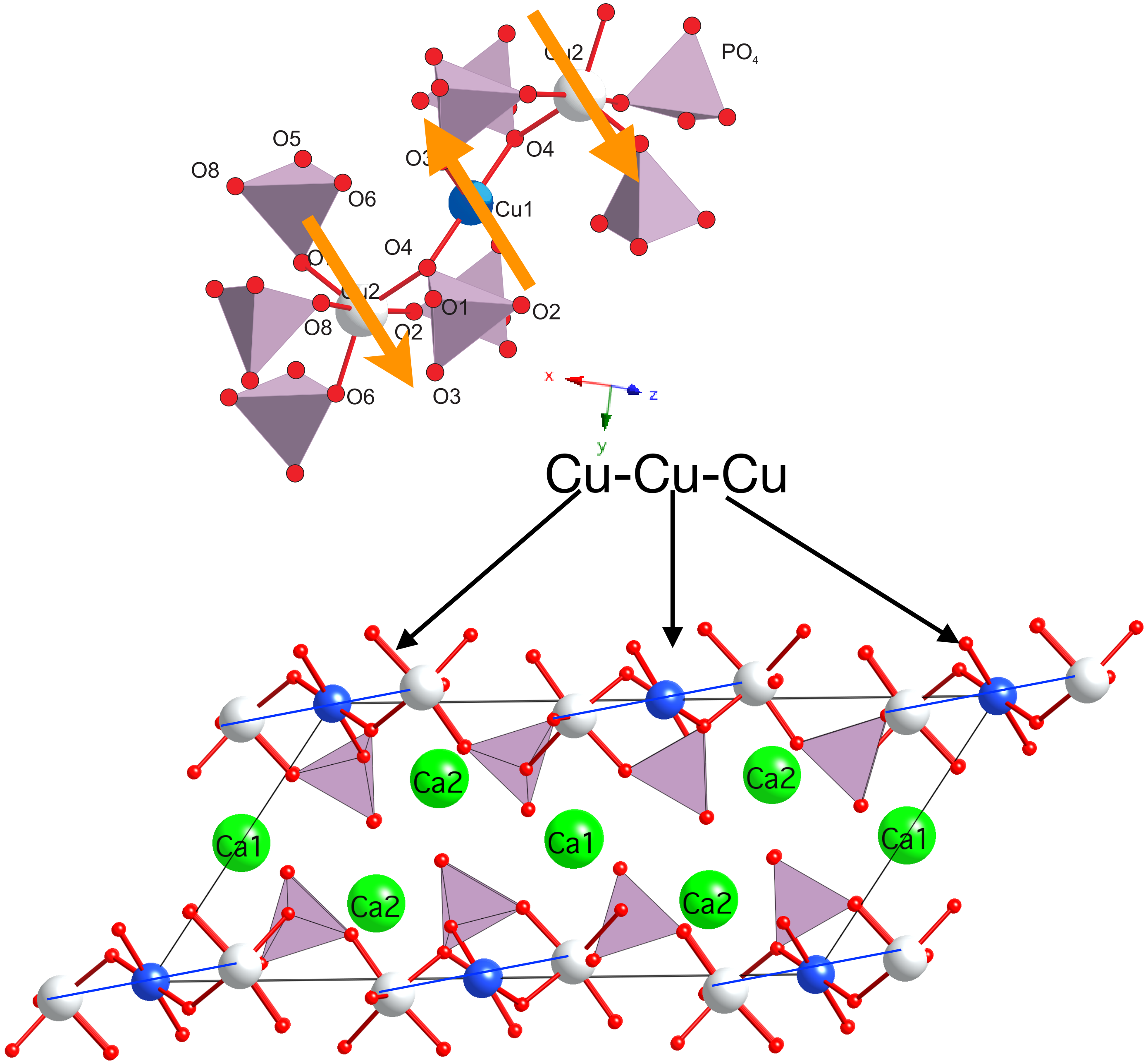

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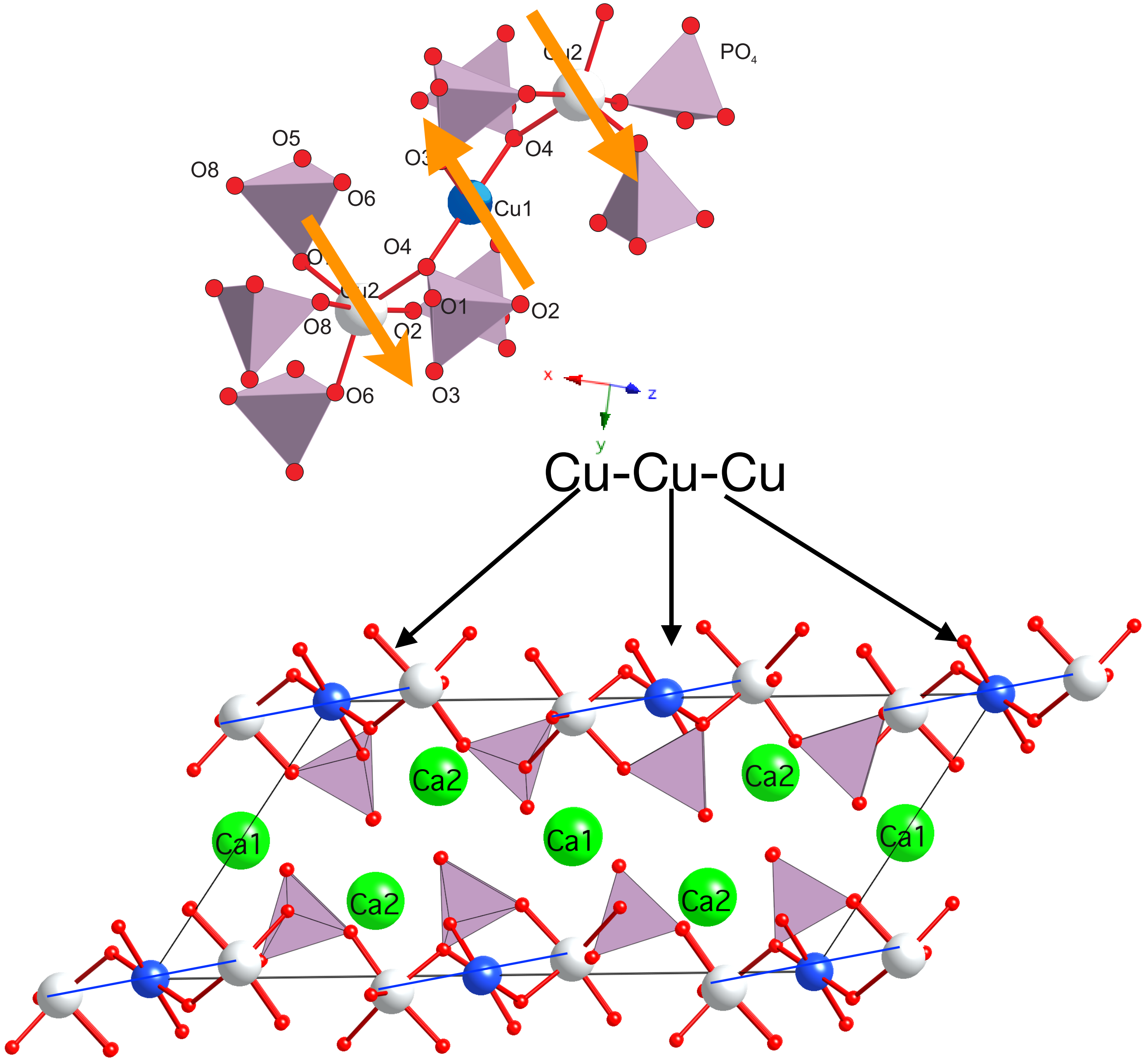

Experiment:
unfortunately, no singlet, no BE…

But!

It happened to be that $Ca_3Cu_1Ni_2(PO_4)_4$ has a multi-arm magnetic structure. It is considered to be unusual, and indeed is rarely reported.

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Cf. with experimental <S> is an independent verification of the multi-arm type of ordering. These types of structures are rarely reported experimentally.

Propagation vector k formalism. Spin amplitudes S_0 are specified in zeroth block of the cell==parent cell w/o centering translations

Magnetic moment or atomic displacement below a phase transition

$$\mathbf{S}(\mathbf{t}_n) = \mathbf{S}_0 \cos(2\pi \mathbf{k} \mathbf{t}_n)$$

Bragg peaks at

$$\mathbf{q} = \mathbf{H} \mp \mathbf{k}$$

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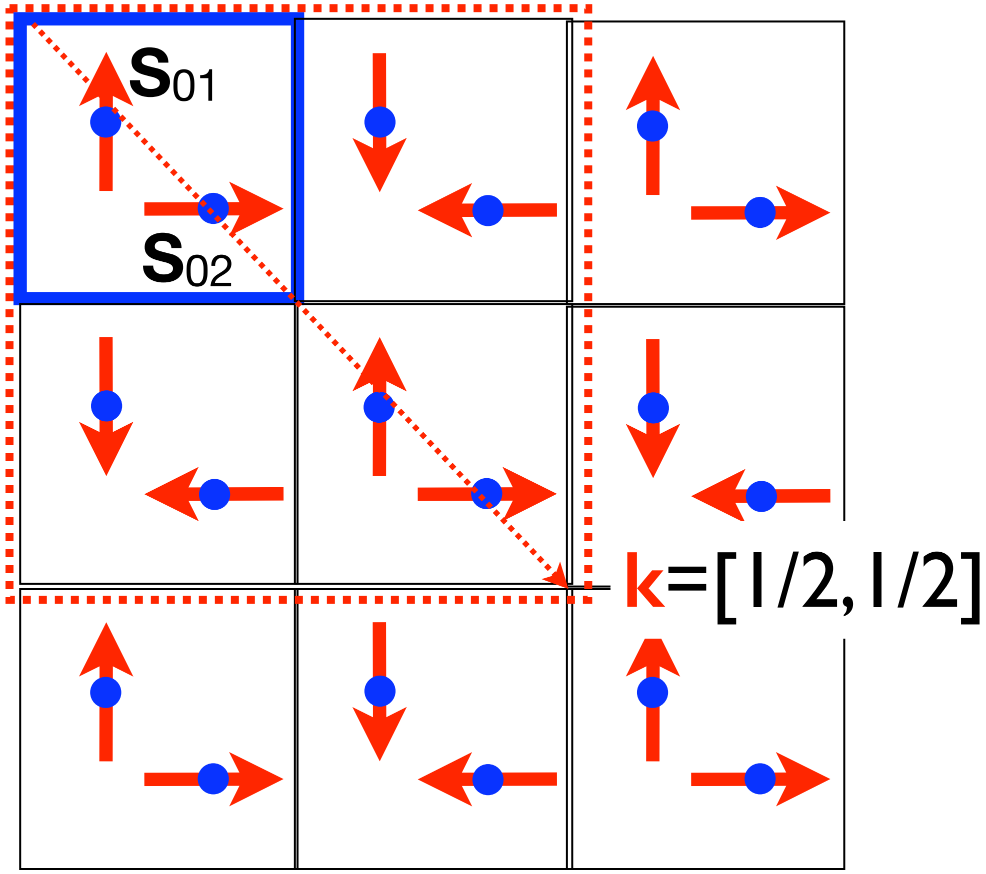

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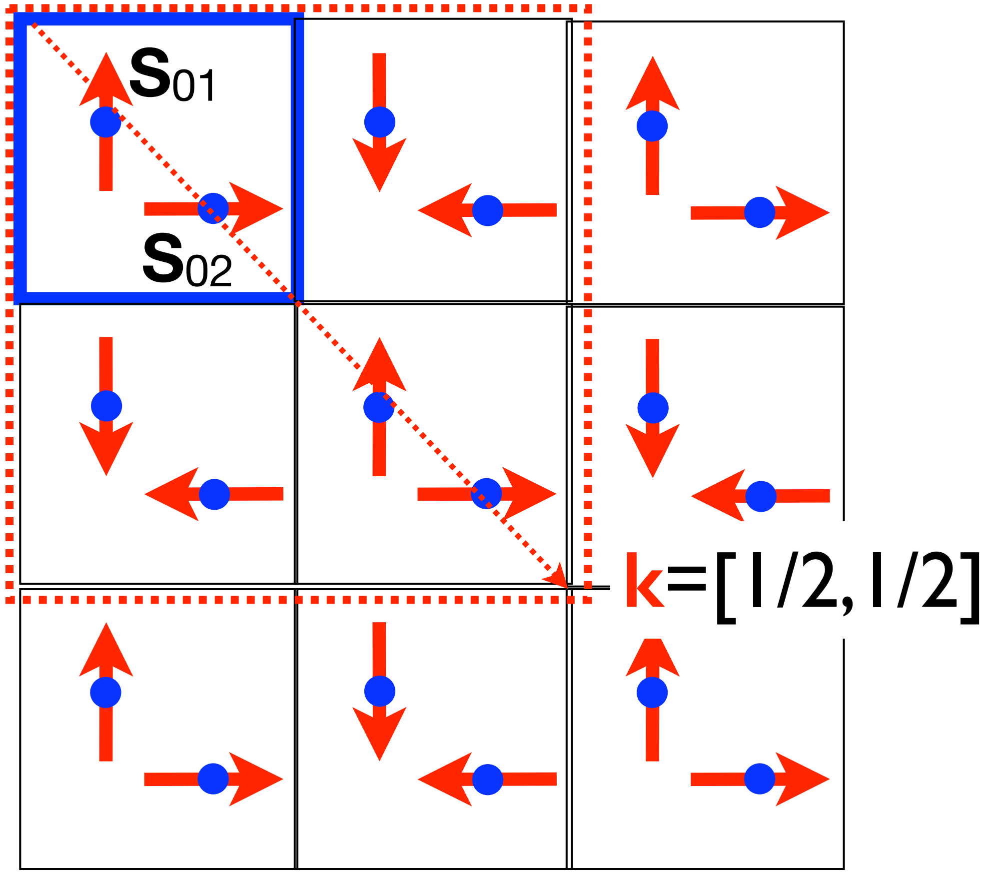

E.g., atom1 $\mathrm{S}_{01} = \mathrm{S}_y$

atom2 $\mathrm{S}_{02} = \mathrm{S}_x$

$$\ldots$$

$$\begin{aligned} \mathbf{S}_1(\mathbf{t}_n) &= \mathbf{S}_y \cos(2\pi \mathbf{t}_n \mathbf{k}) \\ &= \mathbf{S}_y \cos(\pi(t_{nx} + t_{ny})) \end{aligned}$$

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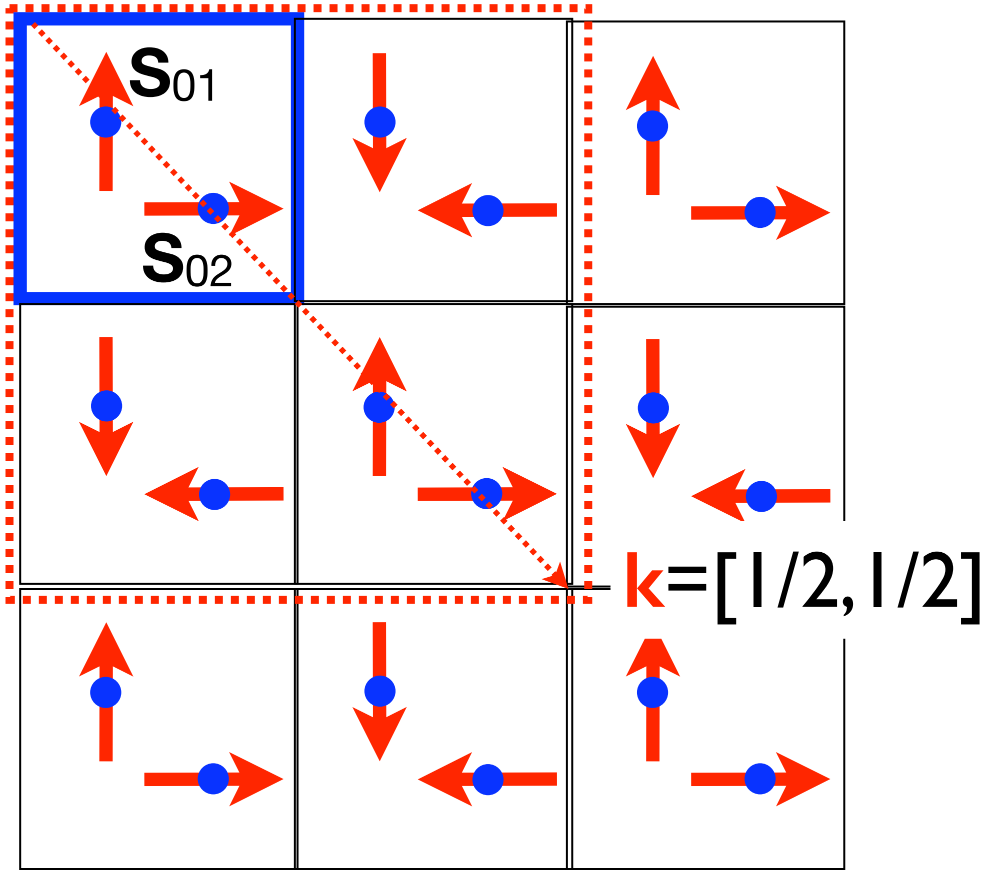

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multi-**k** or multi-*arm** structure (non-equivalent $\mathbf{k}_1$, $\mathbf{k}_2$, … $\mathbf{k}_m$).

$$\mathbf{S}_1(\mathbf{t}_n) = \sum_{l=1}^{m} \mathbf{S}_{01l} \cos(2\pi \mathbf{k}_l \mathbf{t}_n)$$

$\mathbf{k}_1$ is nonequivalent to $\mathbf{k}_2$ if $\mathbf{k}_1 \neq \mathbf{k}_2$+'recip. latt. period'

---

* One must distinguish between the *arms* and the *twin* domains

Symmetry group G_k of propagation vector k. k-star

space group of $Ca_3Cu_1Ni_2(PO_4)_4$

$C2/c$ C^6_{2h} $2/m$ Monoclinic

No. 15 $C12/c1$ Patterson symmetry $C12/m1$

Symmetry operators *zeroth* block of SG

$h_1 = x, y, z$ $h_2 = \bar{x}, y, \bar{z} + \frac{1}{2}$ $h_3 = \bar{x}, \bar{y}, \bar{z}$ $h_4 = x, \bar{y}, z + \frac{1}{2}$

$+T(n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3)$

$(\frac{1}{2}, \frac{1}{2}, 0)+$

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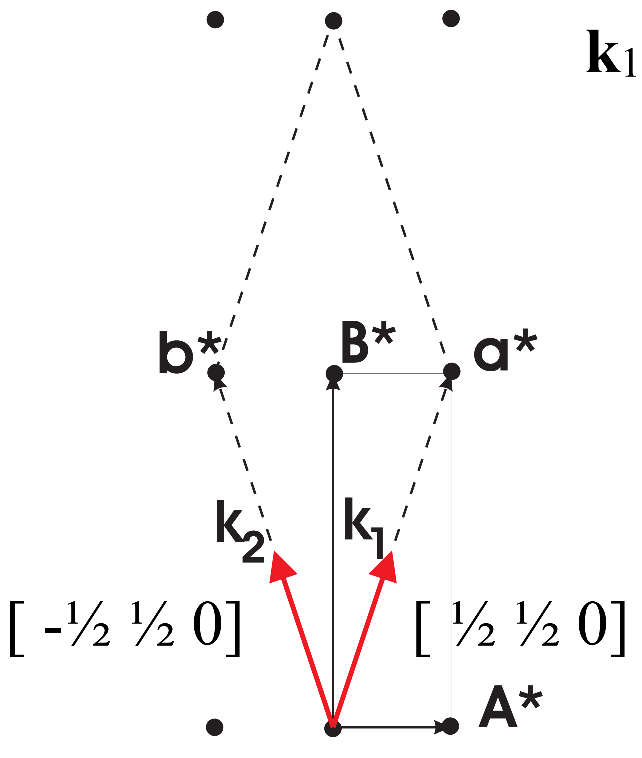
k$_1$=[½ ½ 0] *V*-point of BZ



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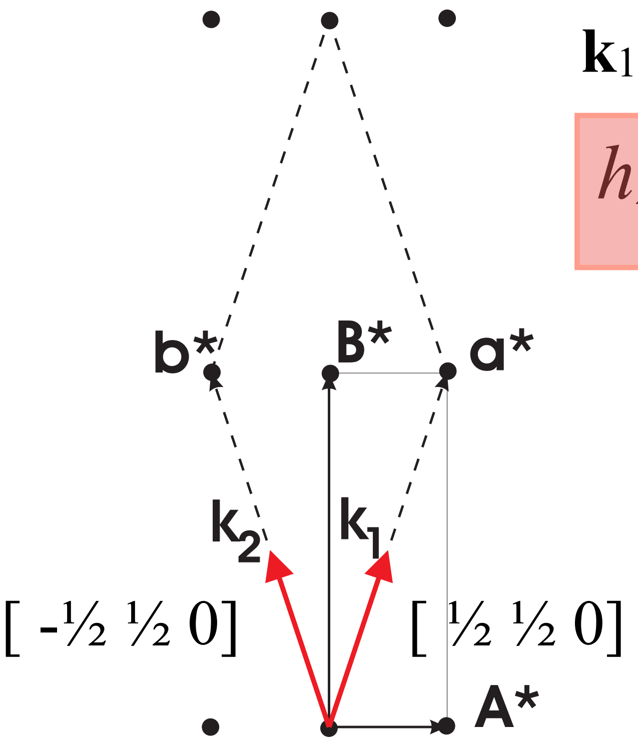

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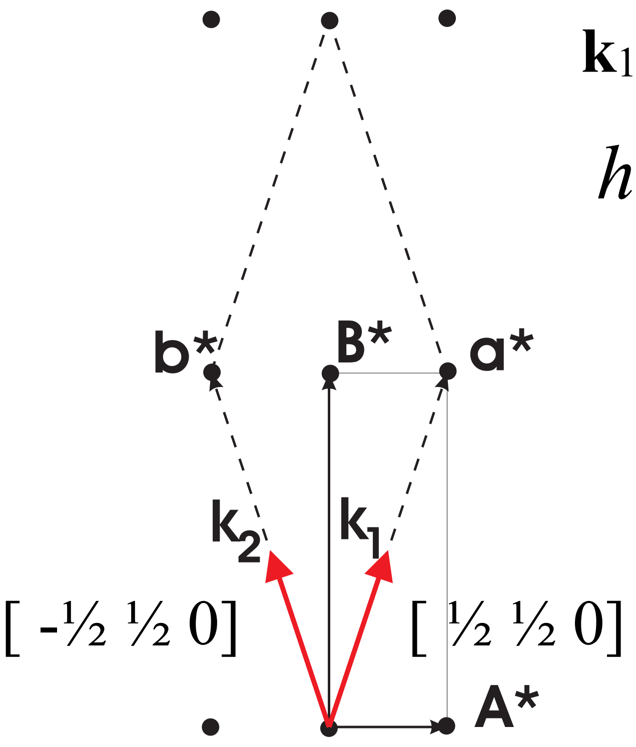

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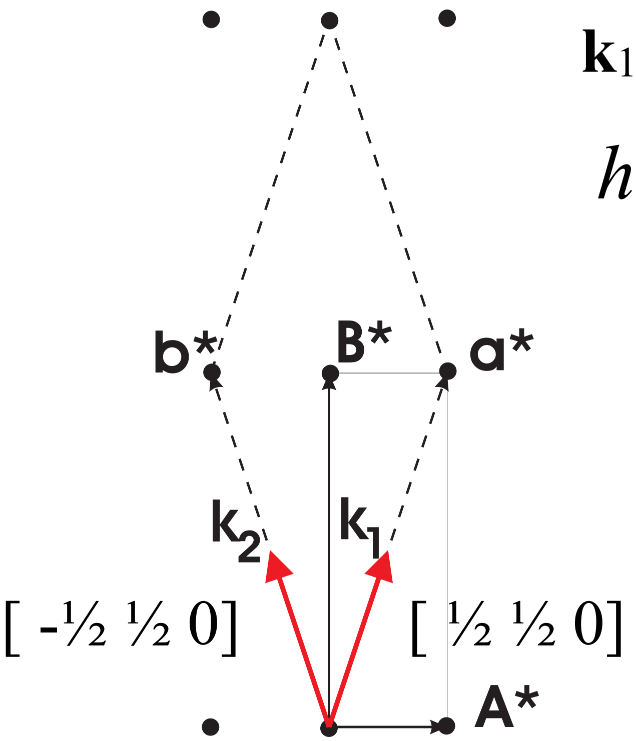

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$G_k \in G$ that leaves ***k*** *invariant* == little group or propagation vector group

h_1 1 h_3 $\bar{1}$ $G_k = C\bar{1}$

zeroth unit cell of $Ca_3Cu_1Ni_2(PO_4)_4$: orbits in k-vector formalism

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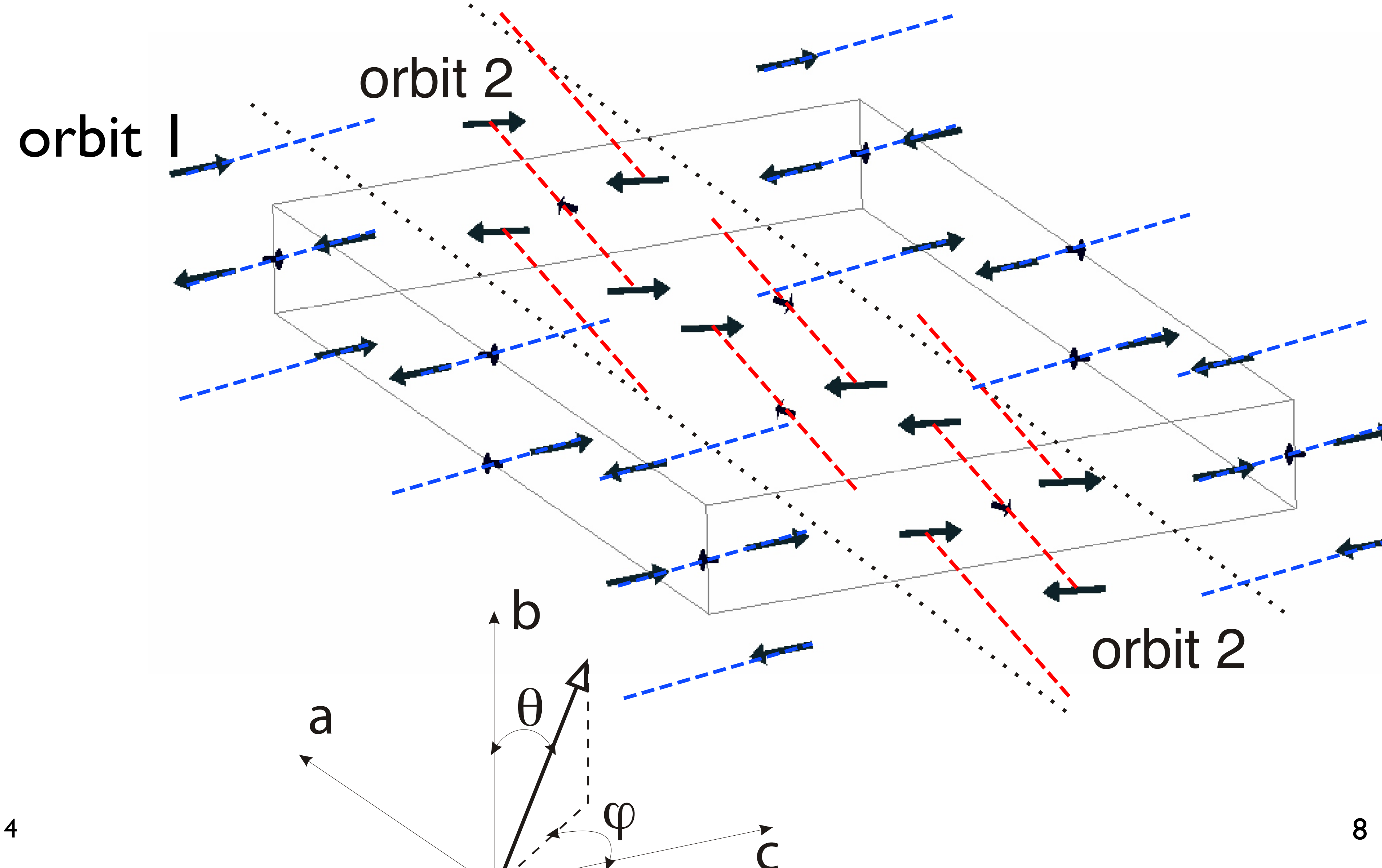

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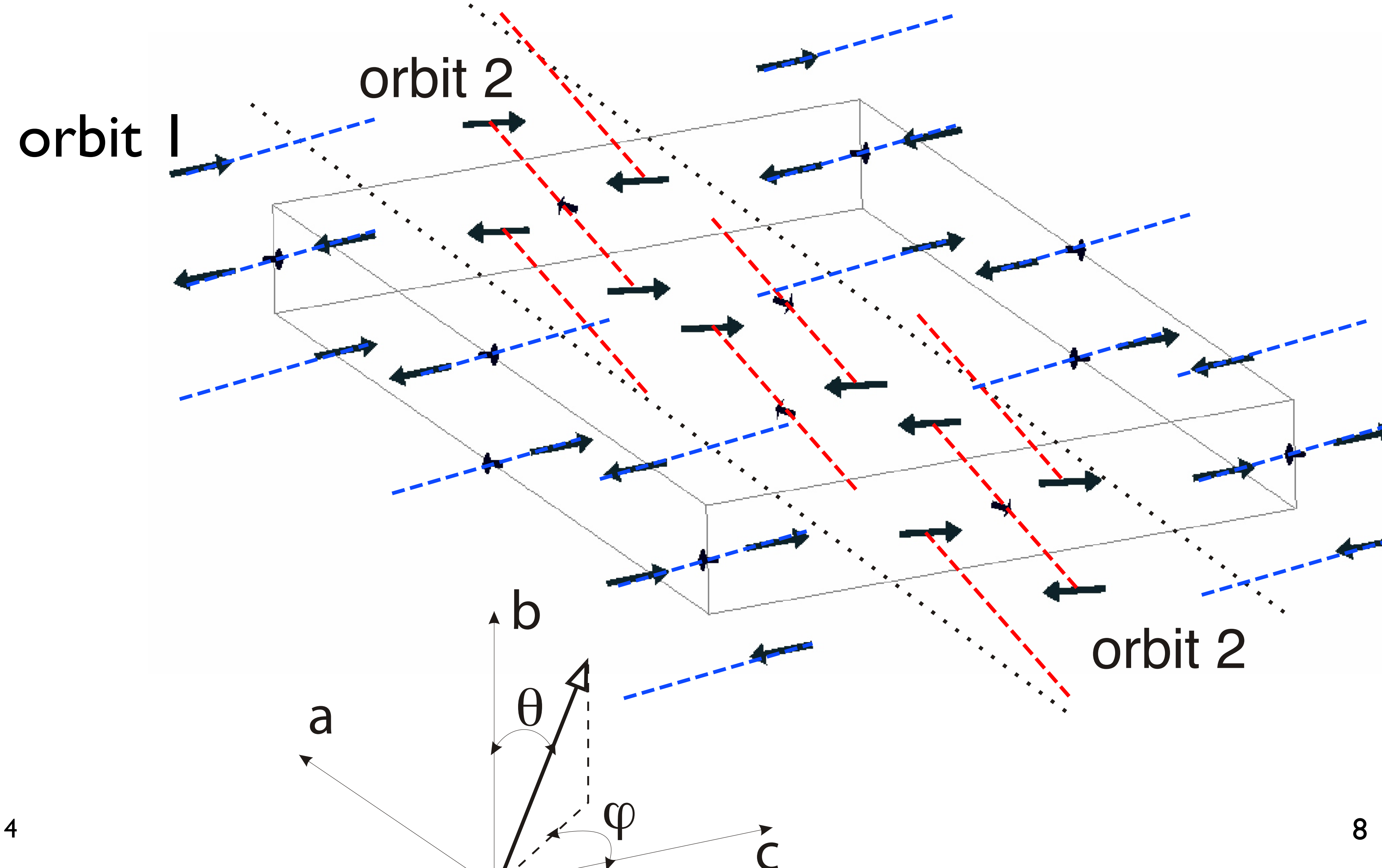

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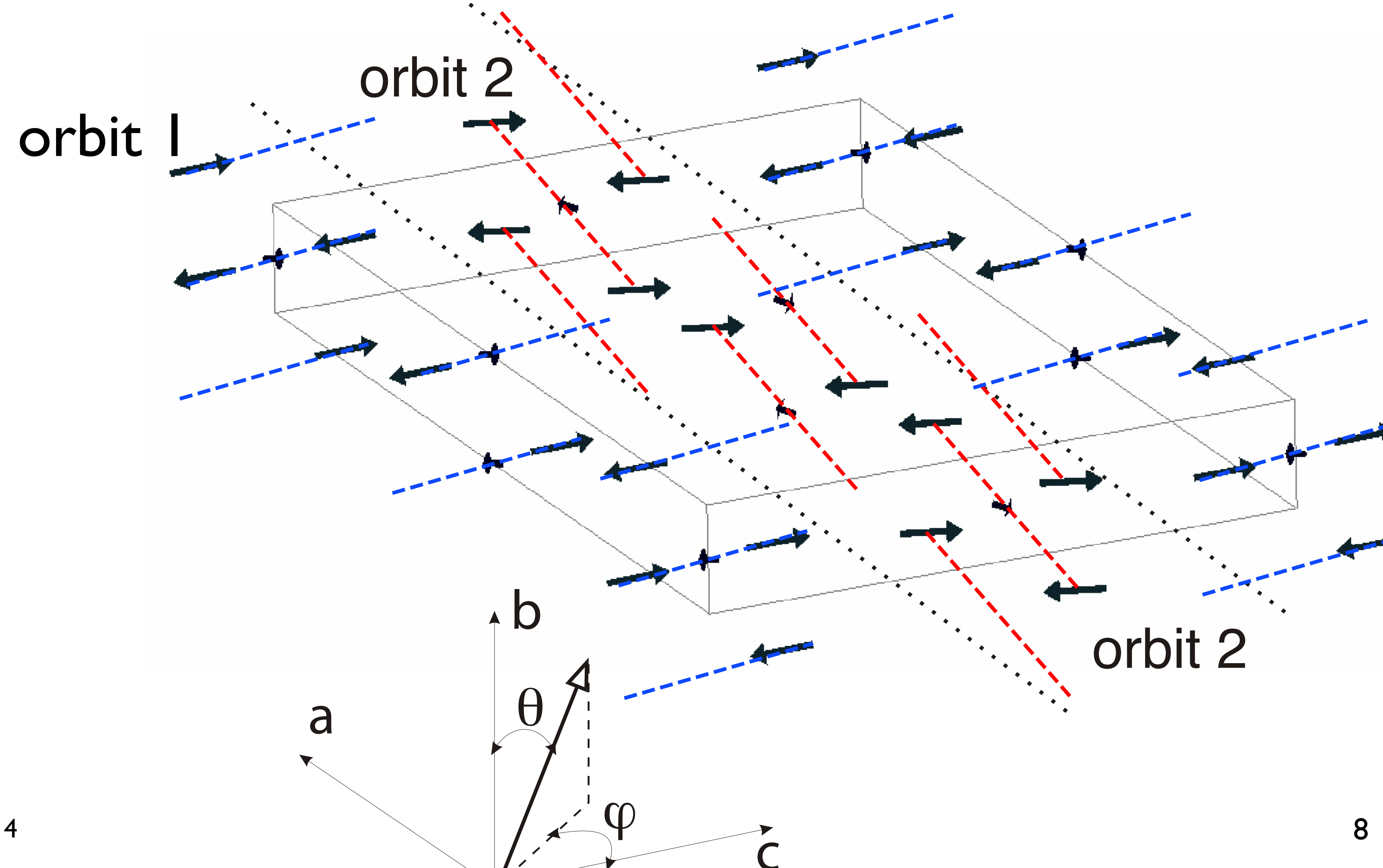

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3. Sort out all symmetry adapted spin configurations in zeroth cell for each *irrep*. Excellent software is available for this way of analysis

Juan Rodríguez Carvajal (ILL) et al, **Fullprof suite**

Wiesława Sikora et al, **program MODY**

Andrew S.Wills (UCL), **program SARAh**

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5. <u>Solutions that are considered do not have maximal possible symmetry</u>

Shubnikov & full star representation analysis in magnetic structure phase transitions

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* J. M. Perez-Mato et al, J. Phys.-Cond. Matt 24 (2012)

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- In some cases rep-analysis & Shubnikov group (or 3D+1*) => "hidden" symmetry
- Regular practice for crystal structure transitions: construct all isotropy subgroups of parent space group using representation analysis for the propagation vector star.
- Magnetic transitions: Usually, representation approach with a single arm of propagation vector star. Possible high symmetry Shubnikov subgroups are lost.

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Full star multi-arm antiferromagnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$

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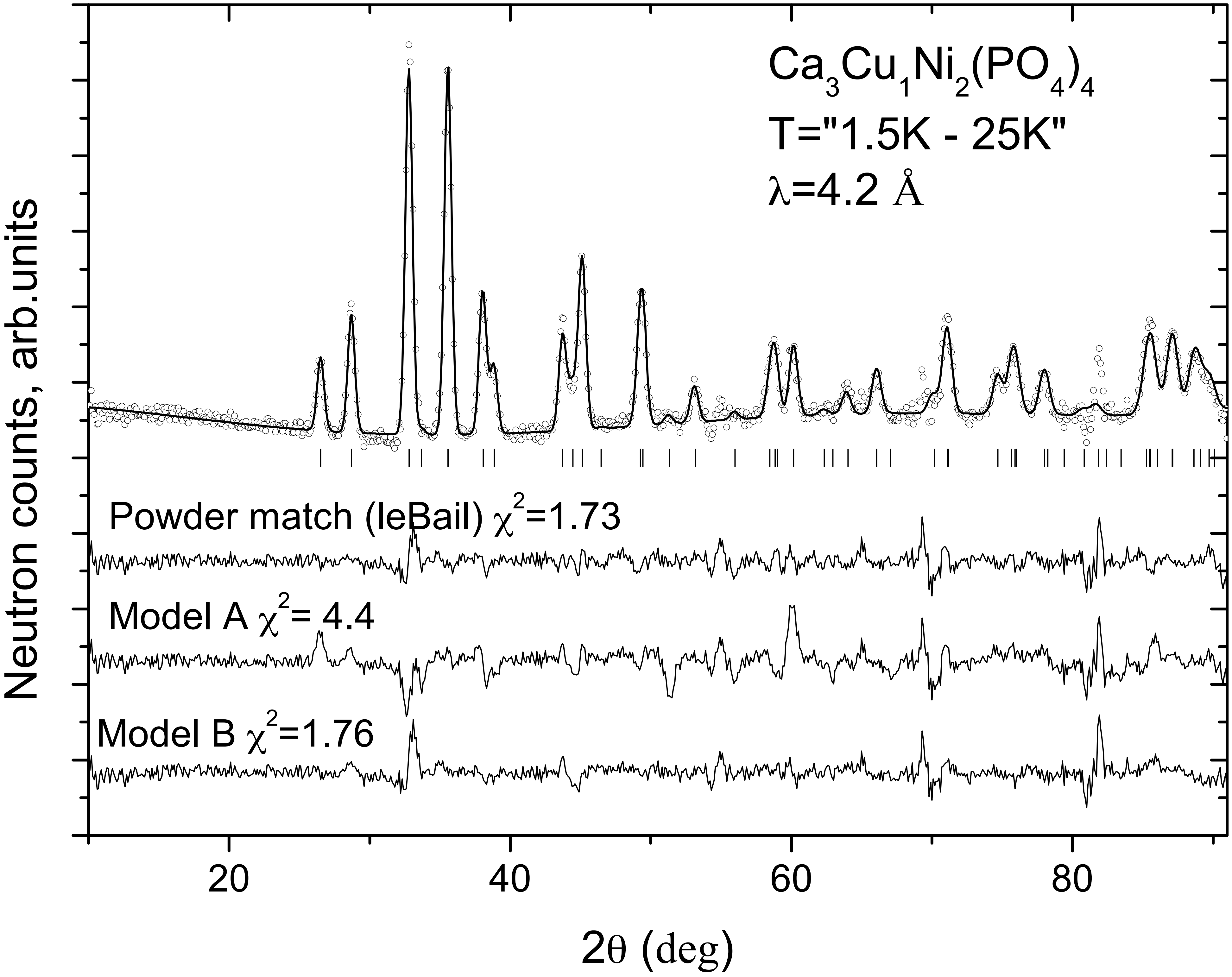
1) propagation vector arms

Magnetic neutron diffraction pattern



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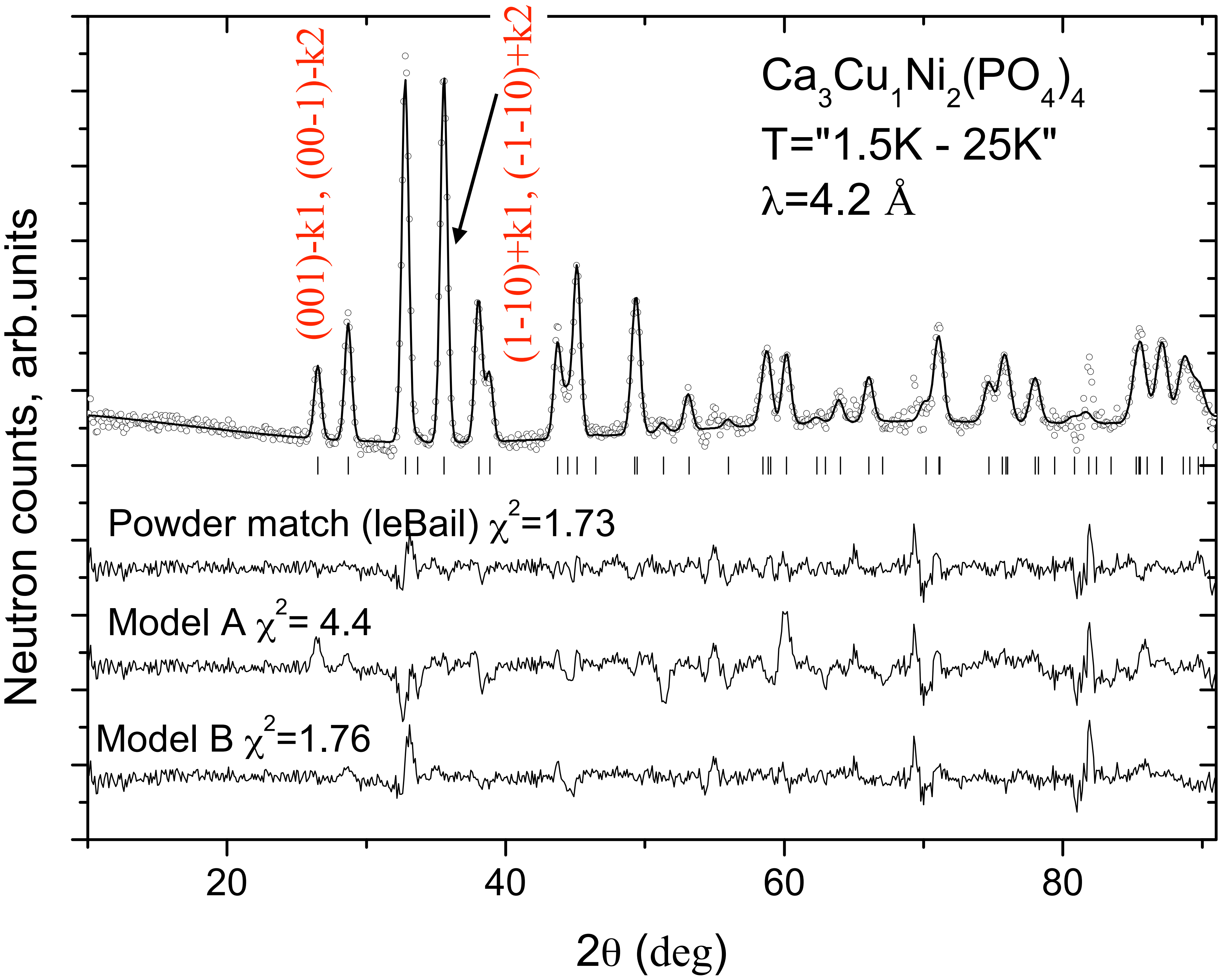

Space group *C2/c*

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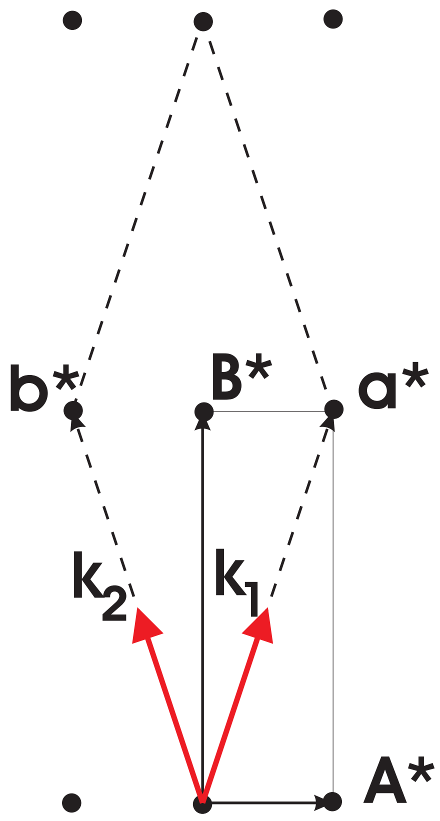
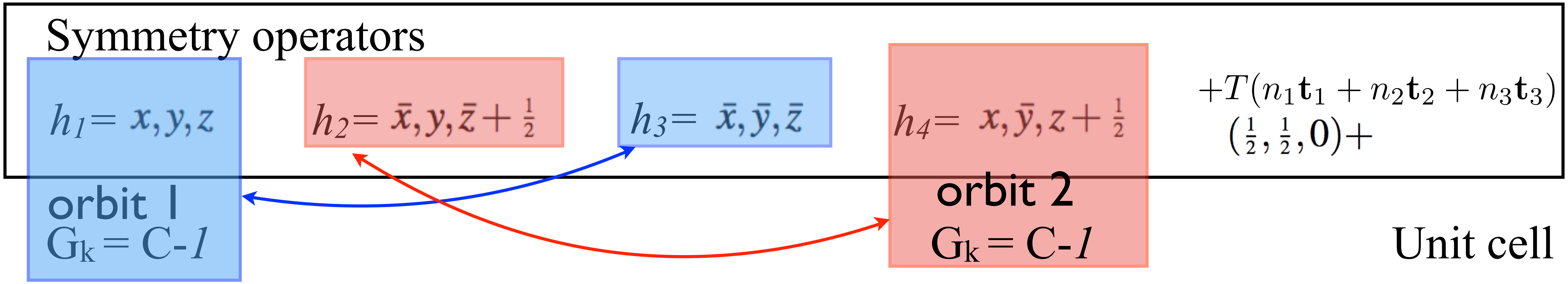


Propagation vector star
{[½ ½ 0], [-½ ½ 0]}

zeroth unit cell of $Ca_3Cu_1Ni_2(PO_4)_4$:

2) orbits, irreps of G_k



Symmetry operators

$h_1 = x, y, z$

$h_2 = \bar{x}, y, \bar{z} + \frac{1}{2}$

$h_3 = \bar{x}, \bar{y}, \bar{z}$

$h_4 = x, \bar{y}, z + \frac{1}{2}$

$+T(n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3)$
$(\frac{1}{2}, \frac{1}{2}, 0)+$

orbit 1
$G_k = C\text{-}1$

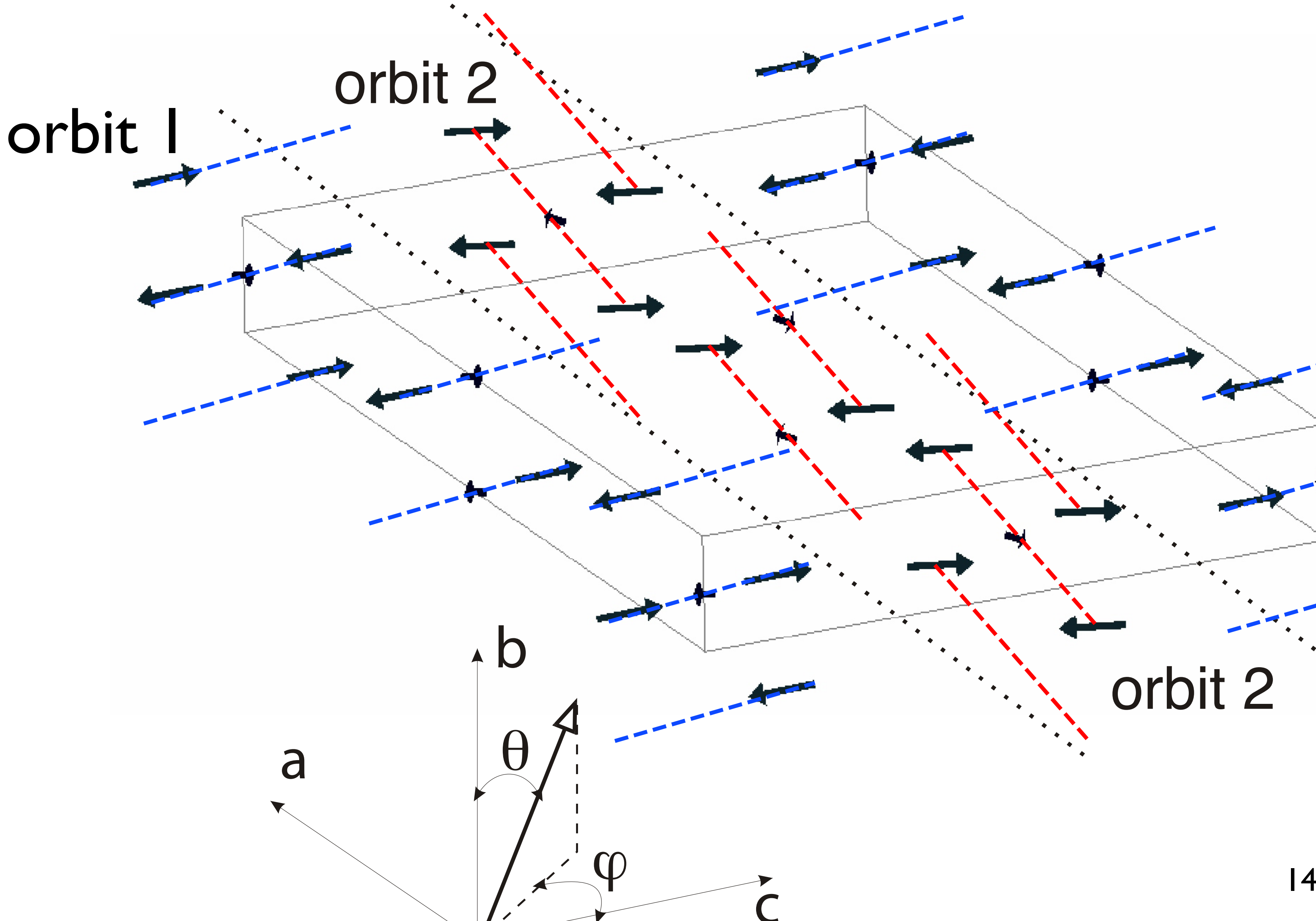
orbit 2
$G_k = C\text{-}1$

Unit cell

$a = 17.724$ Å, $b = 4.815$ Å, $c = 17.836$ Å, $\beta = 123.756°$

Group $G_k = C\bar{1}$ that relates spins in the orbit has **two 1D irreducible representations (irreps) τ_1 and τ_2**

	h_1 1	h_3 $\bar{1}$
τ_1	1	1
τ_2	1	-1



Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} (C_{\lambda,\mathbf{k}_1}\boldsymbol{\psi}_\lambda(\mathbf{k}_1) + C_{\lambda,\mathbf{k}_2}\boldsymbol{\psi}_\lambda(\mathbf{k}_2))$$

$\lambda = x, y, z$

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions or normal modes

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$\lambda = x, y, z$

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

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basis functions or normal modes

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1} \boldsymbol{\psi}_\lambda(\mathbf{k}_1) + C_{\lambda,\mathbf{k}_2} \boldsymbol{\psi}_\lambda(\mathbf{k}_2)\right)$$

$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}_0' = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1} \boldsymbol{\psi}_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2} \boldsymbol{\psi}_\lambda(\mathbf{k}_2)\right)$$

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions or normal modes

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1} \psi_\lambda(\mathbf{k}_1) + C_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2) \right)$$

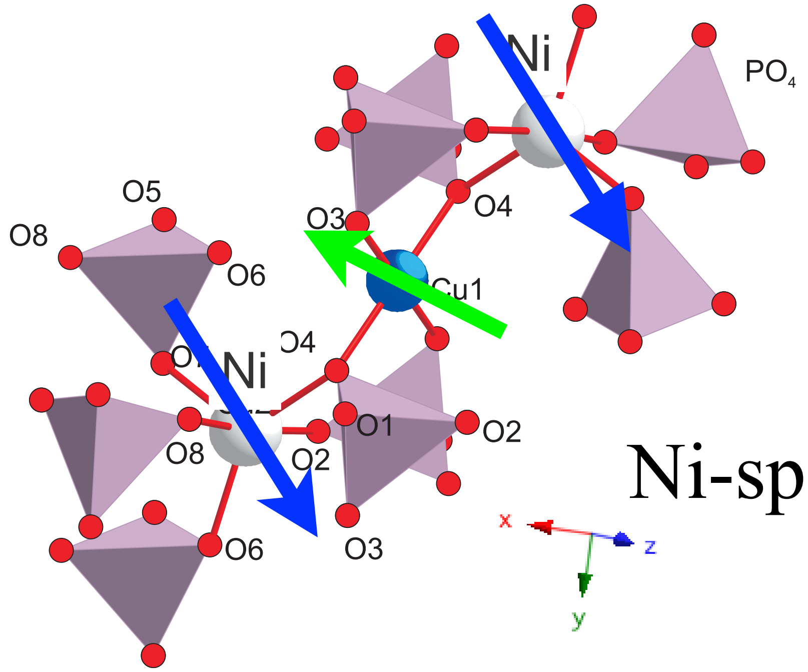
$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1} \psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2) \right)$$

Case 1:

Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$) ⇒ identical trimers on the same orbit



τ_2

Ni-spins ⇈ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

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$$\lambda = x, y, z$$

Orbit 2

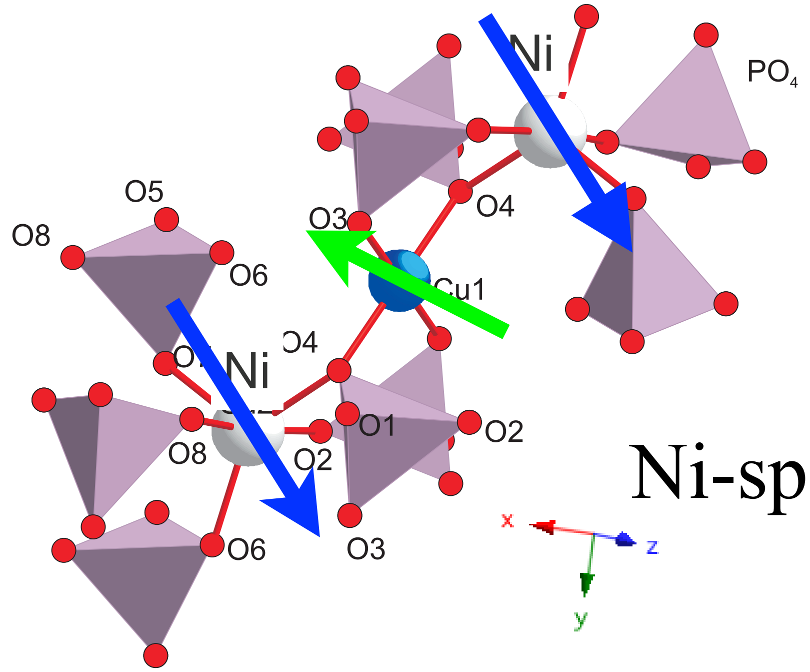
$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1} \psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2)\right)$$

Case 1:

Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$) ⇒ identical trimers on the same orbit

and

the same $\mathbf{k}_1$ for both orbits. orbits are unrelated by symmetry



τ_2

Ni-spins ⇑⇑ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: rep-approach

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions or normal modes

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + \cancel{C_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2)}\right)$$

$\lambda = x, y, z$

Orbit 2

Case 1: $C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_2} = 0$

any $C_{\lambda,\mathbf{k}_2}, C'_{\lambda,\mathbf{k}_1}$

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + \cancel{C'_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2)}\right)$$

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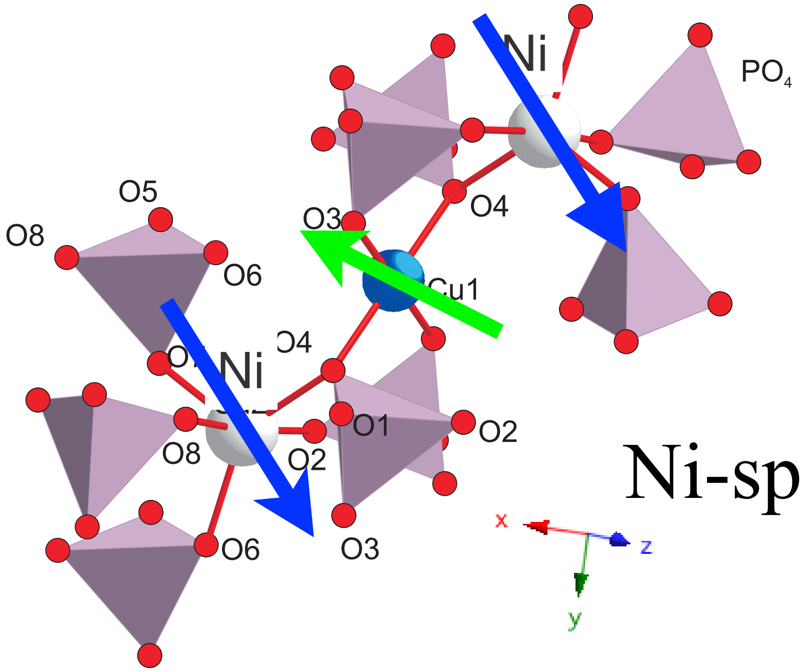


τ_2

Ni-spins ⇑⇑ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 1k

Fit the data under this conditions

Orbit 1

basis functions or normal modes

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1}\boldsymbol{\psi}_\lambda(\mathbf{k}_1) + \cancel{C_{\lambda,\mathbf{k}_2}}\boldsymbol{\psi}_\lambda(\mathbf{k}_2)\right)$$

$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1}\boldsymbol{\psi}_\lambda(\mathbf{k}_1) + \cancel{C'_{\lambda,\mathbf{k}_2}}\boldsymbol{\psi}_\lambda(\mathbf{k}_2)\right)$$

Case 1: $C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_2} = 0$

any $C_{\lambda,\mathbf{k}_2}, C'_{\lambda,\mathbf{k}_1}$

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 1k

Fit the data under this conditions

Experimentally only orbit1 has non-zero spins!

basis functions or normal modes

Orbit 1

$$\mathbf{S}_0 = \sum_{\substack{\lambda=1 \\ \lambda = x,y,z}}^{3} (C_{\lambda,\mathbf{k}_1} \psi_\lambda(\mathbf{k}_1) + \cancel{C_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2)})$$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} (\cancel{C'_{\lambda,\mathbf{k}_1}} \psi_\lambda(\mathbf{k}_1) + \cancel{C'_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2)})$$

Case 1: $C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_2} = 0$

any $C_{\lambda,\mathbf{k}_2}, C'_{\lambda,\mathbf{k}_1}$

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 1k

Fit the data under this conditions

Experimentally only orbit1 has non-zero spins!

Orbit 1

basis functions or normal modes

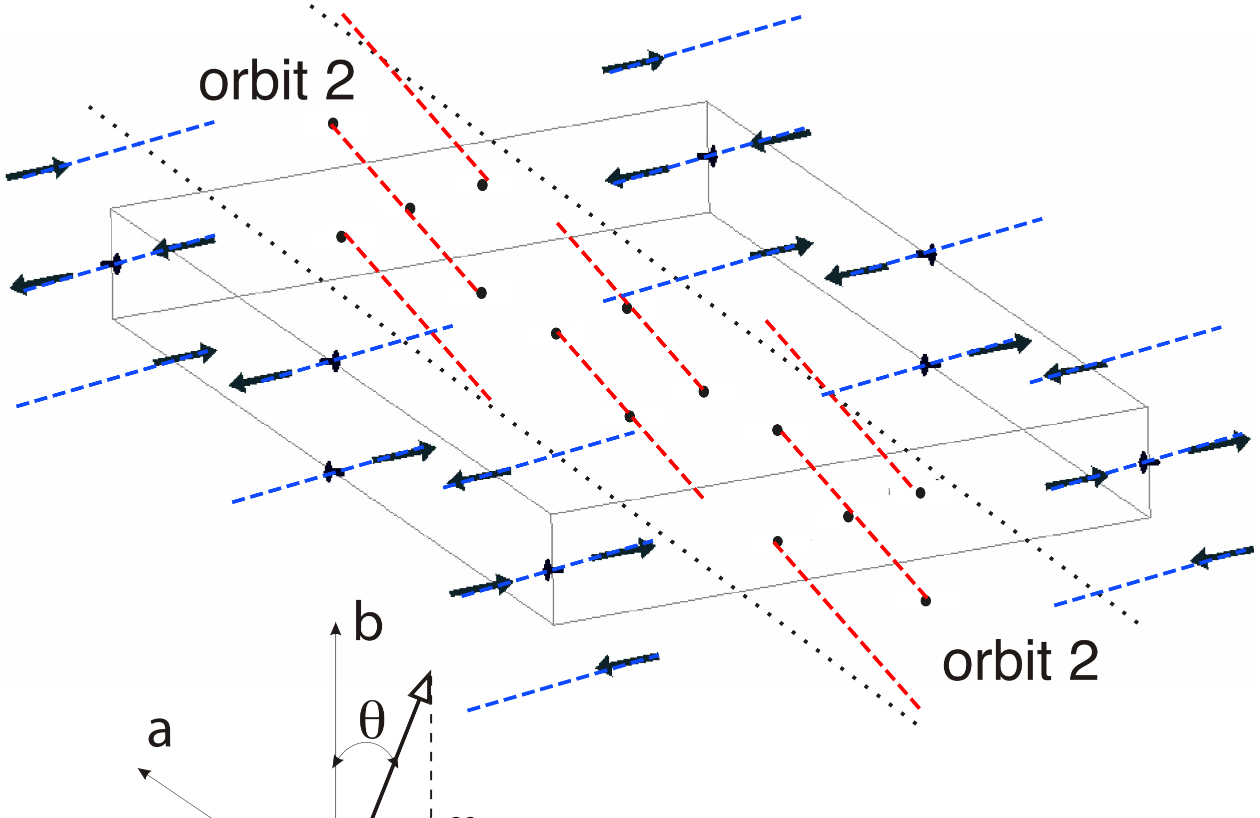
$$\mathbf{S}_0 = \sum_{\substack{\lambda=1 \\ \lambda = x,y,z}}^{3} (\boxed{C_{\lambda,\mathbf{k}_1}}\psi_\lambda(\mathbf{k}_1) + \cancel{C}_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2))$$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} (\cancel{C'_{\lambda,\mathbf{k}_1}}\psi_\lambda(\mathbf{k}_1) + \cancel{C}_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2))$$

Case 1: $C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_2} = 0$

any $C_{\lambda,\mathbf{k}_2}, C'_{\lambda,\mathbf{k}_1}$



Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 2k

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

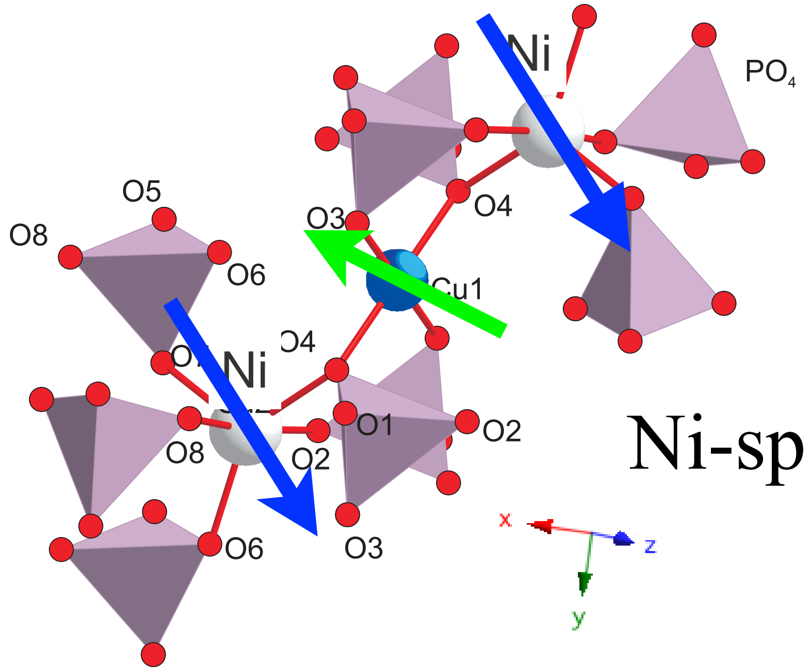
basis functions

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1} \boldsymbol{\psi}_\lambda(\mathbf{k}_1) + C_{\lambda,\mathbf{k}_2} \boldsymbol{\psi}_\lambda(\mathbf{k}_2) \right)$$

$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1} \boldsymbol{\psi}_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2} \boldsymbol{\psi}_\lambda(\mathbf{k}_2) \right)$$



Ni-spins ⇈ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 2k

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions

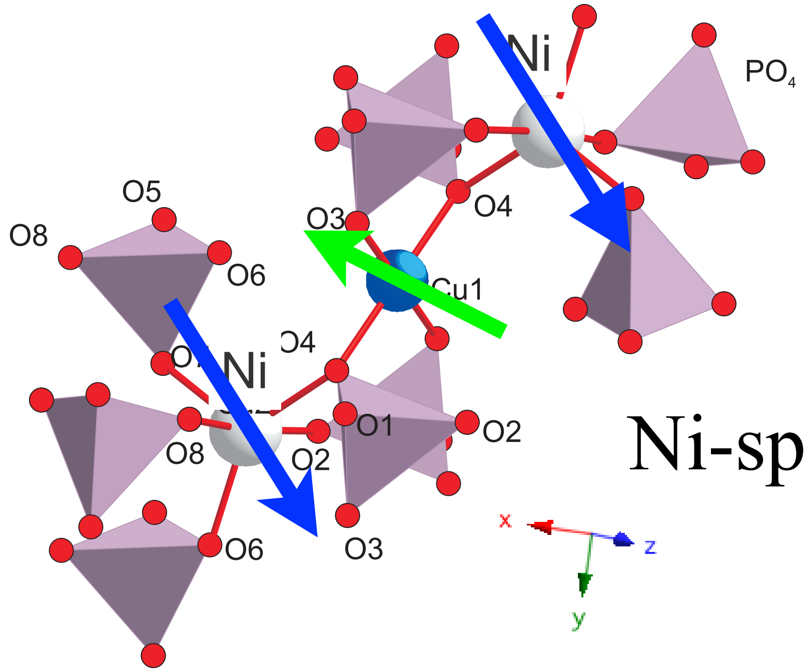
$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + C_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2)\right)$$

$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} \left(C'_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2)\right)$$

Case 2:
Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$)
and



Ni-spins ⇈ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 2k

irrep τ_2

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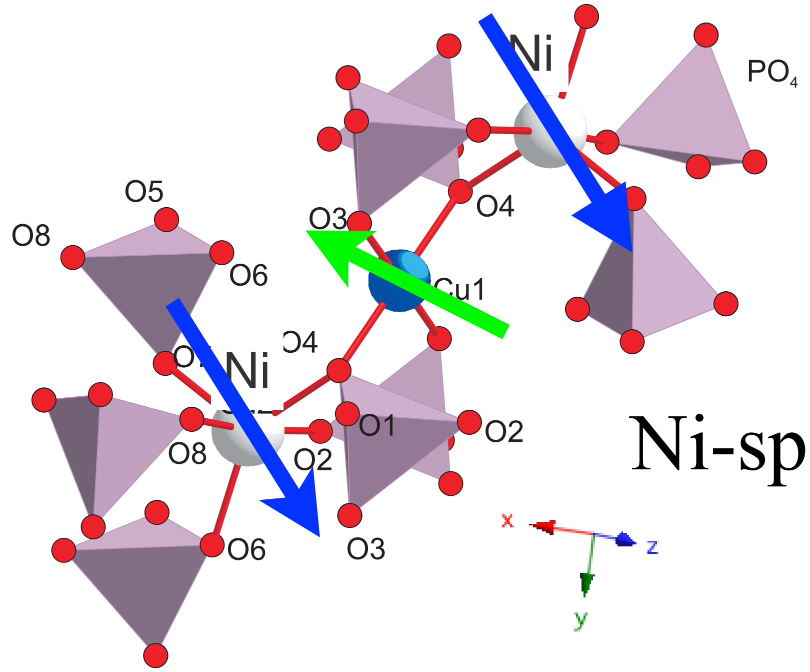
$\lambda = x, y, z$

Orbit 2

$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} (C'_{\lambda,\mathbf{k}_1} \psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2} \psi_\lambda(\mathbf{k}_2))$$

Case 2:
Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$)
and
$\mathbf{k}_1$ for orbit 1 and $\mathbf{k}_2$ for orbit 2



Ni-spins ⇈ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 2k

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} (C_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + \xcancel{C_{\lambda,\mathbf{k}_2}}\psi_\lambda(\mathbf{k}_2))$$

$\lambda = x, y, z$

$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$

Orbit 2

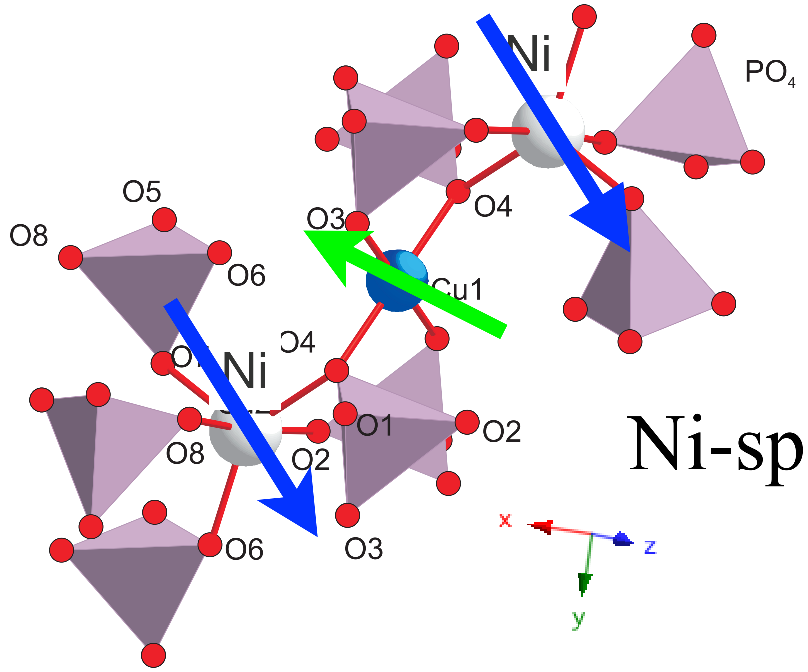
$$\mathbf{S}'_0 = \sum_{\lambda=1}^{3} (\xcancel{C'_{\lambda,\mathbf{k}_1}}\psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2))$$

Case 2:

$$C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_1} = 0$$

Case 2:
Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$)
and
$\mathbf{k}_1$ for orbit 1 and $\mathbf{k}_2$ for orbit 2

$$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$$



Ni-spins ⇈ in trimer

Magnetic order in $Ca_3Cu_1Ni_2(PO_4)_4$: 2k

irrep τ_2

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basis functions

Orbit 1

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$\lambda = x, y, z$

$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$

Orbit 2

$$\mathbf{S}'_0 = \sum^{3} \left(\cancel{C_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1)} + C'_{\lambda,\mathbf{k}_2}\boldsymbol{\psi}_\lambda(\mathbf{k}_2)\right)$$

Case 2: $C_{\lambda,\mathbf{k}_2} = C'_{\lambda,\mathbf{k}_1} = 0$

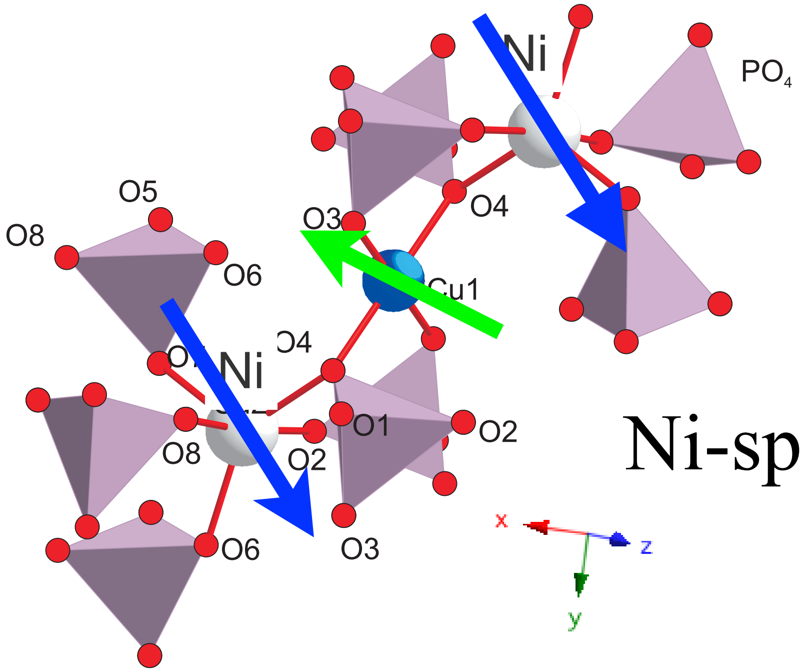
Ideally fits experimental data!

Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$)

and

$\mathbf{k}_1$ for orbit 1 and $\mathbf{k}_2$ for orbit 2

$$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$$



Ni-spins ⇈ in trimer

Magnetic order in Ca$_3$Cu$_1$Ni$_2$(PO$_4$)$_4$: 2k

irrep τ_2

Independently for both Cu-spins and Ni-spins we have:

Orbit 1

basis functions

$$\mathbf{S}_0 = \sum_{\lambda=1}^{3} \left(C_{\lambda,\mathbf{k}_1}\psi_\lambda(\mathbf{k}_1) + \cancel{C_{\lambda,\mathbf{k}_2}}\psi_\lambda(\mathbf{k}_2)\right)$$

$\lambda = x, y, z$

$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$

Orbit 2

$$\mathbf{S}'_0 = \sum^{3} \left(\cancel{C'_{\lambda,\mathbf{k}_1}}\psi_\lambda(\mathbf{k}_1) + C'_{\lambda,\mathbf{k}_2}\psi_\lambda(\mathbf{k}_2)\right)$$

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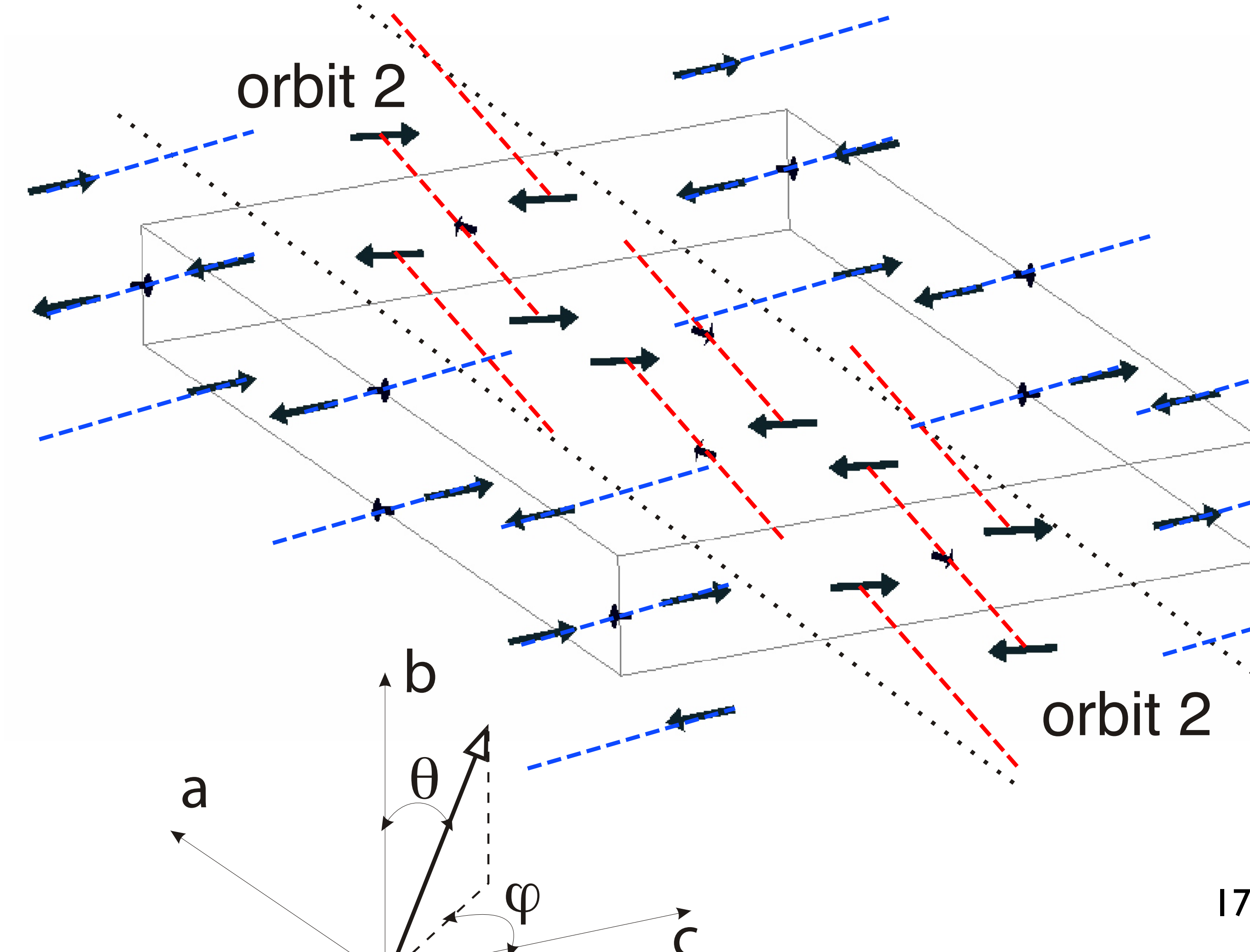
Ideally fits experimental data!

Both Cu and Ni propagate with the same k-arm (e.g. $\mathbf{k}_1$)

and

$\mathbf{k}_1$ for orbit 1 and $\mathbf{k}_2$ for orbit 2

$$C_{\lambda,\mathbf{k}_1} = C'_{\lambda,\mathbf{k}_2}$$



Symmetry analysis using full star {k} & Shubnikov

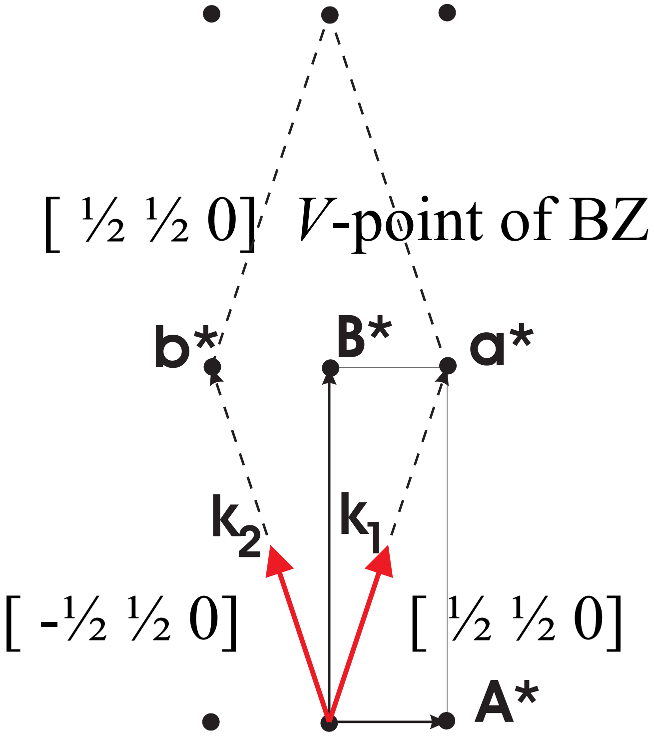
$C2/c$ C_{2h}^6 $2/m$ Monoclinic

No. 15 $C\,1\,2/c\,1$ Patterson symmetry $C\,1\,2/m\,1$

Symmetry operators

$h_1 = x, y, z$ $h_2 = \bar{x}, y, \bar{z}+\frac{1}{2}$ $h_3 = \bar{x}, \bar{y}, \bar{z}$ $h_4 = x, \bar{y}, z+\frac{1}{2}$ $+T(n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3)$ $(\frac{1}{2}, \frac{1}{2}, 0)+$

{k}-star has two arms



h_1 1
h_3 -1

$G_k = C\text{-}\mathit{1}$

http://stokes.byu.edu/iso/

ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA,

Symmetry analysis using full star {k} & Shubnikov

$C2/c$ C_{2h}^{6} $2/m$ Monoclinic

No. 15 $C12/c1$ Patterson symmetry $C12/m1$

Symmetry operators

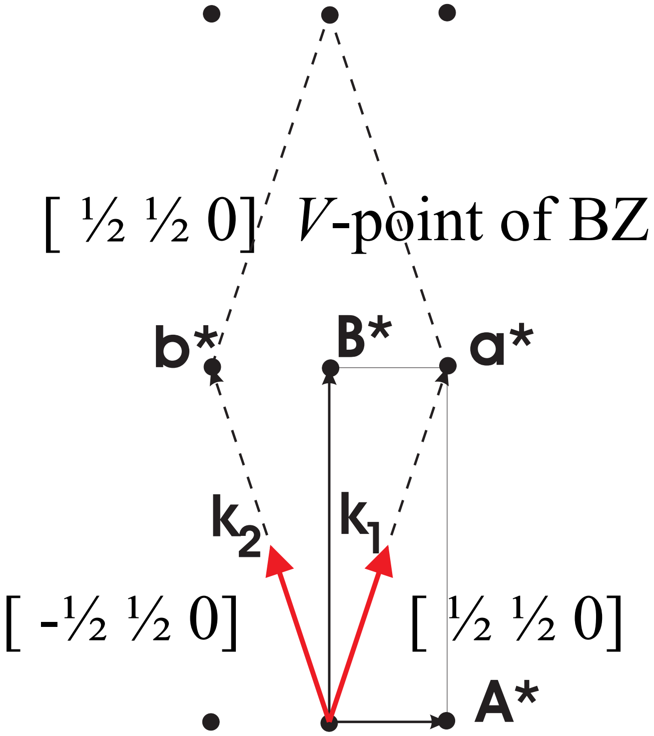
$h_1 = x,y,z$ $h_2 = \bar{x},y,\bar{z}+\frac{1}{2}$ $h_3 = \bar{x},\bar{y},\bar{z}$ $h_4 = x,\bar{y},z+\frac{1}{2}$ $+T(n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3)$ $(\frac{1}{2},\frac{1}{2},0)+$

$\{[\frac{1}{2},\frac{1}{2},0],[-\frac{1}{2},\frac{1}{2},0]\}$ in $C2/c$ has 2D *irrep* (mV-), based on 1D *irrep* τ_2 of $G_k = C\text{-}1$

……

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$$

{k}-star has two arms



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h_3 -1

$G_k = C\text{-}1$

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Symmetry analysis using full star {k} & Shubnikov

$C2/c$ C_{2h}^{6} $2/m$ Monoclinic

No. 15 $C\,1\,2/c\,1$ Patterson symmetry $C\,1\,2/m\,1$

Symmetry operators

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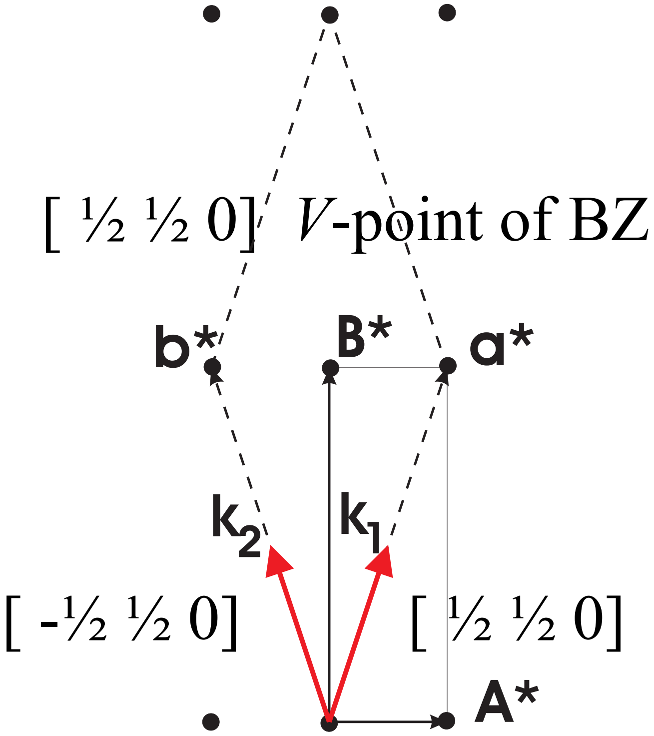
$\{[\frac{1}{2},\frac{1}{2},0],[-\frac{1}{2},\frac{1}{2},0]\}$ in $C2/c$ has 2D *irrep* (mV-), based on 1D *irrep* τ_2 of $G_k = C$-1

……

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$$

{k}-star has two arms



h_1 1
h_3 -1

$G_k = C$-*1*

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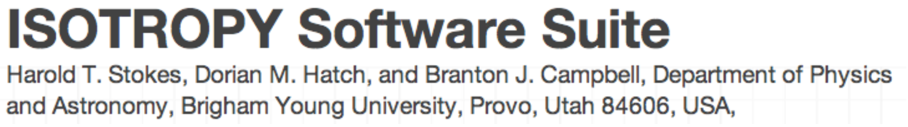
$\boxed{\{[\frac{1}{2},\frac{1}{2},0],[-\frac{1}{2},\frac{1}{2},0]\}\text{ in }C2/c}$ has 2D *irrep* (mV-), based on 1D *irrep* τ_2 of $G_k = C$-1

……

http://stokes.byu.edu/iso/



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Symmetry analysis using full star {k} & Shubnikov

$\{[\frac{1}{2},\frac{1}{2},0],[-\frac{1}{2},\frac{1}{2},0]\}$ in $C2/c$ has 2D *irrep* (mV-), based on 1D *irrep* τ_2 of $G_k = C$-1

……

Space Group: 15 C2/c C2h-6, Lattice parameters: a=17.71770, b=4.82100, c=17.84720, alpha=90.00000, beta=123.63700, gamma=90.00000

Cu 4b (0,1/2,0), Ni 8f (x,y,z), x=-0.12000 , y=0.03750 , z=-0.46700

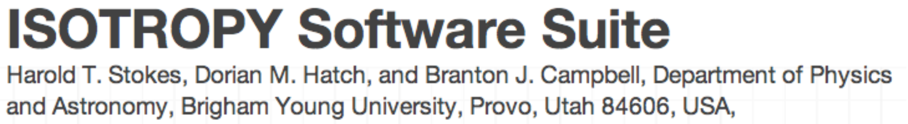
k point: V, k4 (1/2,1/2,0)
IR: mV1-, mk4t2

P1 (a,a) 15.91 C_a2/c, basis={(2,0,2),(0,-2,0),(0,0,-1)}, origin=(0,1/2,0), s=4, i=4, k-active= (1/2,1/2,0),(-1/2,1/2,0)

P3 (0,a) 2.7 P_S-1, basis={(-1/2,-1/2,-1),(-1/2,-1/2,0),(0,2,0)}, origin=(-1/4,1/4,0), s=2, i=4, k-active= (-1/2,1/2,0)

C1 (a,b) 2.7 P_S-1, basis={(0,0,-1),(1,1,1),(0,-2,0)}, origin=(0,1/2,0), s=4, i=8, k-active= (1/2,1/2,0),(-1/2,1/2,0)

http://stokes.byu.edu/iso/



ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA,

Symmetry analysis using full star {k} & Shubnikov

$\{[\frac{1}{2},\frac{1}{2},0],[-\frac{1}{2},\frac{1}{2},0]\}$ in $C2/c$ has 2D *irrep* (mV-), based on 1D *irrep* τ_2 of $G_k = C$-1

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Space Group: 15 C2/c C2h-6, Lattice parameters: a=17.71770, b=4.82100, c=17.84720, alpha=90.00000, beta=123.63700, gamma=90.00000

Cu 4b (0,1/2,0), Ni 8f (x,y,z), x=-0.12000 , y=0.03750 , z=-0.46700

k point: V, k4 (1/2,1/2,0)
IR: mV1-, mk4t2

Order parameter direction

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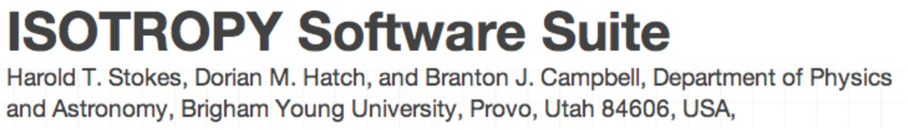
http://stokes.byu.edu/iso/



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Active arms of propagation vector star

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"Conventional" one-**k** case does not give physically reasonable solution

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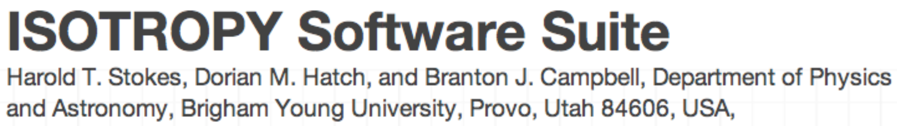

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Shubnikov group

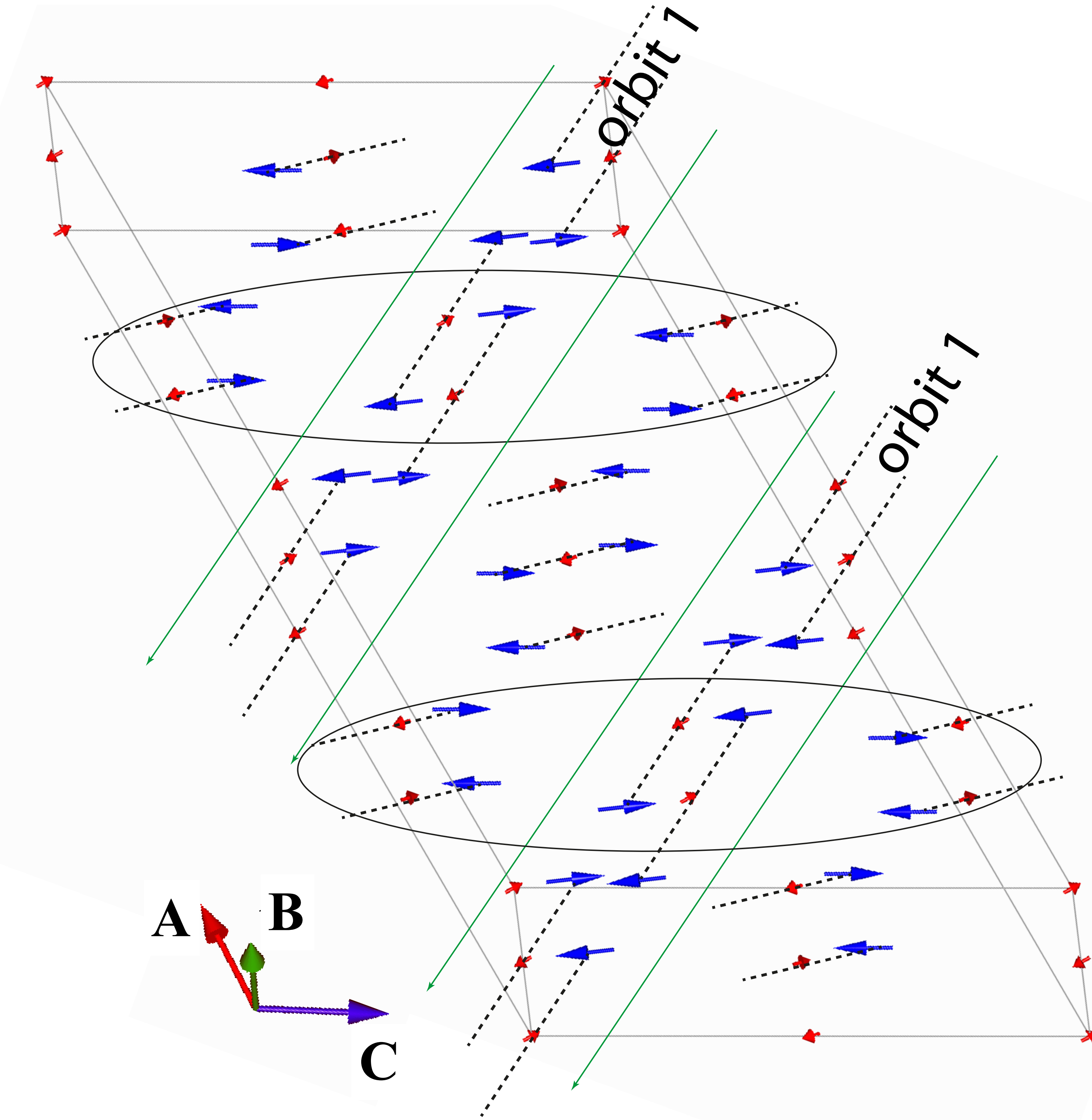
C_a2/c 15.91 BNS
P_c2/c 13.8.84 OG

Shubnikov subgroup generated by *2*D-*irrep mV*- and P1 (a,a)

$C2/c$ —> Sh. group C_a2/c

Basis transformation

$\mathbf{A} = 2\mathbf{a} + 2\mathbf{c}, \mathbf{B} = -2\mathbf{b}, \mathbf{C} = -\mathbf{c}$



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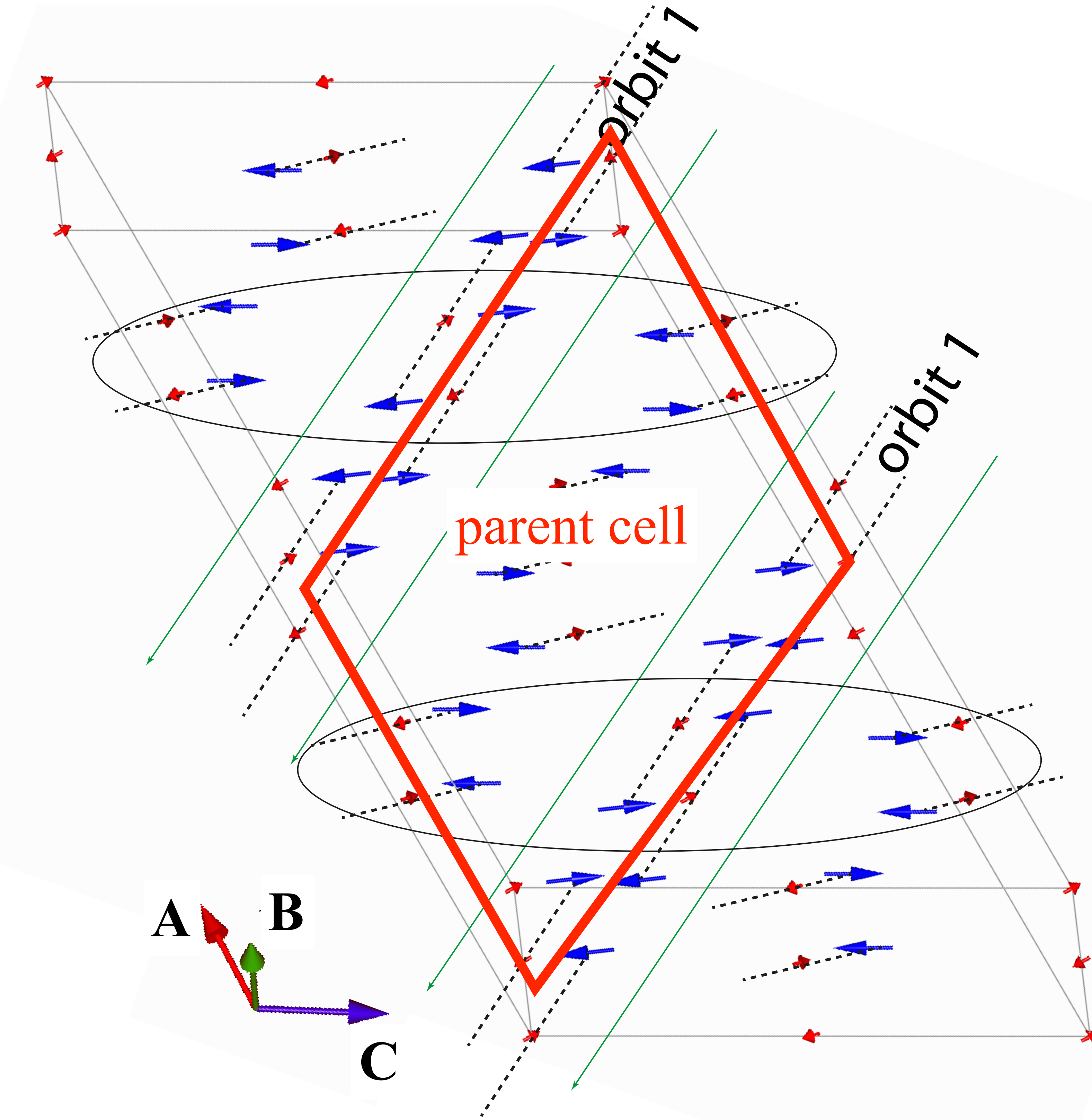

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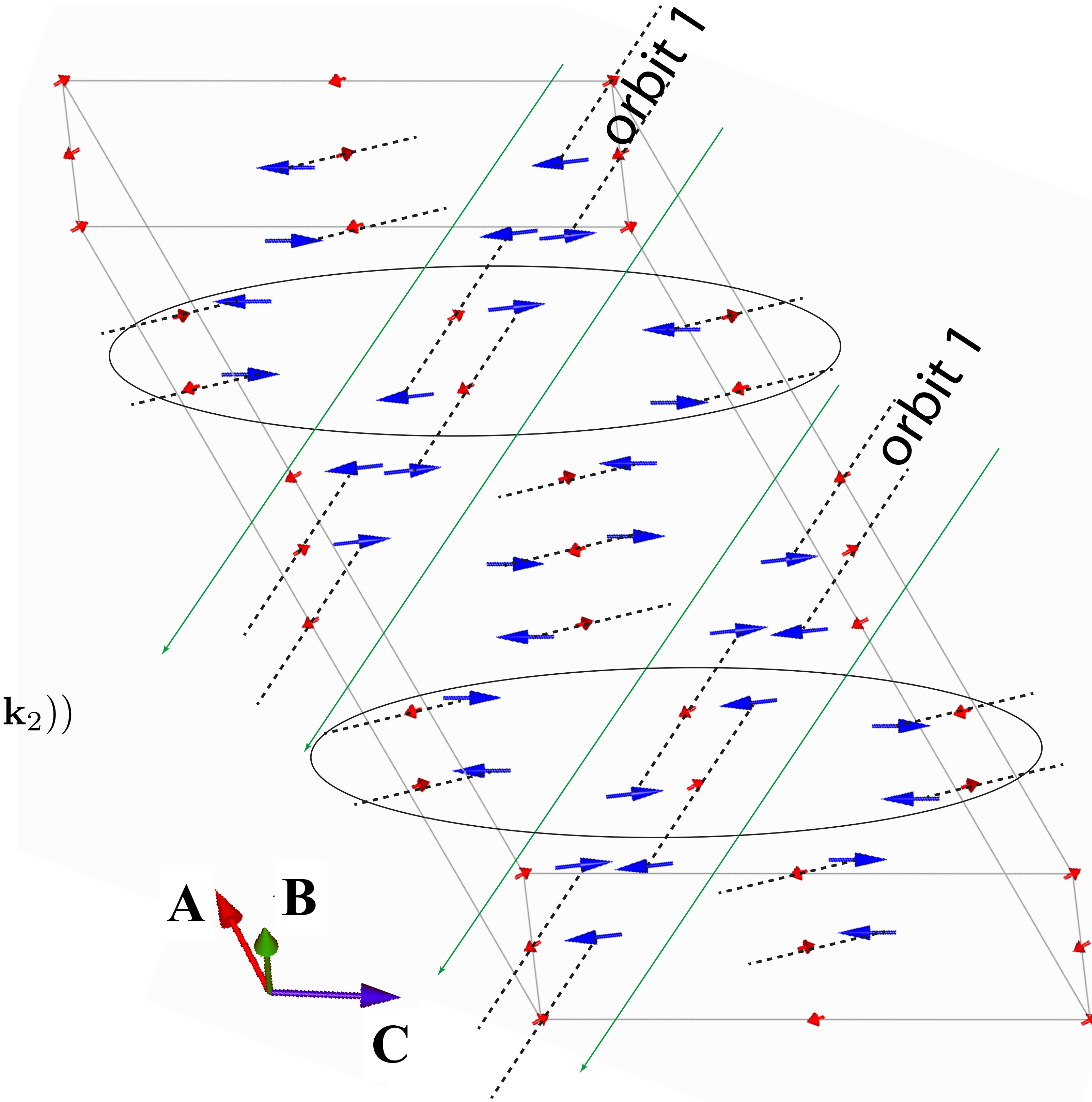
Spin configuration

two Ni in (16g), two Cu in (8a)

Independently for both Cu-spins and Ni-spins we have two normal modes, constructed from parent *C2/c*::

$$\mathbf{S} = \sum_{\lambda=1}^{3} (C_{\lambda,o_1\mathbf{k}_1}\psi_\lambda(o_1\mathbf{k}_1) + C_{\lambda,o_1\mathbf{k}_2}\psi_\lambda(o_1\mathbf{k}_2))$$

$\lambda = x, y, z$



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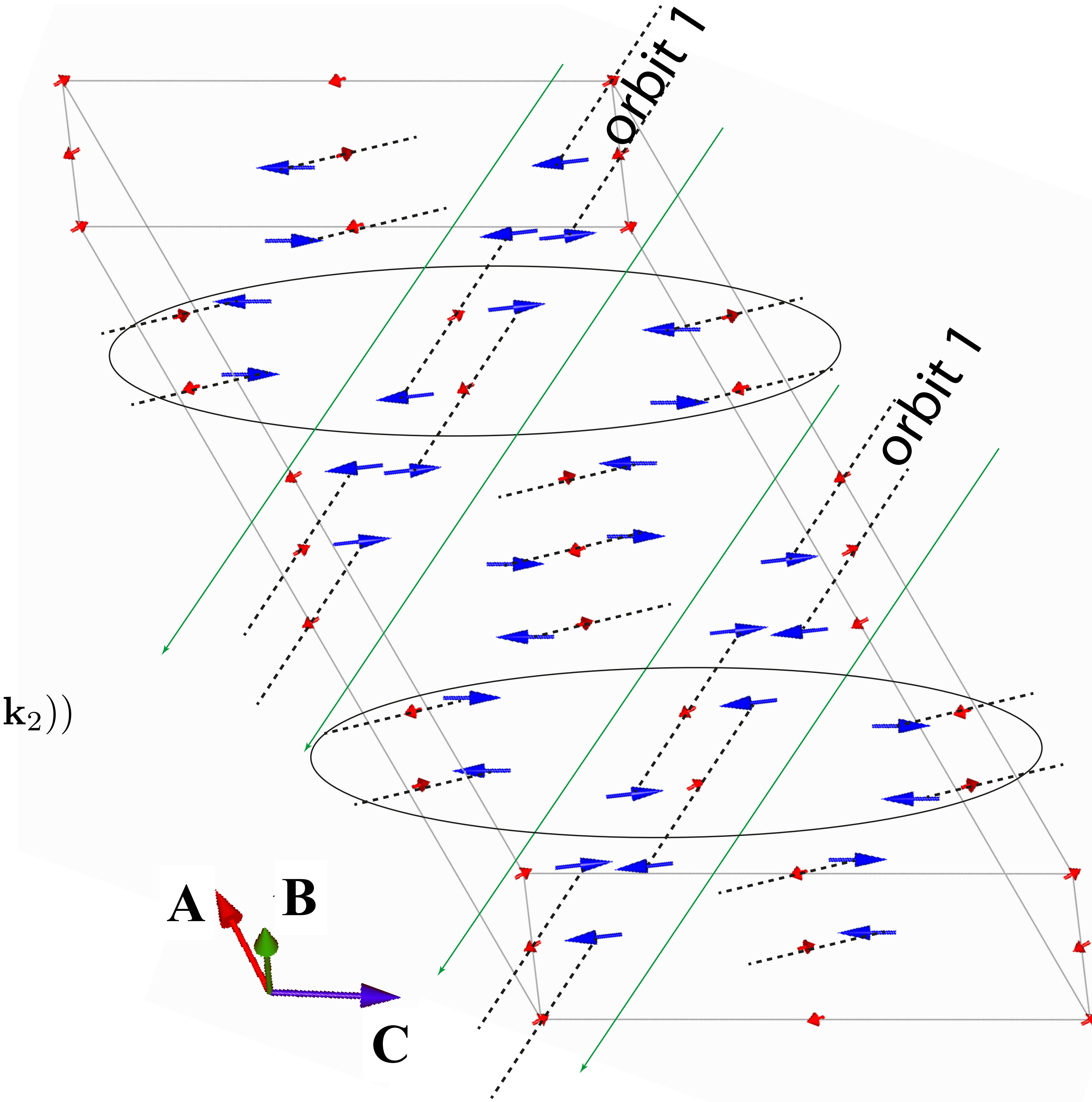
$\lambda = x, y, z$

In parent *C-1* group →

orbit1 with $\mathbf{k}_1$
+
orbit2 with $\mathbf{k}_2$



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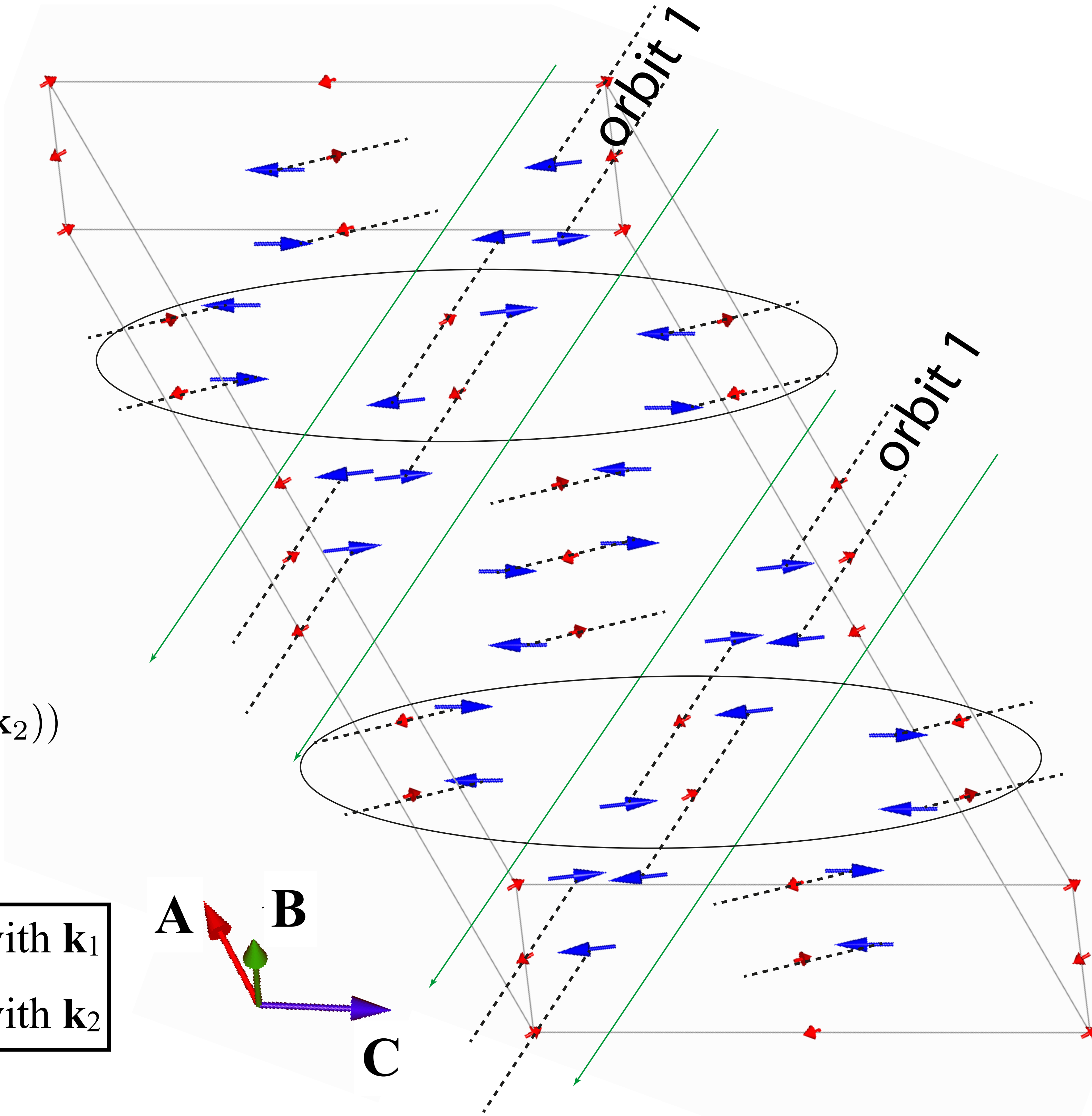
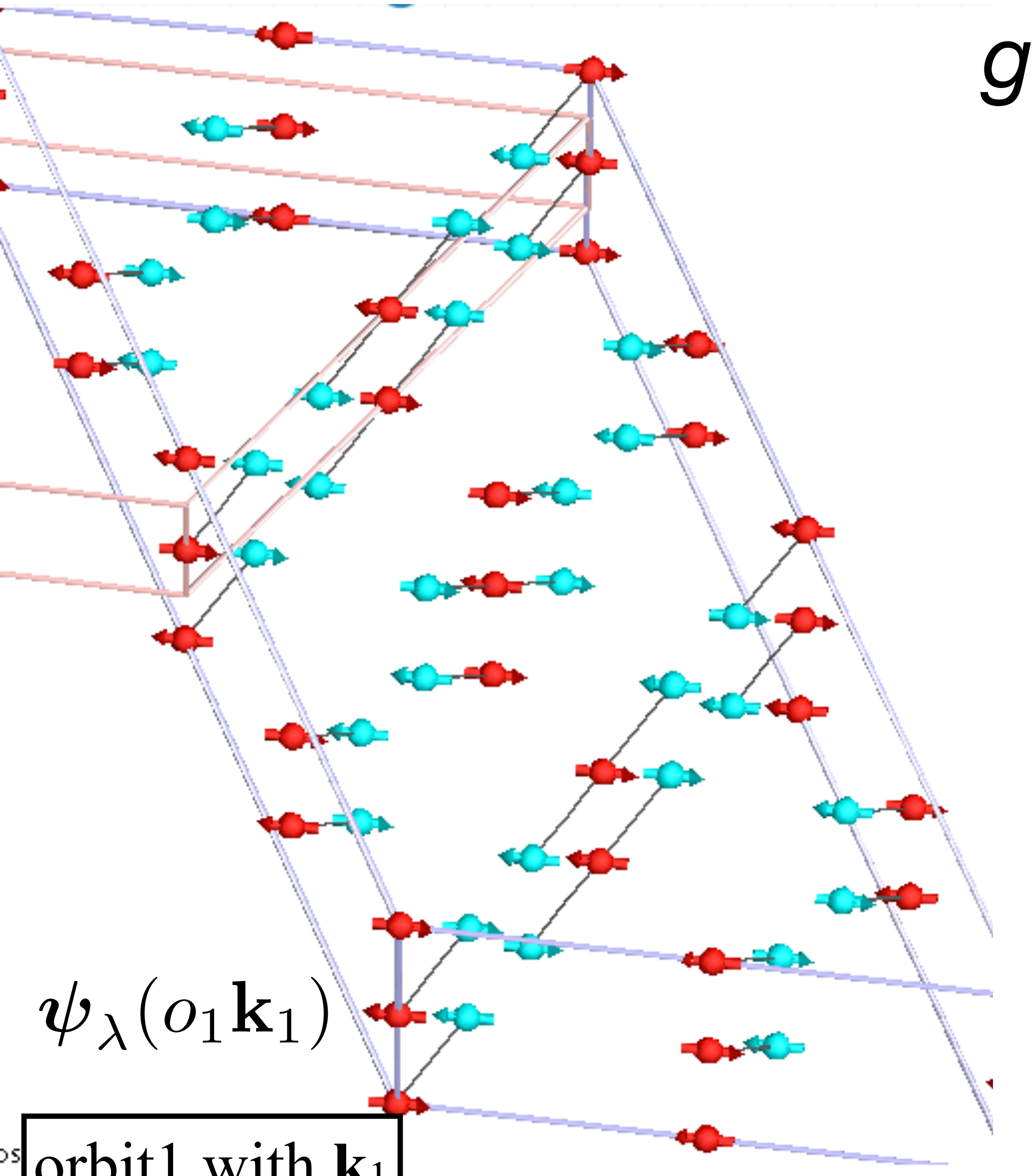


Only one mode fits experimental data

Shubnikov group C_a2/c
*g*enerated by full propagation vector star

experimental values
$<S_{Ni}>=0.945(5)$, $<S_{Cu}>=0.31(1)$
angle between $<\mathbf{S}_{Ni}>$ and $<\mathbf{S}_{Cu}>$
$\cong$ 160 degrees



orbit1 with $\mathbf{k}_1$
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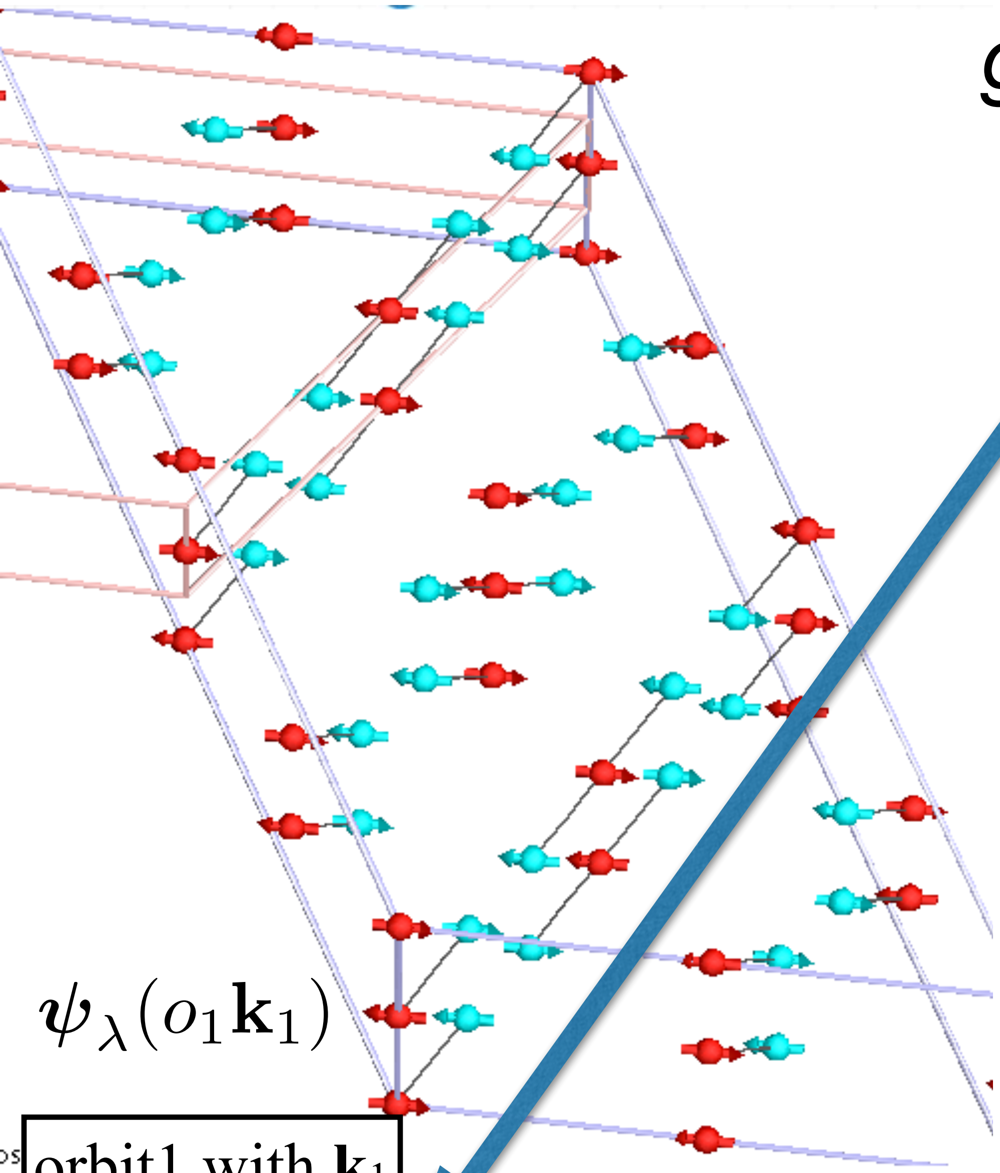

$\psi_\lambda(o_1\mathbf{k}_1)$

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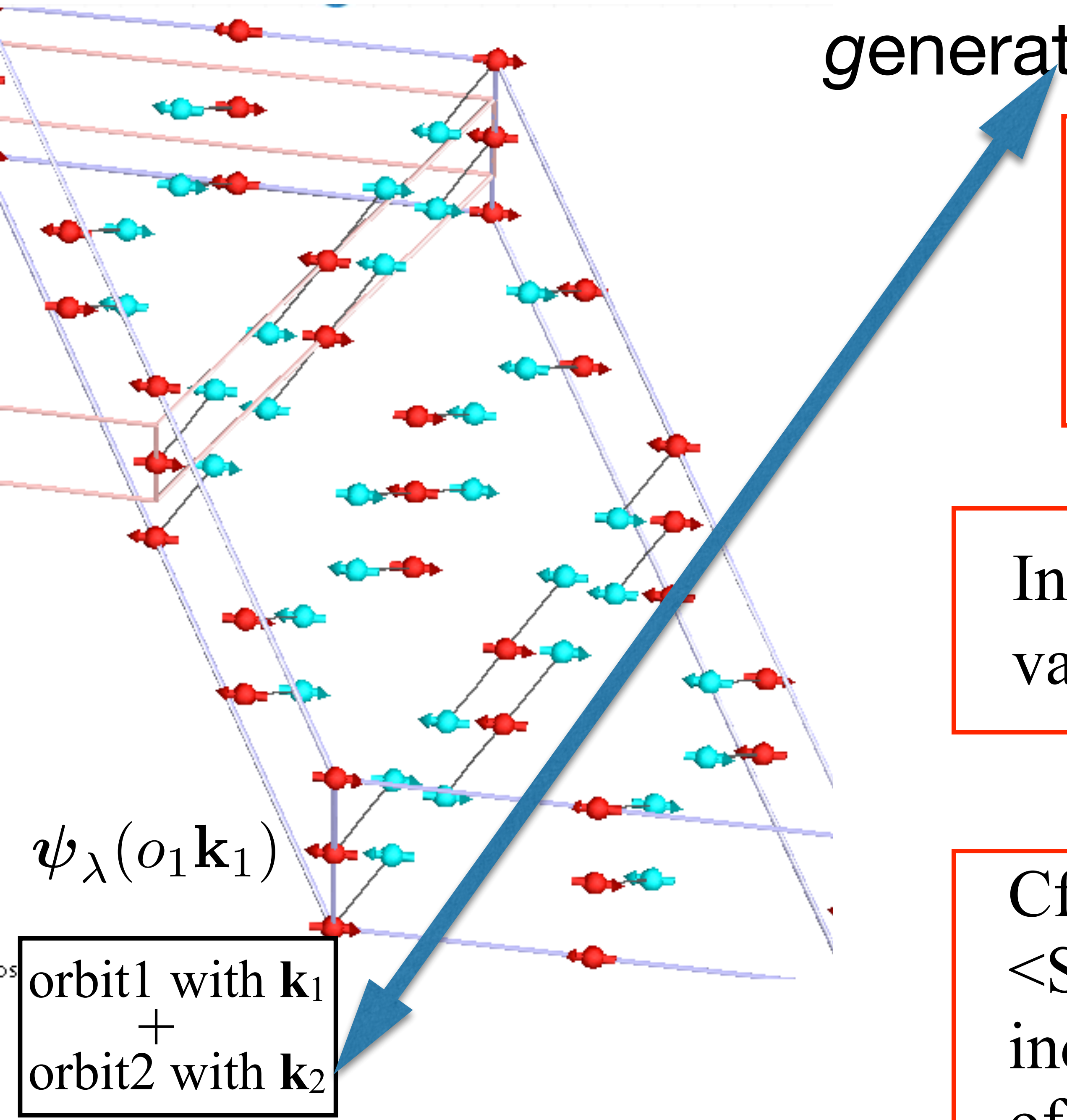

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In $Ca_3Cu_1Ni_2(PO_4)_4$ the trimer Ni-Cu-Ni spin values: $S(Ni^{2+}) <1$, $S(Cu^{2+}) <1/2$

↓

Cf. theoretical spin expectation values $<S_{Ni}>$, $<S_{Cu}>$ with experimental $<S>$ is an independent verification of the multi-arm type of ordering

Spin expectation values <S> in quantum trimer in molecular field

Ni - Cu - Ni
S$_1$ - **S**$_2$ - **S**$_3$
spin = 1 - ½ - 1

basis
$\chi_{m_1,m_2,m_3} = |m_1, m_2, m_3 >$
m_1,m_3=-1,0,1
m_2= -½, ½

$$H = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + d\sum_{i=1}^{3}(S_i^z)^2 - \mathbf{hS}$$

exchange

anisotropy

mol. field

$$\mathbf{S} = \sum_{i=1}^{3} \mathbf{S}_i$$

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mol. field

$$\mathbf{S} = \sum_{i=1}^{3}\mathbf{S}_i$$

d=0

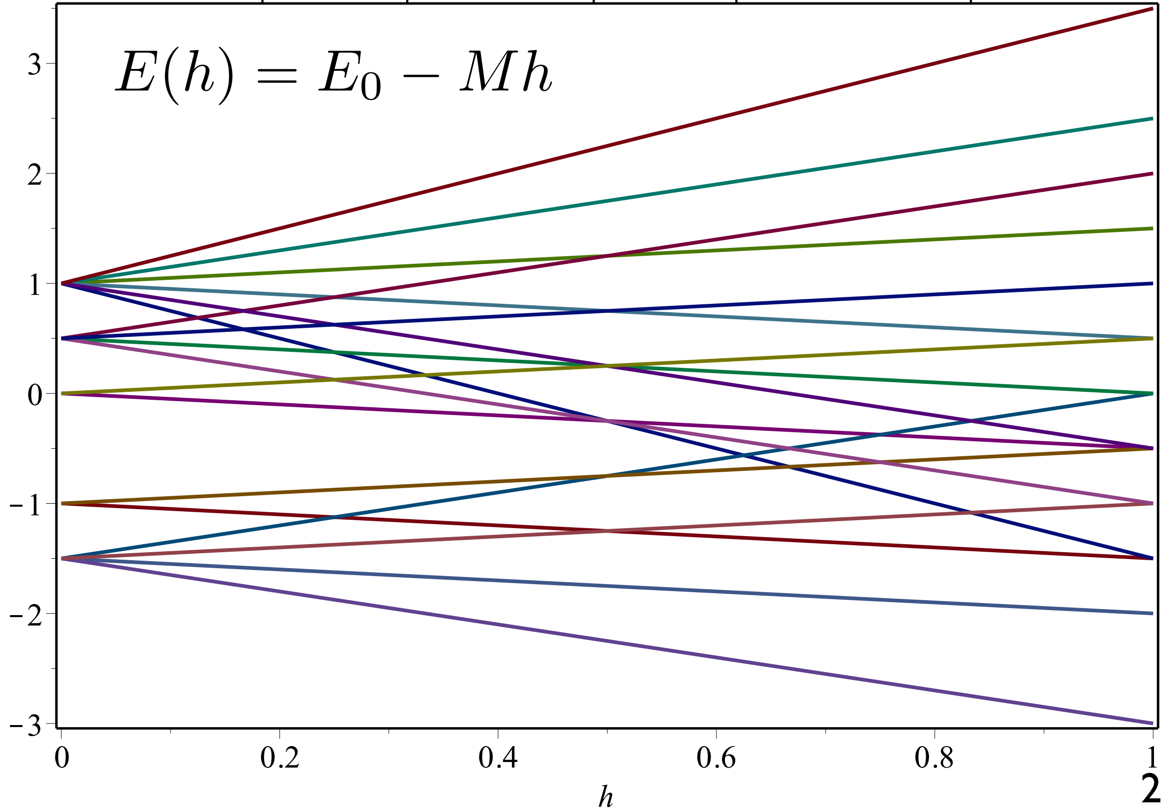
$$\mathbf{S}_{13}^2 = (\mathbf{S}_1 + \mathbf{S}_3)^2$$

$$[H, \mathbf{S}^2] = [H, \mathbf{S}_{13}^2] = 0$$

total S^2, S_h

M=2<S_1>+<S_2>

E_0	S	M	S_{13}	$< S_1 >$	$< S_2 >$
-3/2	3/2	±3/2	2	±9/10	∓3/10
-3/2	3/2	±1/2	2	±3/10	∓1/10
-1	1/2	±1/2	1	±1/3	∓1/6
0	1/2	±1/2	0	0	±1/2
1/2	3/2	±3/2	1	±1/2	±1/2
1/2	3/2	±1/2	1	±1/6	±1/6
1	5/2	±5/2	2	±1	±1/2
1	5/2	±3/2	2	±3/5	±3/10
1	5/2	±1/2	2	±1/5	±1/10



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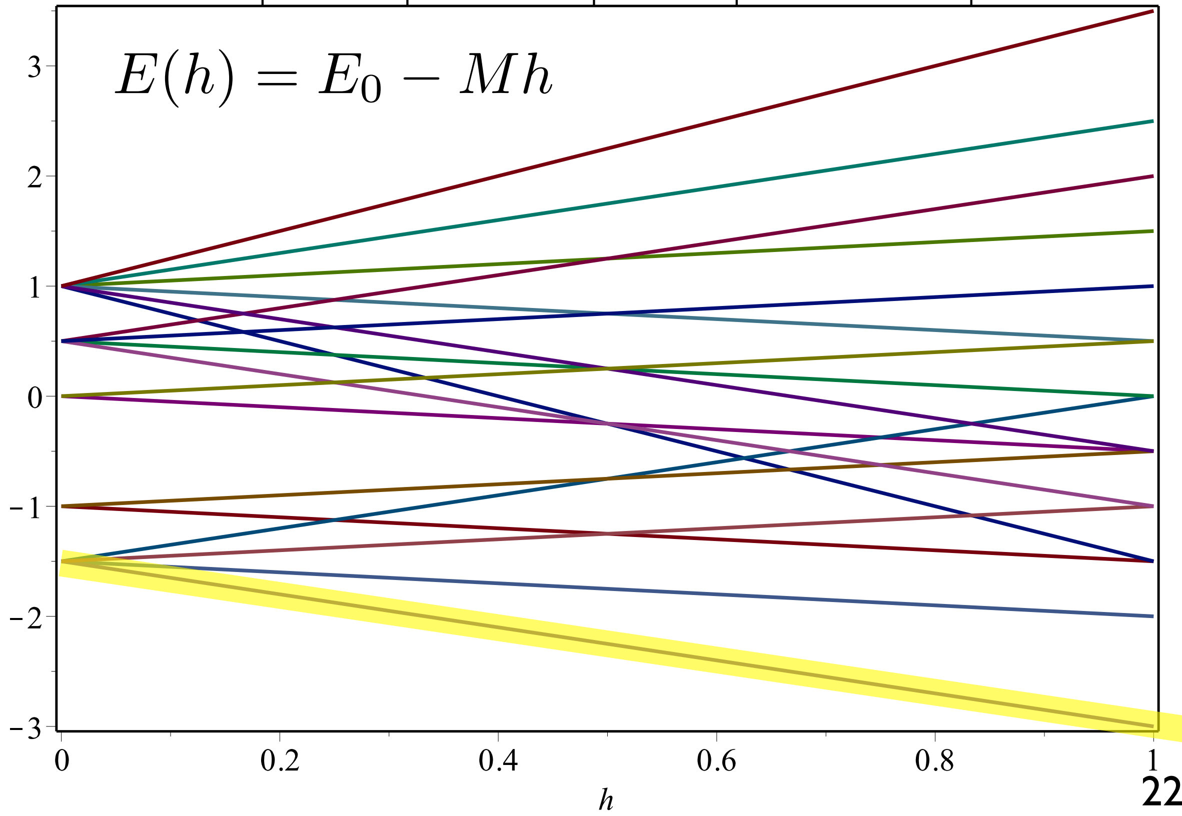
-3/2	3/2	±1/2	2	±3/10	∓1/10
-1	1/2	±1/2	1	±1/3	∓1/6
0	1/2	±1/2	0	0	±1/2
1/2	3/2	±3/2	1	±1/2	±1/2
1/2	3/2	±1/2	1	±1/6	±1/6
1	5/2	±5/2	2	±1	±1/2
1	5/2	±3/2	2	±3/5	±3/10
1	5/2	±1/2	2	±1/5	±1/10

Ground state |ket> for d=0, h<5/2

$$\frac{\sqrt{10}}{10}\left(|\pm1,\pm\frac{1}{2},0> -2\sqrt{2}|\pm1,\mp\frac{1}{2},\pm1> +|0,\pm\frac{1}{2},\pm1>\right)$$



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exchange   anisotropy   mol. field

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d=0

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	total S², S$_\mathbf{h}$			Ni	Cu
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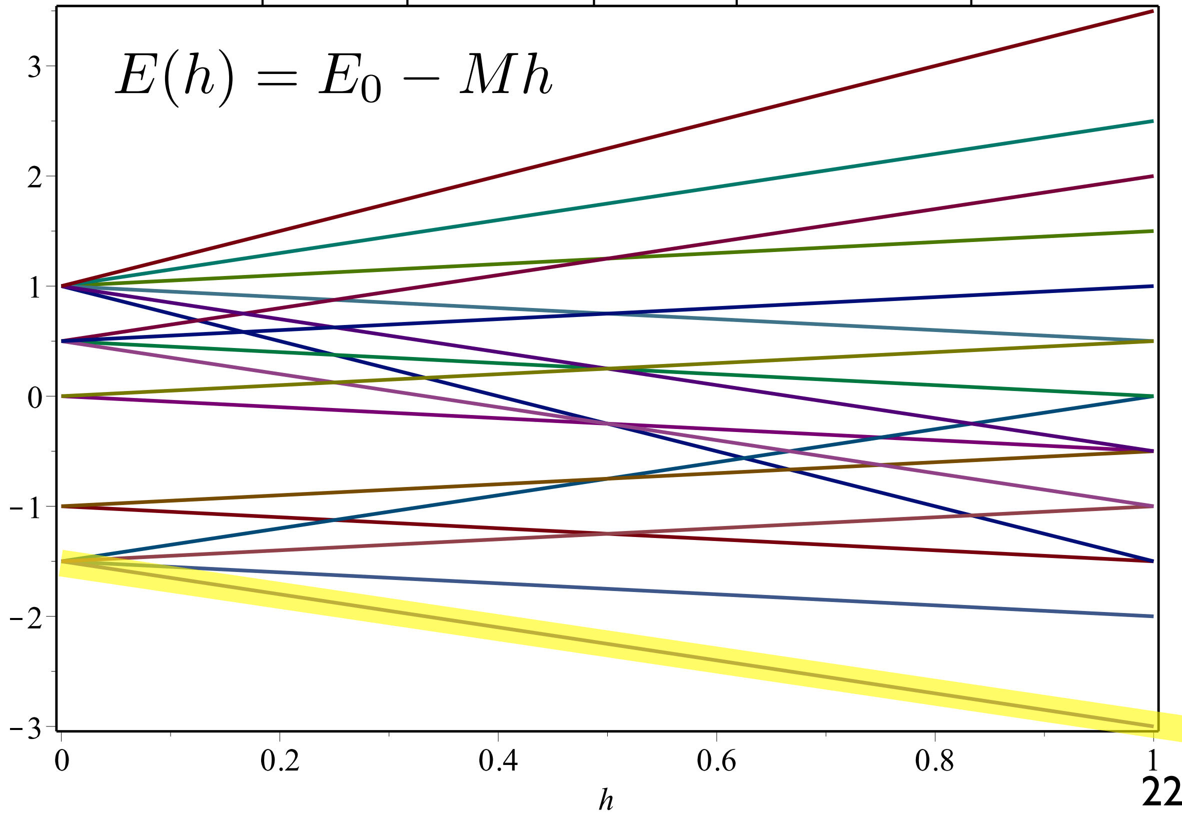
-3/2	3/2	±1/2	2	±3/10	∓1/10
-1	1/2	±1/2	1	±1/3	∓1/6
0	1/2	±1/2	0	0	±1/2
1/2	3/2	±3/2	1	±1/2	±1/2
1/2	3/2	±1/2	1	±1/6	±1/6
1	5/2	±5/2	2	±1	±1/2
1	5/2	±3/2	2	±3/5	±3/10
1	5/2	±1/2	2	±1/5	±1/10

Ground state |ket> for d=0, h<5/2

$$\frac{\sqrt{10}}{10}\left(|\pm1,\pm\frac{1}{2},0> -2\sqrt{2}|\pm1,\mp\frac{1}{2},\pm1> +|0,\pm\frac{1}{2},\pm1>\right)$$

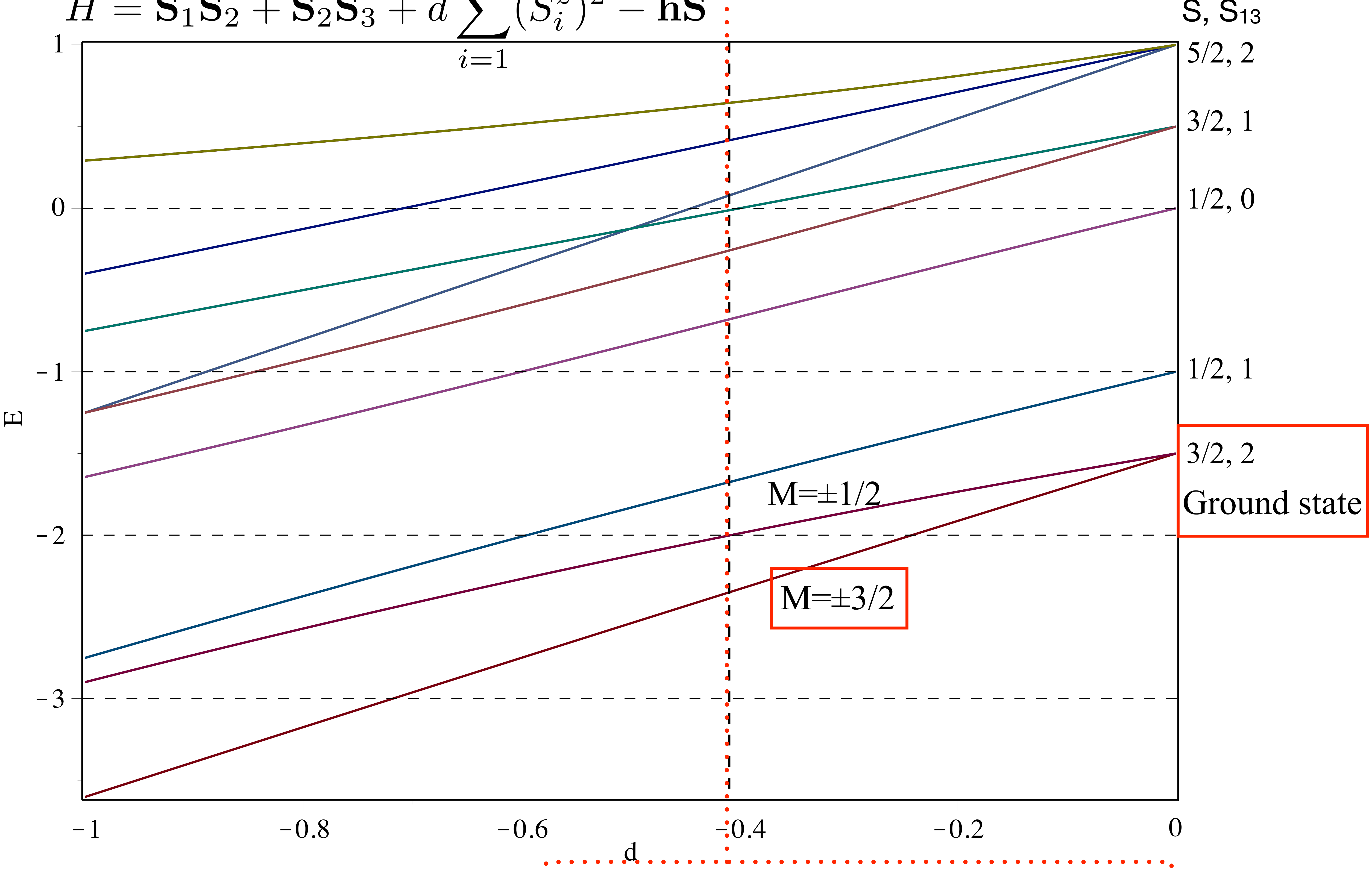
theory
<S$_{\rm Ni}$>=0.9000, <S$_{\rm Cu}$>=0.3000

experimental values
<S$_{\rm Ni}$>=0.945(5), <S$_{\rm Cu}$>=0.31(1)



Energy spectrum E(Single ion anisotropy d_{Ni}), h=0

$$H = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + d\sum_{i=1}^{3}(S_i^z)^2 - \mathbf{hS}$$



Experimental anisotropy from INS

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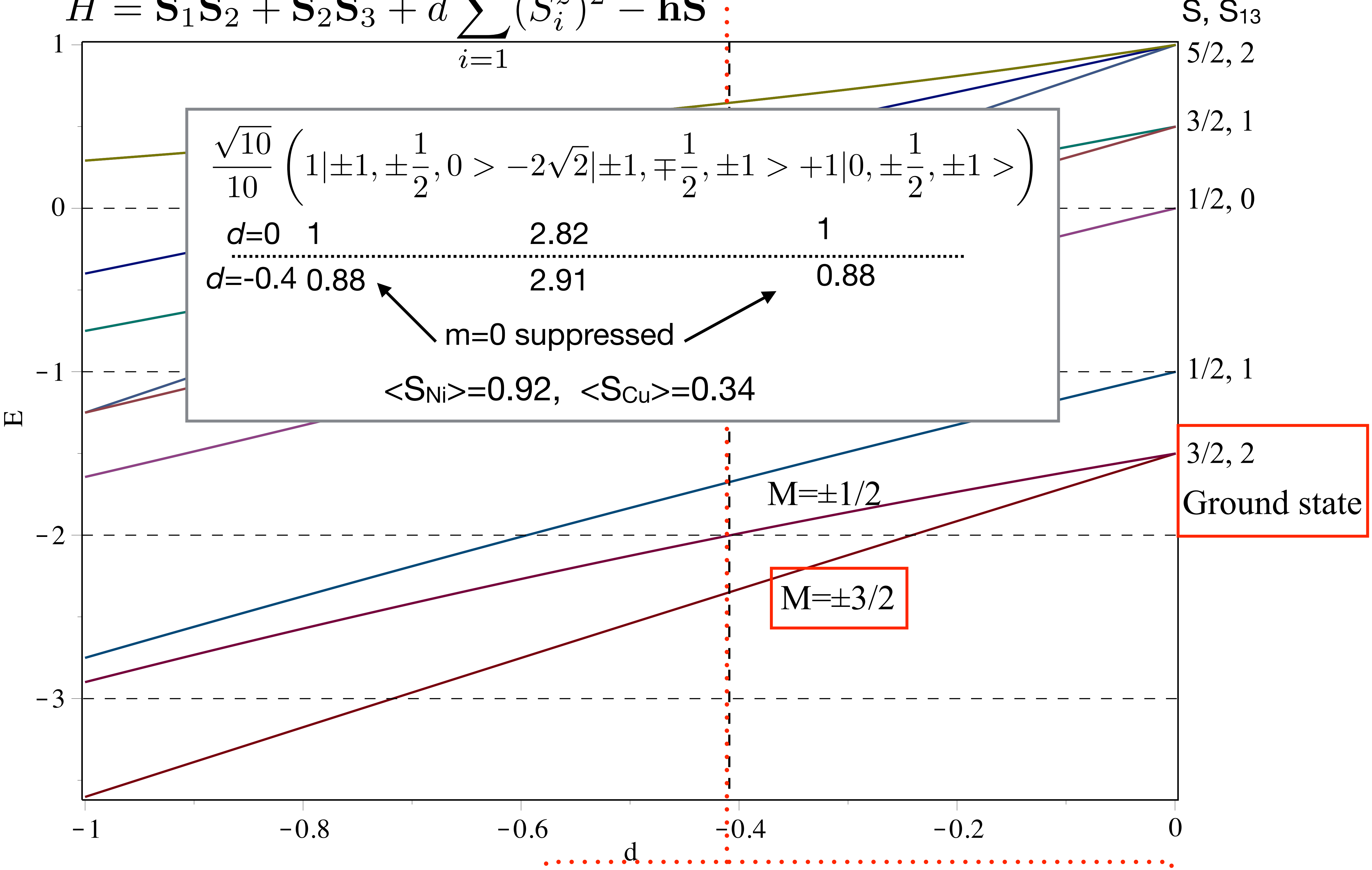


$$\frac{\sqrt{10}}{10}\left(1|\pm1,\pm\frac{1}{2},0> -2\sqrt{2}|\pm1,\mp\frac{1}{2},\pm1> +1|0,\pm\frac{1}{2},\pm1>\right)$$

d=0	1	2.82	1
d=-0.4	0.88	2.91	0.88

m=0 suppressed

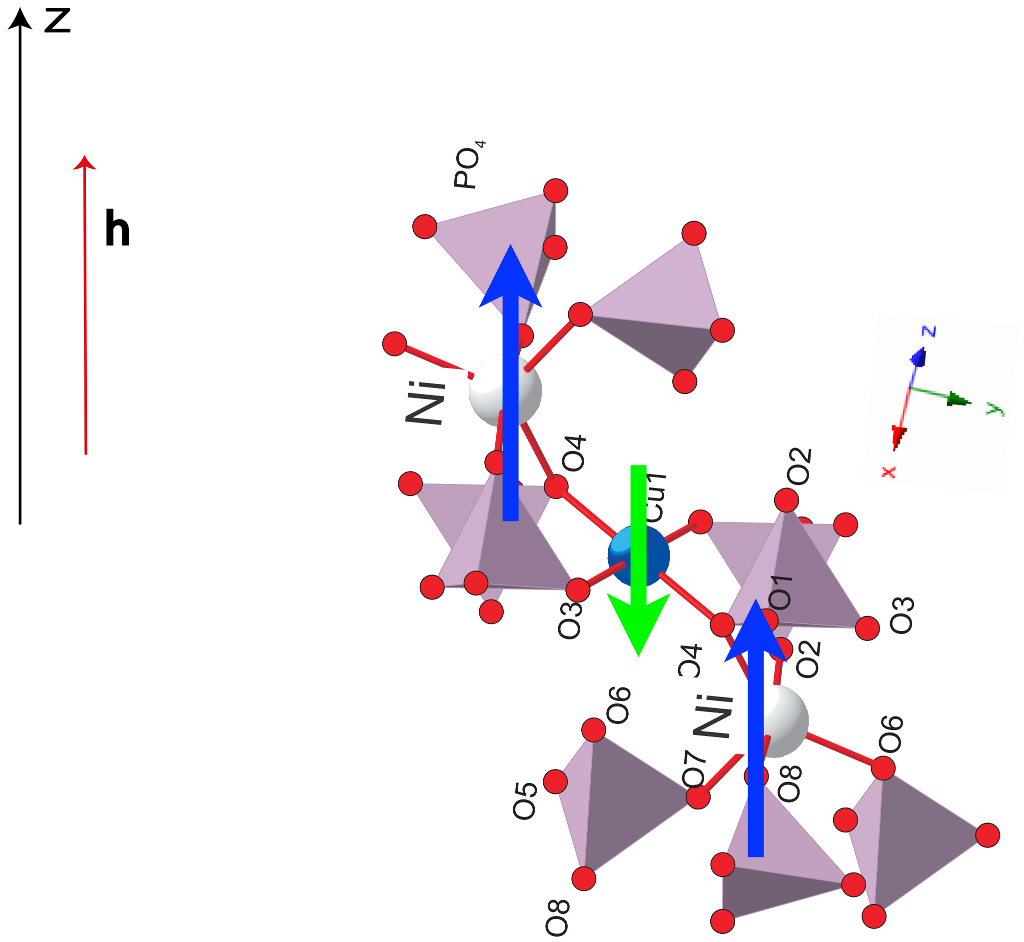
$\langle S_{Ni}\rangle=0.92$, $\langle S_{Cu}\rangle=0.34$

Experimental anisotropy from INS

Interplay between molecular field and anisotropy

$$H = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + d\sum_{i=1}^{3}(S_i^z)^2 - \mathbf{hS}$$

experimental values from
INS $h \cong 0.56$ and $d_{Ni}=-0.4$



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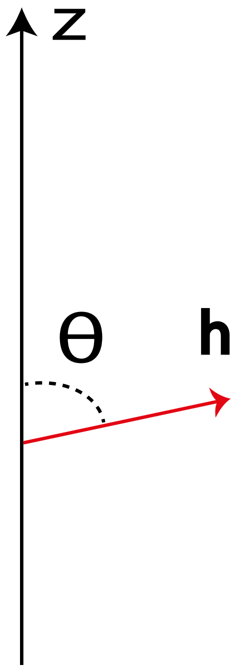

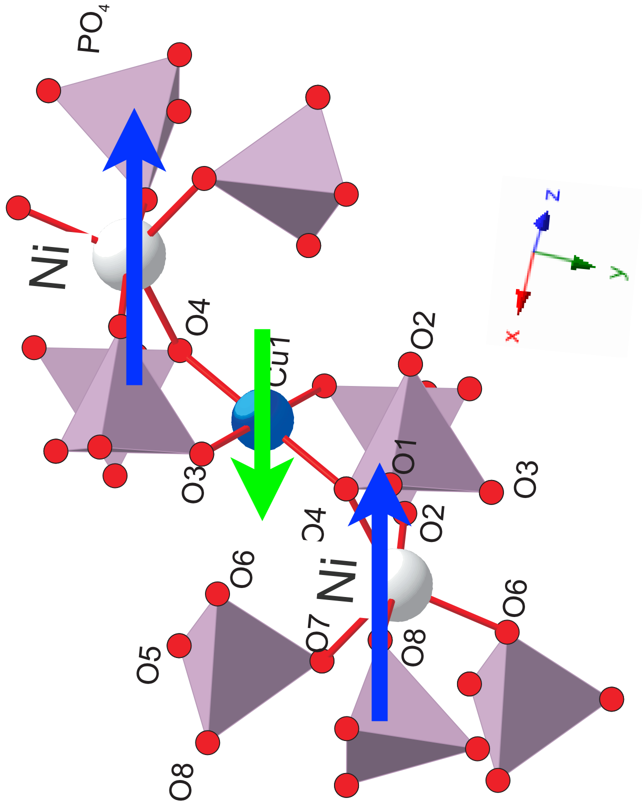

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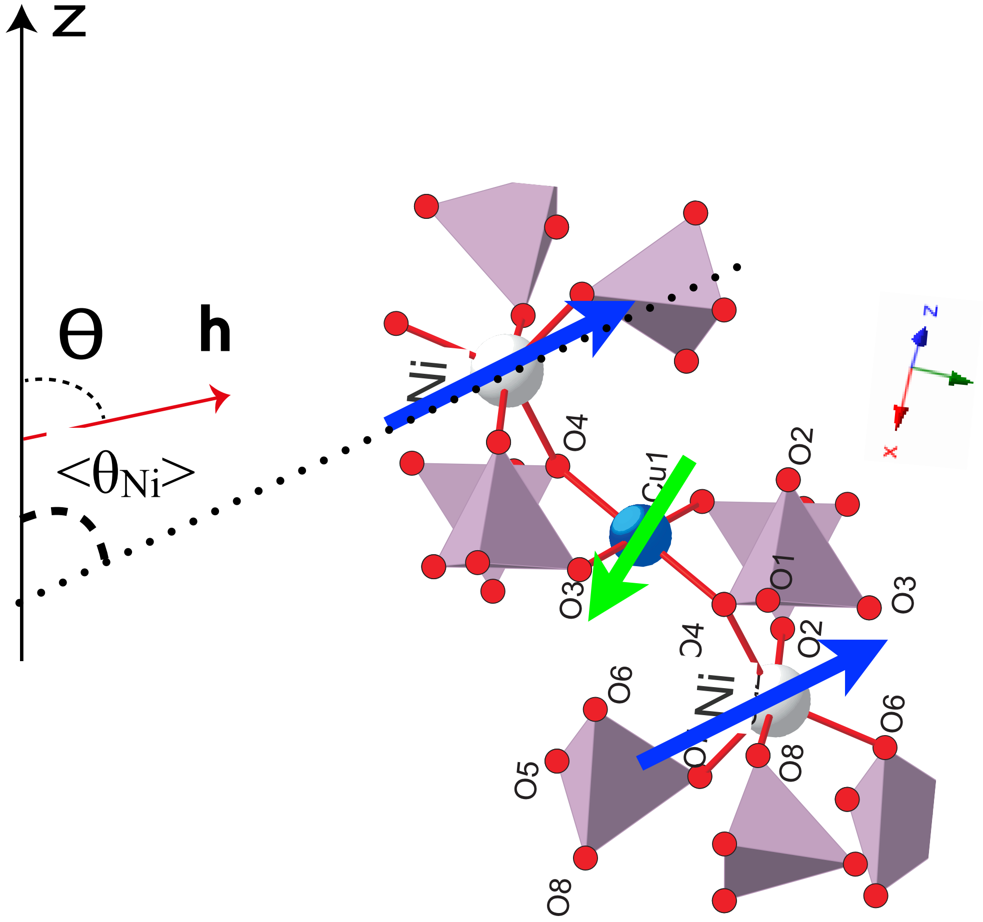

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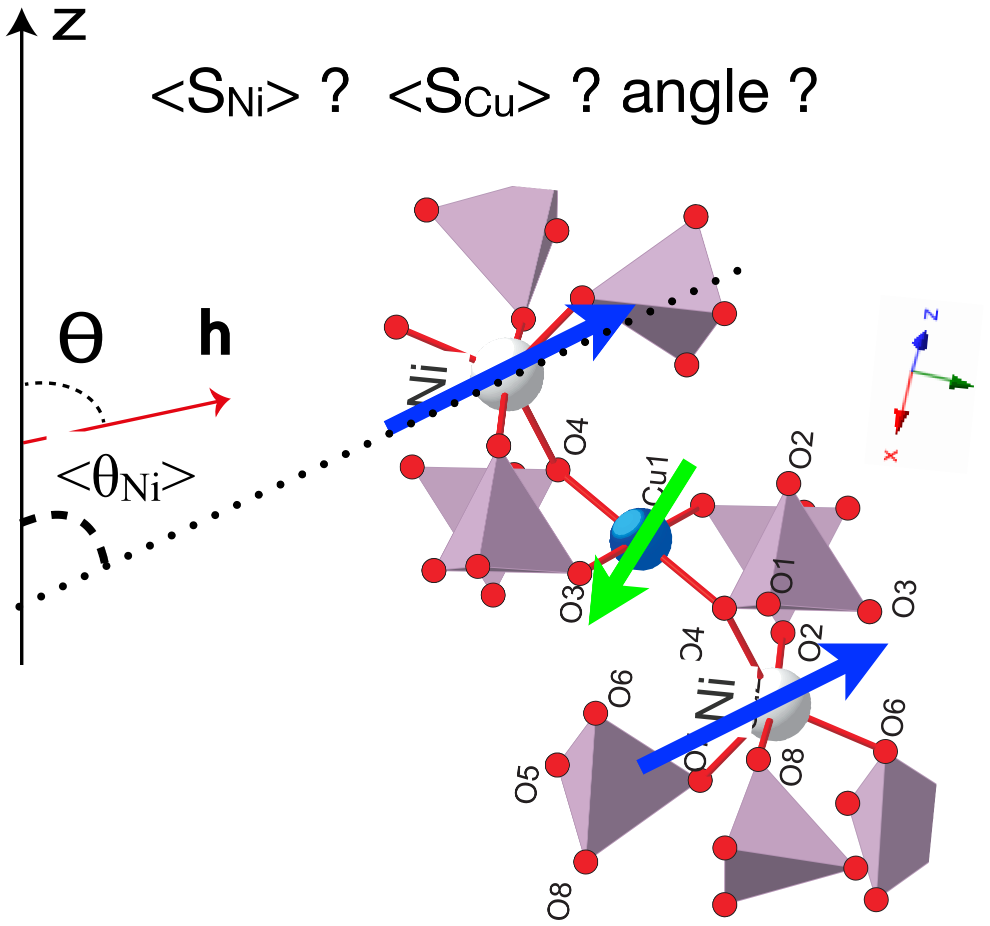

<S_{Ni}> ? <S_{Cu}> ? angle ?

Interplay between molecular field and anisotropy

$$H = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + d\sum_{i=1}^{3}(S_i^z)^2 - \mathbf{hS}$$

experimental values from
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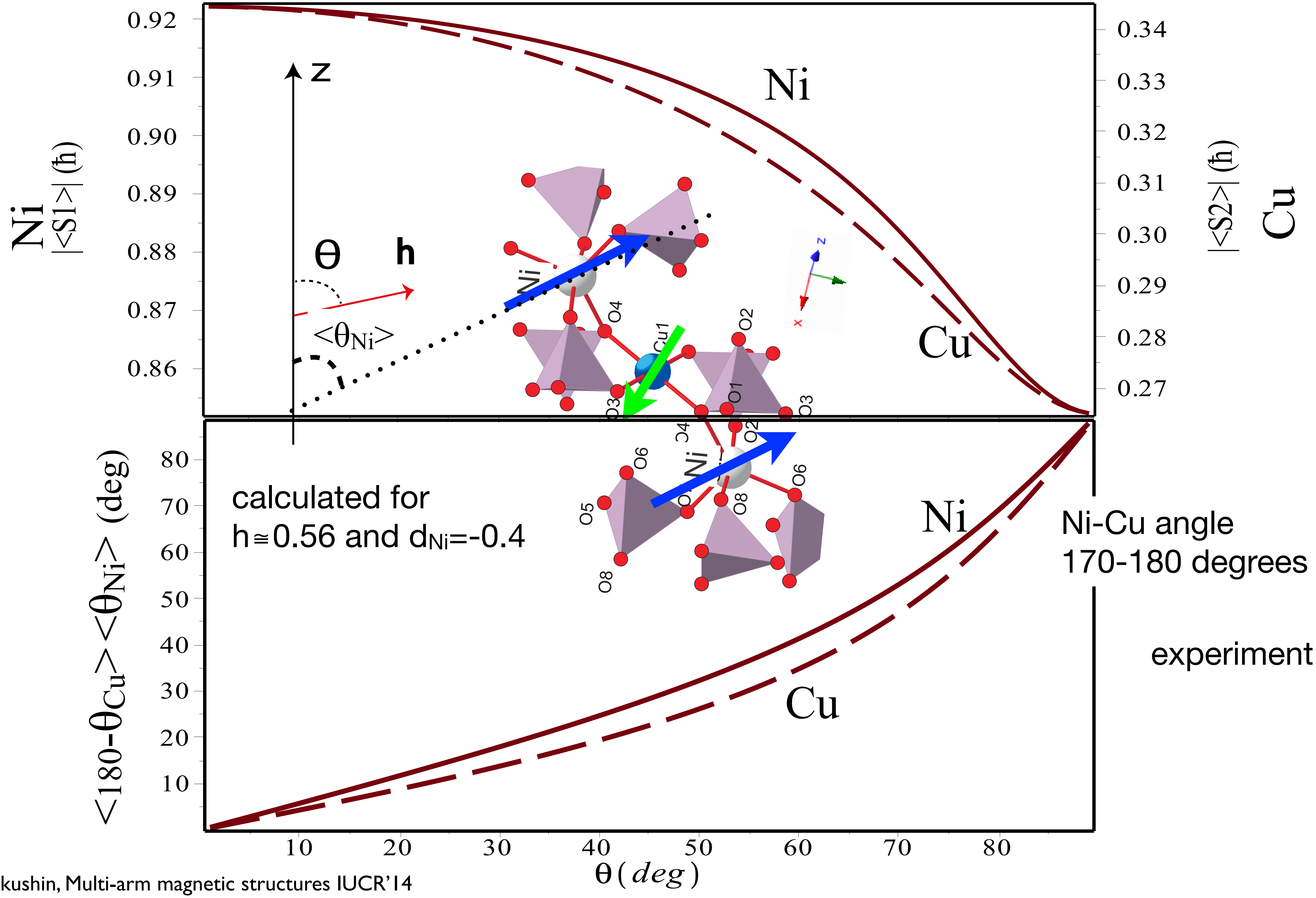

calculated for
h≅0.56 and d_{Ni}=-0.4

Ni-Cu angle
170-180 degrees

experiment: ≅160

Conclusions on: antiferromagnetic order in quantum spin trimer $Ca_3Cu_1Ni_2(PO_4)_4$

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- The relation between Shubnikov symmetry and representation analysis in k-vector formalism is examined in details

- multi-arm AFM is further supported by the calculations of the spin expt. values in the trimer Ni-Cu-Ni
  experiment: $\langle S_{Cu} \rangle$=0.31(1) $\langle S_{Ni} \rangle$ =0.945(5)
  theory (exact): $\langle S_{Cu} \rangle$=3/10 $\langle S_{Ni} \rangle$=9/10
  theory (realistic H): $\langle S_{Cu} \rangle$=0.305(35) $\langle S_{Ni} \rangle$=0.885(35)

Acknowledgements next slide

Acknowledgements

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Andrey Podlesnyak
Laboratory for Neutron Scattering, Paul Scherrer Institute PSI ; Oak Ridge Natl Lab, Quantum Condensed Matter Div, USA

Thank you!

k-vector and Shubnikov description

C2/c —> Sh. group C_a2/c

$\mathbf{A} = 2\mathbf{a} + 2\mathbf{c}, \mathbf{B} = -2\mathbf{b}, \mathbf{C} = -\mathbf{c}$

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(8f)-Ni and (4b)-Cu in *C2/c*
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		C-1 with $\mathbf{k}_1$& $\mathbf{k}_2$
	a, Å	17.68079
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(4i)	Ni11 xyz	0.62065 0.5353 0.96795
orbit 1	$m_xm_ym_z$	0.1539 -0.1984 -1.7917
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generated by **k**

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$\mathbf{t} = -(\frac{1}{2}, \frac{1}{2}, 0)$	$m_xm_ym_z$	-0.1539 0.1[illegible] [illegible]917	
	Cu1c xyz	$-\frac{1}{2}$ 0 [illegible]	
	$m_xm_ym_z$	-[illegible] [illegible].1426 0.3601	

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(2c)	Cu1 xyz	0 $\frac{1}{2}$ 0	0 0 0	Cu1 (8a)
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(2c)	Cu2 xyz	0 $\frac{1}{2}$ $\frac{1}{2}$		
	$m_xm_ym_z$	-0.3238 -0.1426 0.3601		
	Ni11c xyz	0.12065 0.0353 [illegible].96795	0.06033 0.23235 -0.8473	Ni11c (16g)
$\mathbf{t} = -(\frac{1}{2}, \frac{1}{2}, 0)$	$m_xm_ym_z$	-0.1539 0.1[illegible]917	-0.1456 -0.19843 -1.9466	
	Cu1c xyz	$-\frac{1}{2}$ 0 [illegible]	$-\frac{1}{4}$ $\frac{1}{4}$ -$\frac{1}{2}$	Cu1c (8b)
	$m_xm_ym_z$	-[illegible].1426 0.3601	-0.3063 -0.1426 -0.6860	

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	Cu1c xyz	$-\frac{1}{2}$ 0 [illegible]	$-\frac{1}{4}$ $\frac{1}{4}$ -$\frac{1}{2}$	Cu1c (8b)
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generated by Sh. group

generated by **k**

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$\mathbf{A}=2\mathbf{a}+2\mathbf{c}, \mathbf{B}=-2\mathbf{b}, \mathbf{C}=-\mathbf{c}$

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C_a2/c 15.91 BNS

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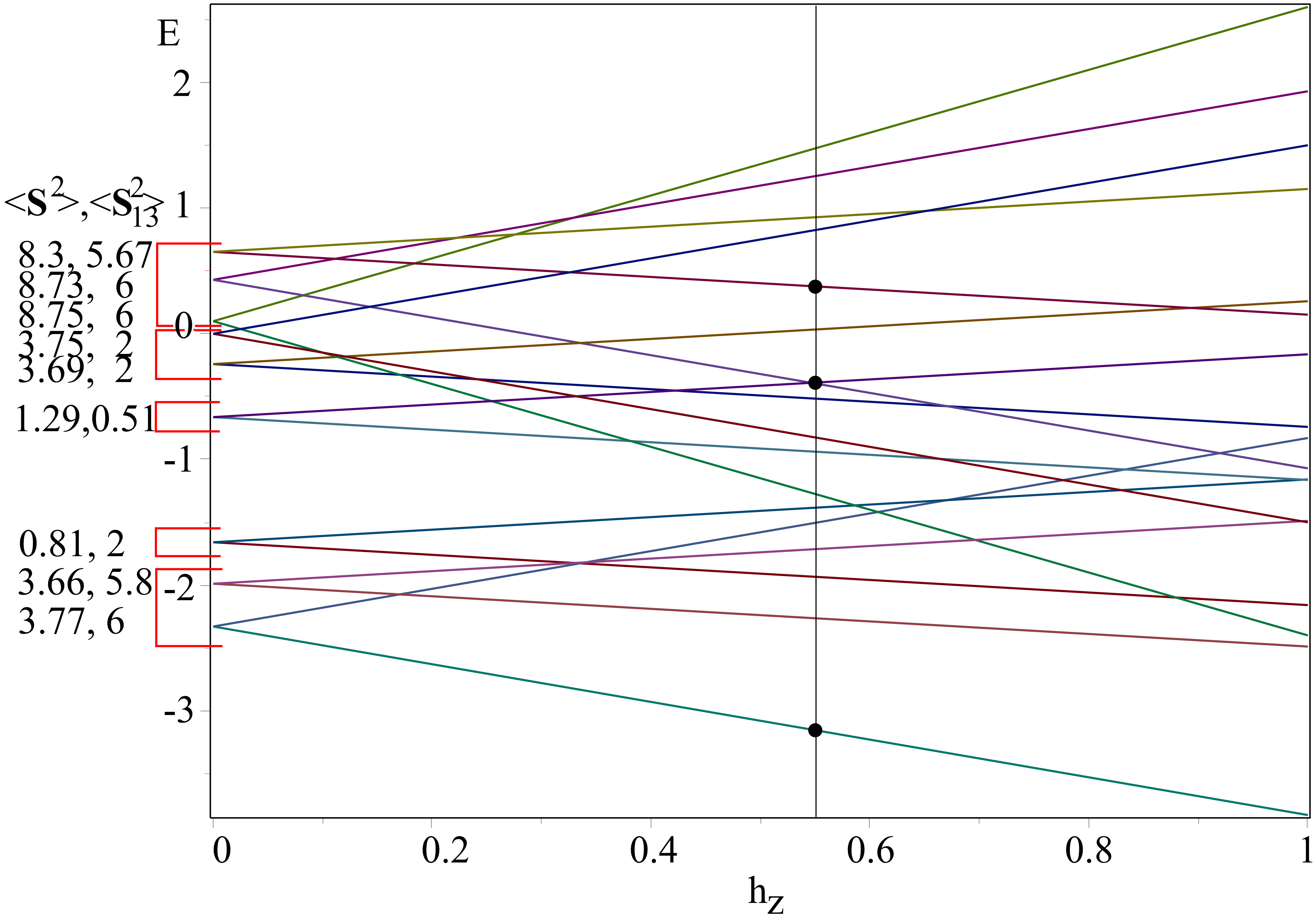
$$\mathbf{m}(\mathbf{t})=\mathbf{m}_0\cos(2\pi\mathbf{k}_1\mathbf{t})$$

Molecular field h_z



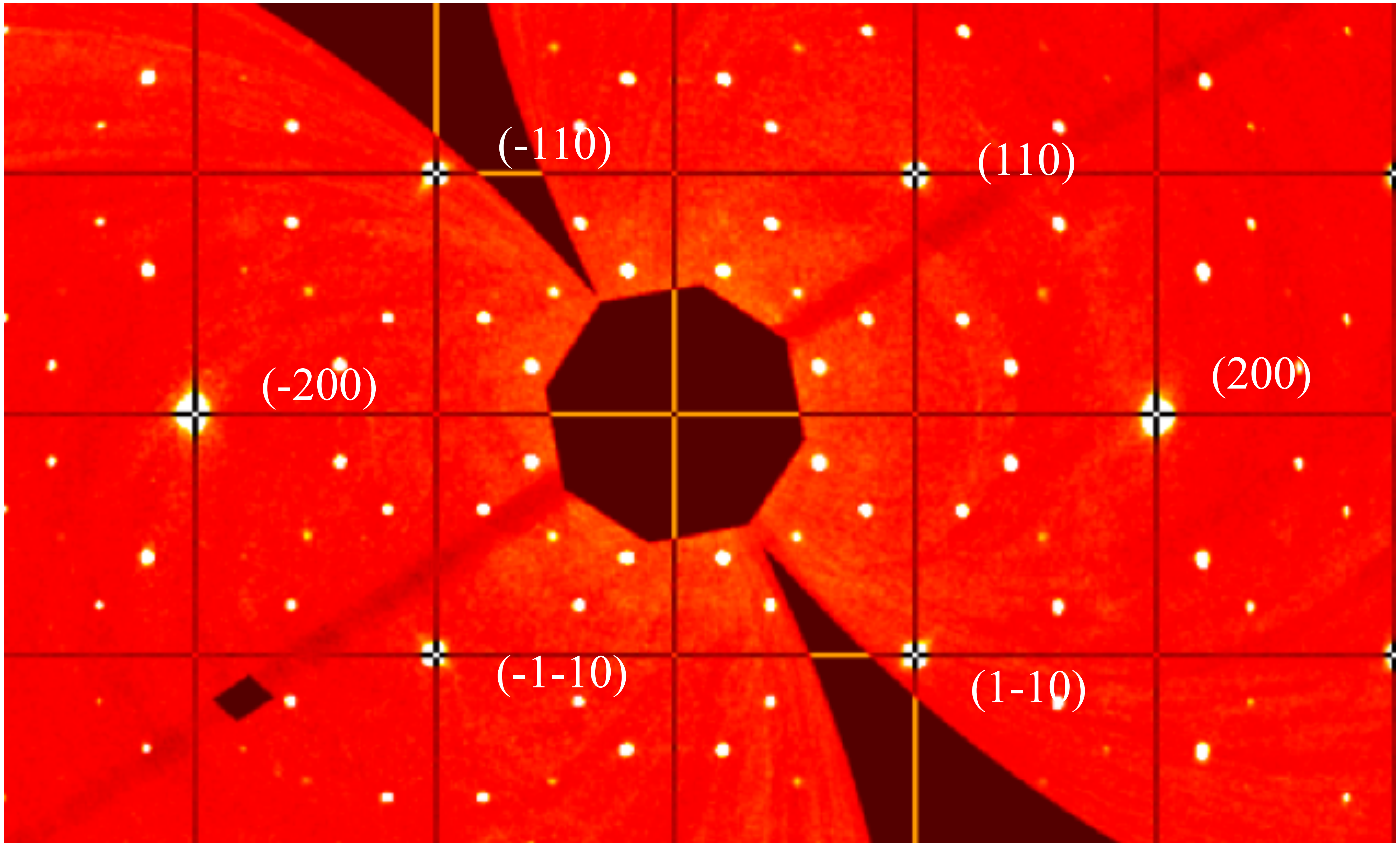
Example of modulated crystal structure

4-arms k-vector stars

$$\{\mathbf{k}_1\} = \{[\frac{2}{5}, \frac{1}{5}, 1]\}$$

$$\{\mathbf{k}_2\} = \{[\frac{1}{5}, \frac{2}{5}, \bar{1}]\}$$

superstructure satellites



the mesh is for the parent I4/mmm cell
T=300K, (hk0) plane of $Cs_yFe_{2-x}Se_2$

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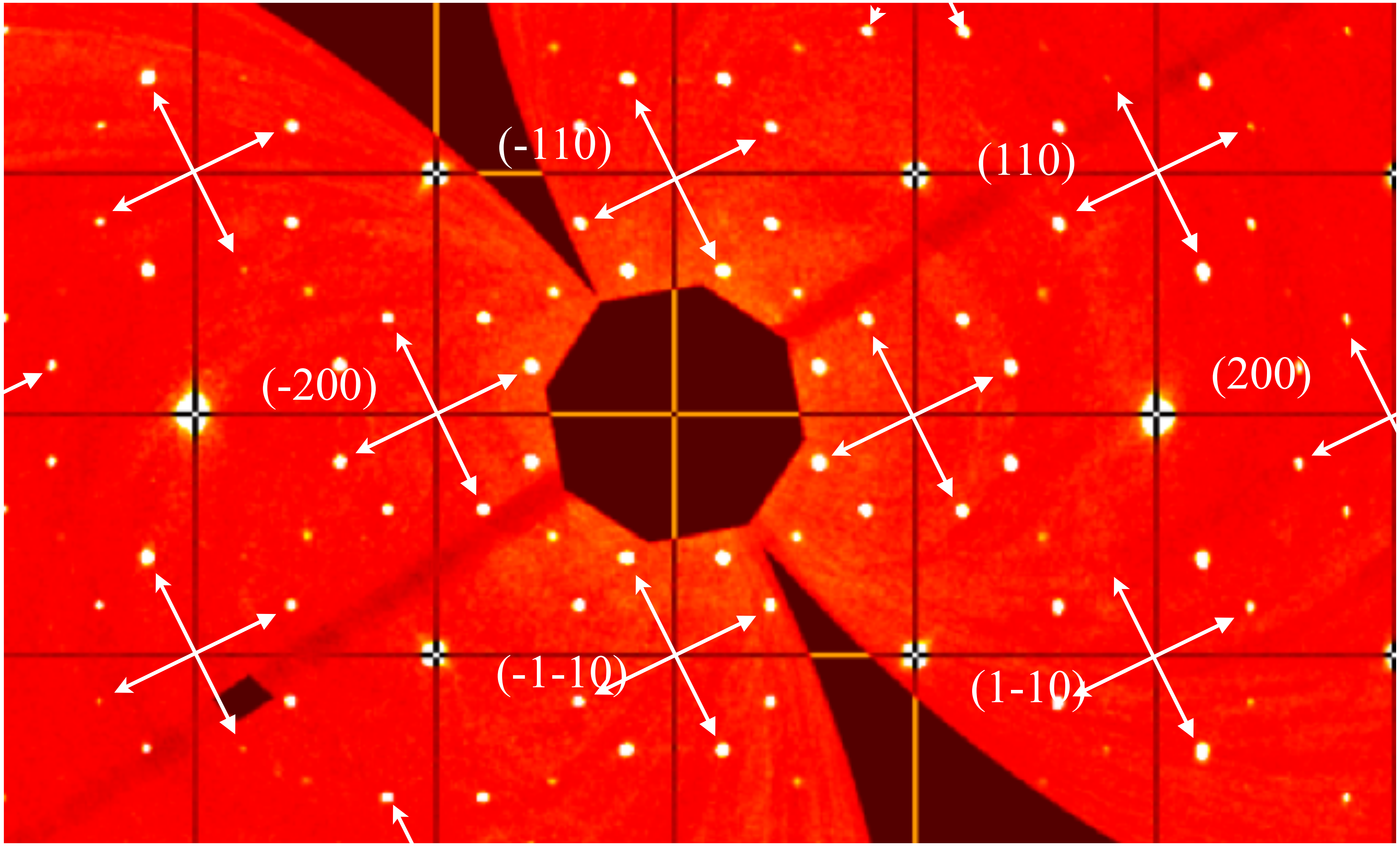
4-arms k-vector stars

$$\boxed{\{\mathbf{k}_1\} = \{[\frac{2}{5}, \frac{1}{5}, 1]\}}$$

$$\{\mathbf{k}_2\} = \{[\frac{1}{5}, \frac{2}{5}, \bar{1}]\}$$

superstructure satellites



the mesh is for the parent I4/mmm cell
T=300K, (hk0) plane of $Cs_yFe_{2-x}Se_2$

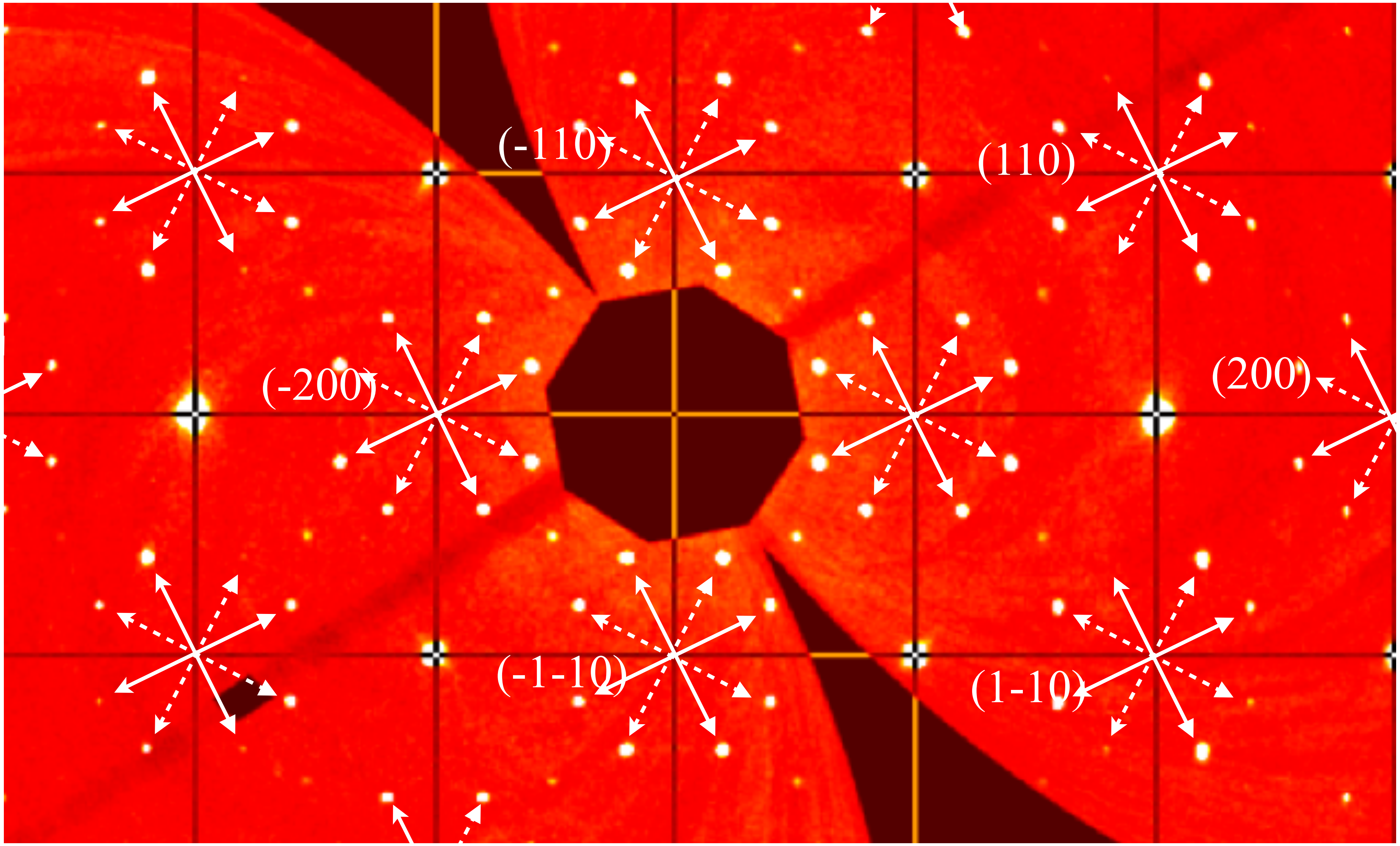
Example of modulated crystal structure

4-arms k-vector stars

$$\{\mathbf{k}_1\} = \{[\frac{2}{5}, \frac{1}{5}, 1]\}$$

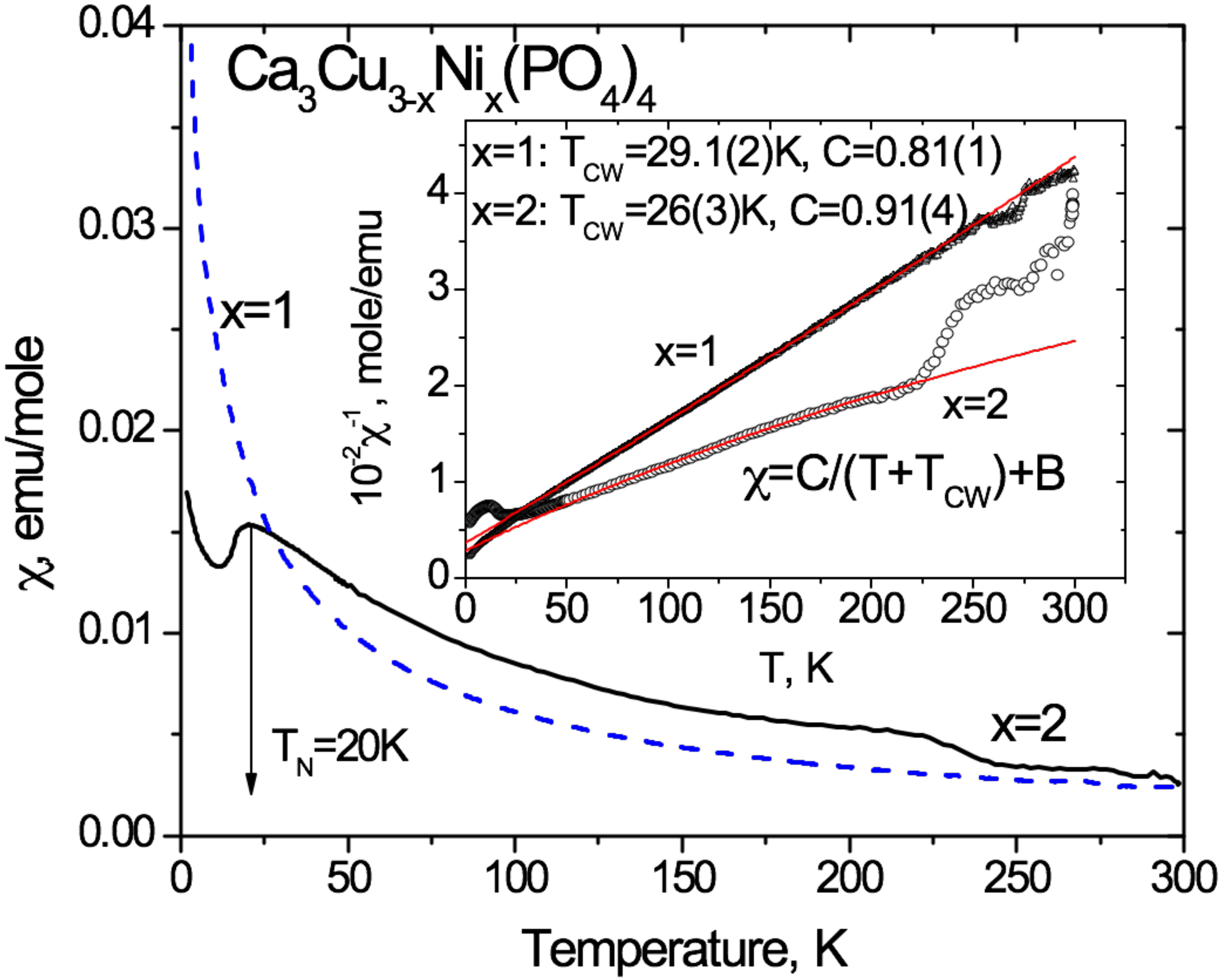
$$\{\mathbf{k}_2\} = \{[\frac{1}{5}, \frac{2}{5}, \bar{1}]\}$$

superstructure satellites



the mesh is for the parent I4/mmm cell
T=300K, (hk0) plane of $Cs_yFe_{2-x}Se_2$

Magnetic susceptibility

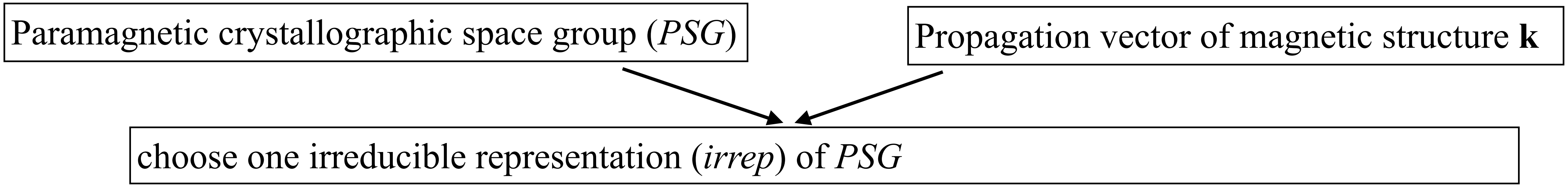


Relation of magnetic Shubnikov symmetry and irreducible representation of space group

Paramagnetic crystallographic space group (*PSG*)

Propagation vector of magnetic structure **k**

Relation of magnetic Shubnikov symmetry and irreducible representation of space group



Paramagnetic crystallographic space group (*PSG*)

Propagation vector of magnetic structure **k**

choose one irreducible representation (*irrep*) of *PSG*

Relation of magnetic Shubnikov symmetry and irreducible representation of space group

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choose one irreducible representation (*irrep*) of *PSG*

magnetic symmetry

representatio

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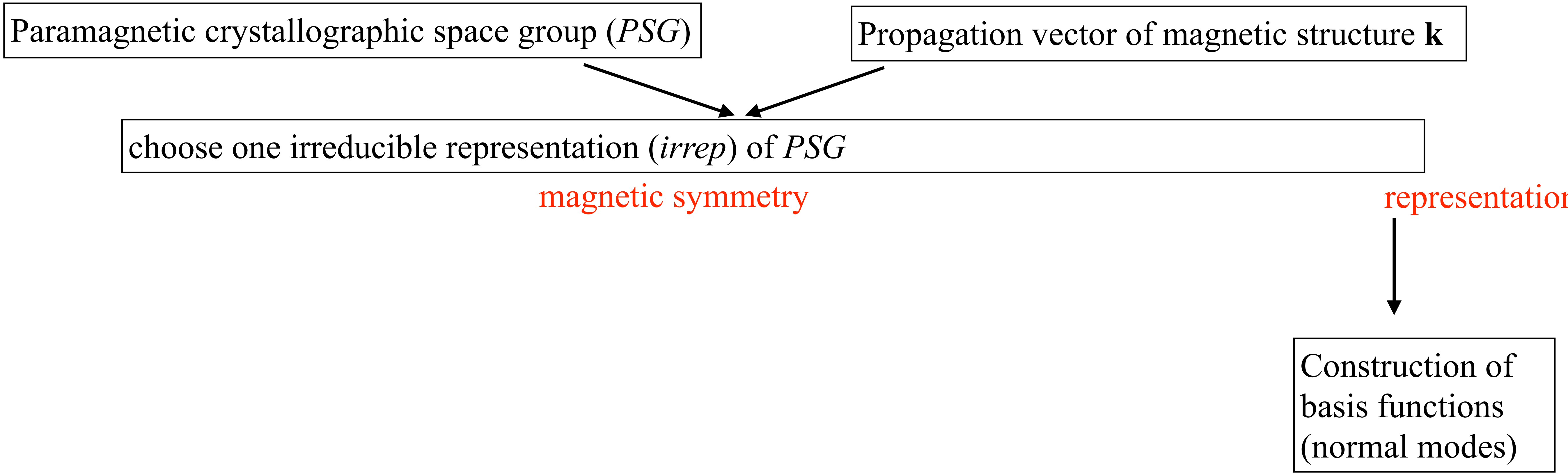

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magnetic symmetry

representatio

Construction of
basis functions
(normal modes)

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constrains on the components of basis function for >1D irrep

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Magnetic structure made from linear combination of basis functions (normal modes)

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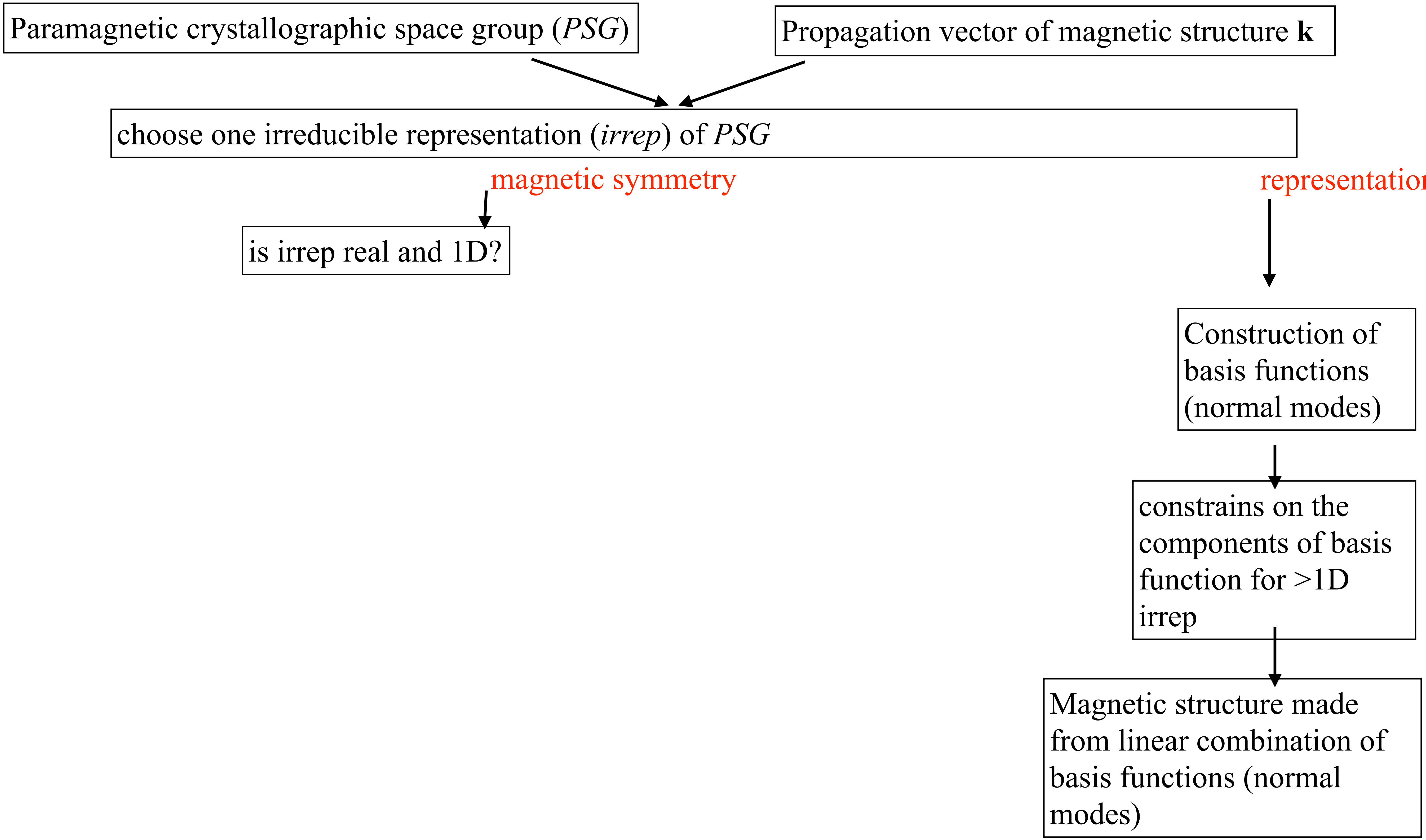

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is irrep real and 1D?

representatio

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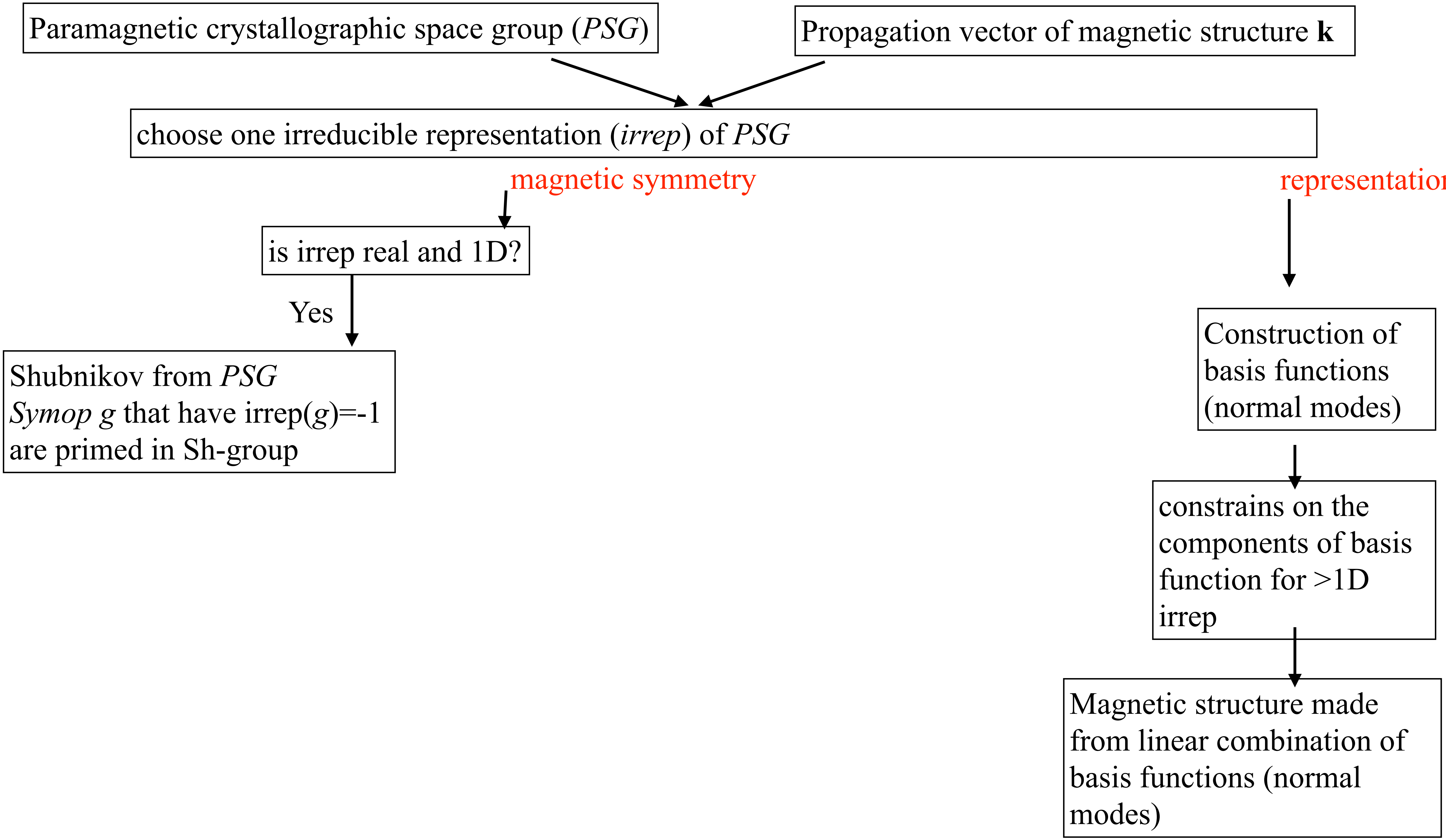

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Shubnikov from *PSG*
Symop g that have irrep(*g*)=-1 are primed in Sh-group

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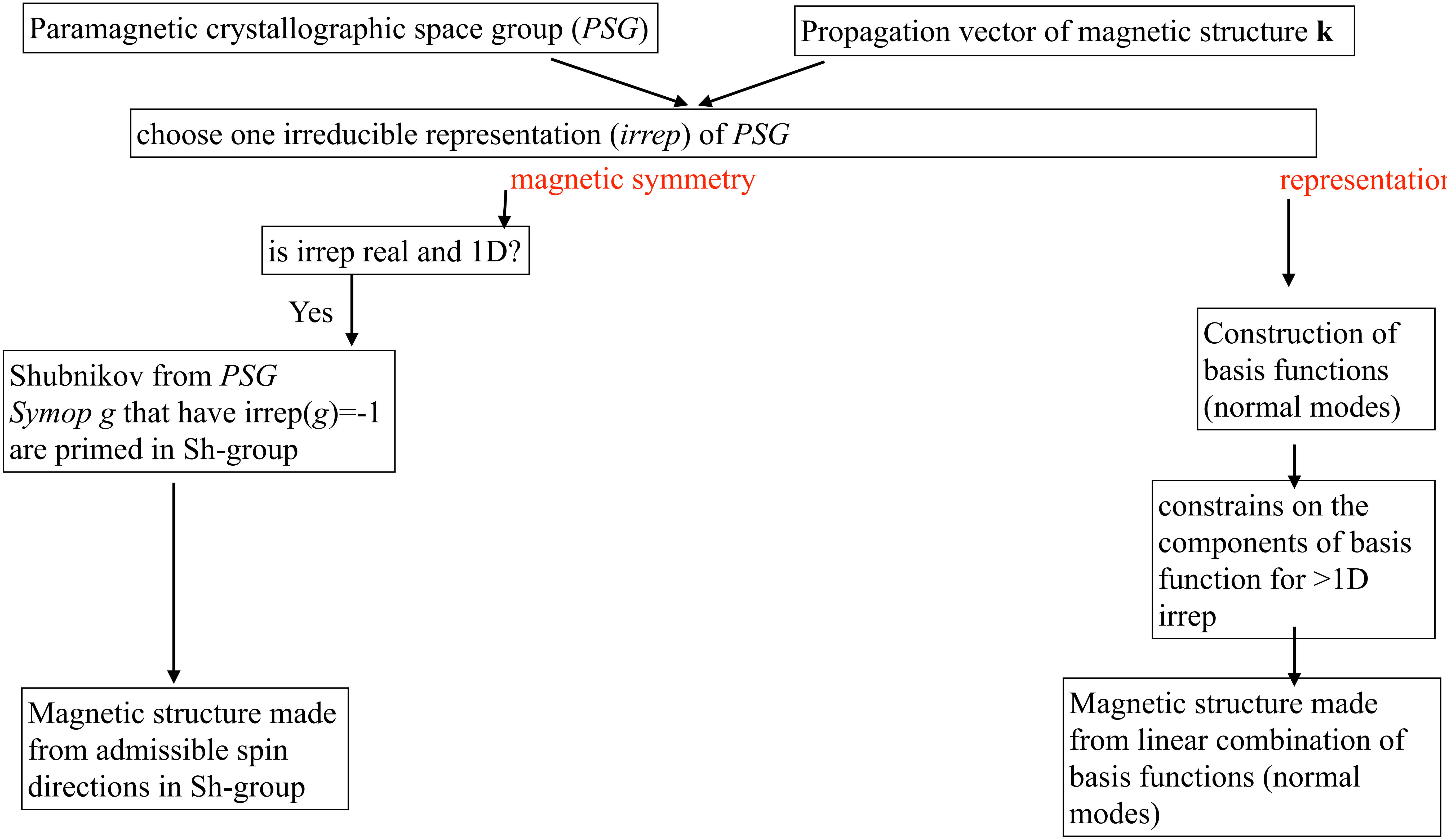

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Magnetic structure made from admissible spin directions in Sh-group

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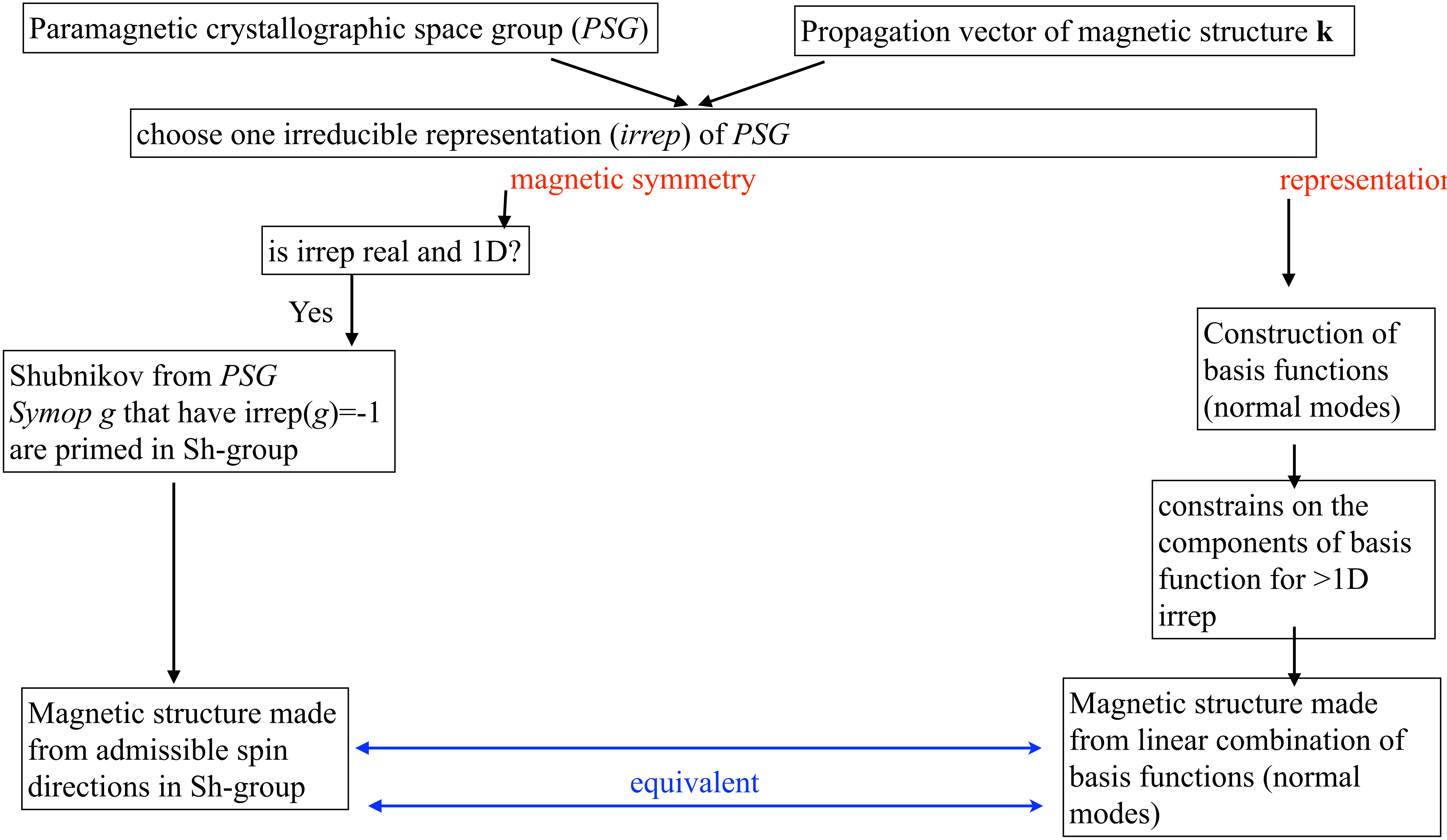

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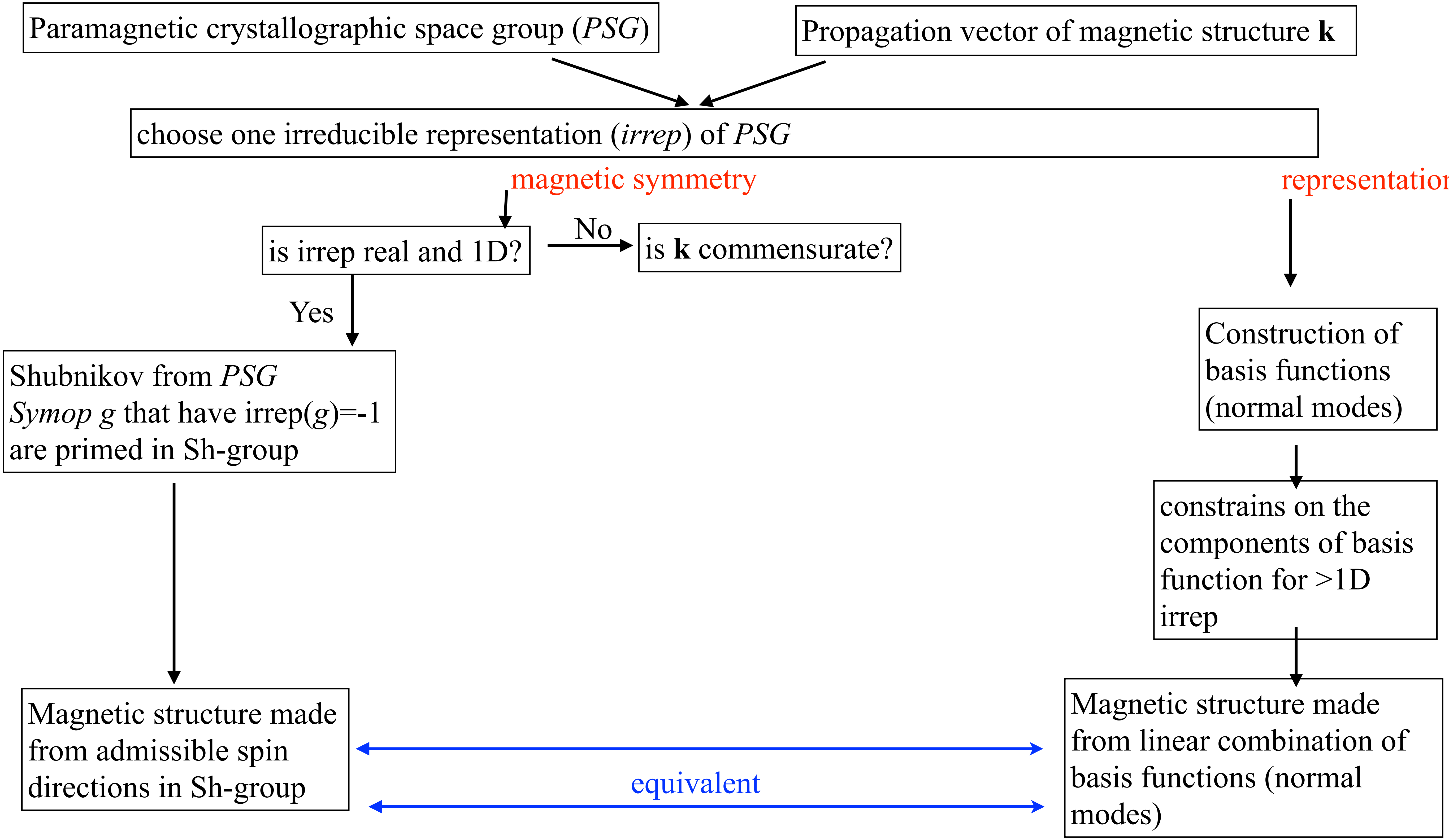
Magnetic structure made from linear combination of basis functions (normal modes)

equivalent

Relation of magnetic Shubnikov symmetry and irreducible representation of space group



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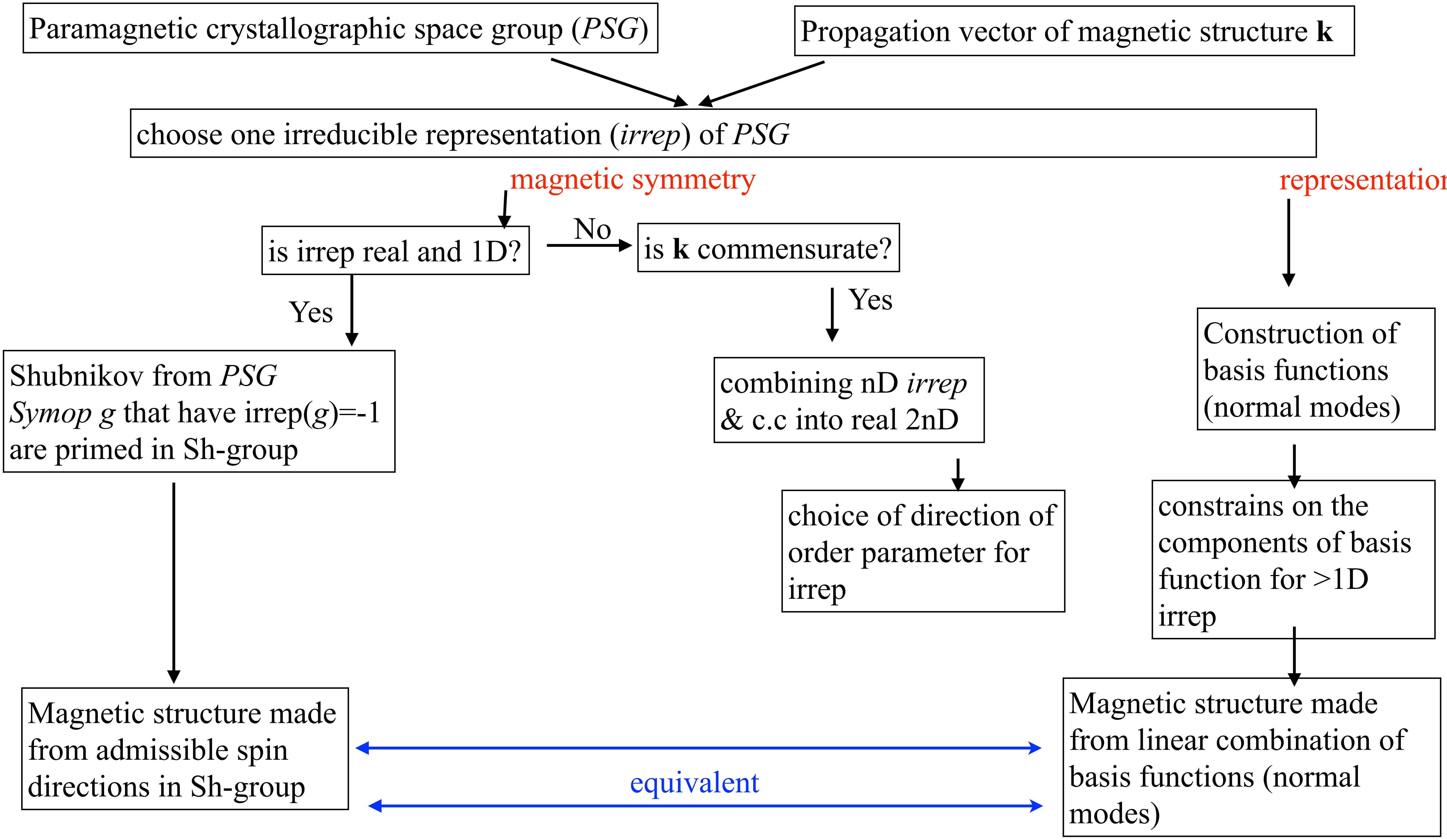

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is **k** commensurate?

Yes

combining nD *irrep* & c.c into real 2nD

choice of direction of order parameter for irrep

Yes

Shubnikov from *PSG* *Symop g* that have irrep(*g*)=-1 are primed in Sh-group

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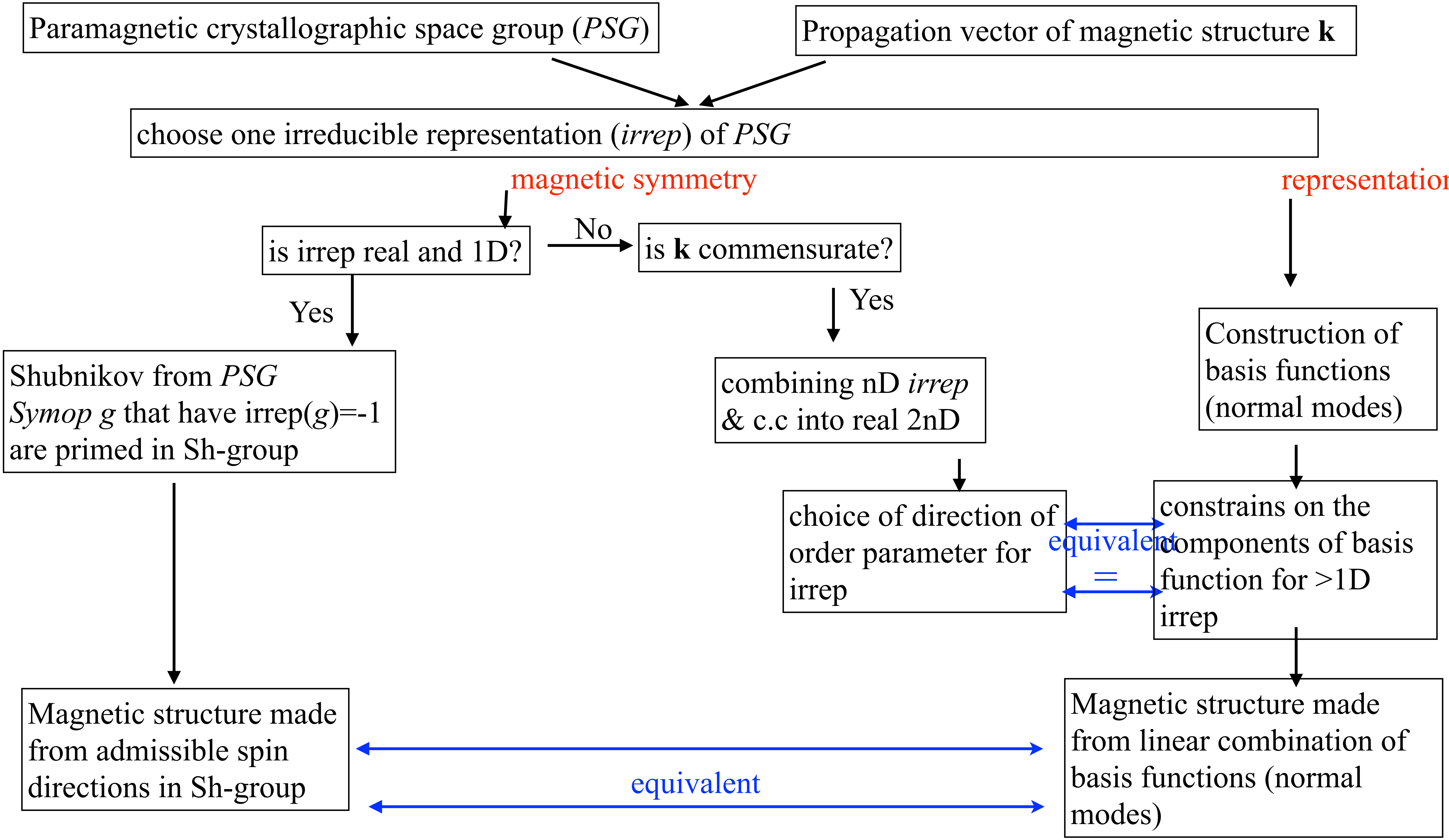

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Construction of
basis functions
(normal modes)

choice of direction of
order parameter for
irrep

equivalent

=

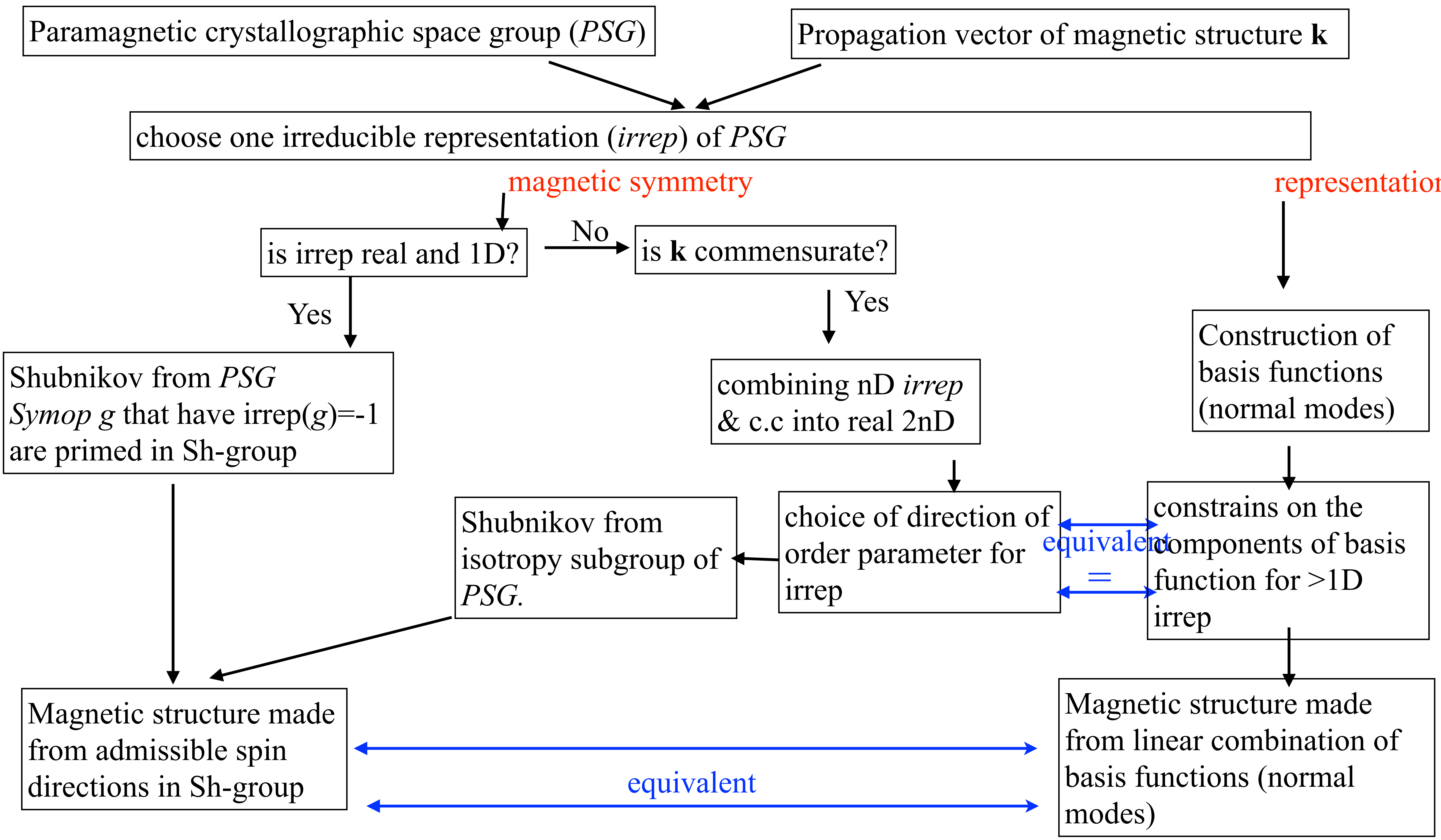
constrains on the
components of basis
function for >1D
irrep

Magnetic structure made
from admissible spin
directions in Sh-group

equivalent

Magnetic structure made
from linear combination of
basis functions (normal
modes)

Relation of magnetic Shubnikov symmetry and irreducible representation of space group



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combining nD *irrep* & c.c into real 2nD

Shubnikov from isotropy subgroup of *PSG*.

choice of direction of order parameter for irrep

equivalent

=

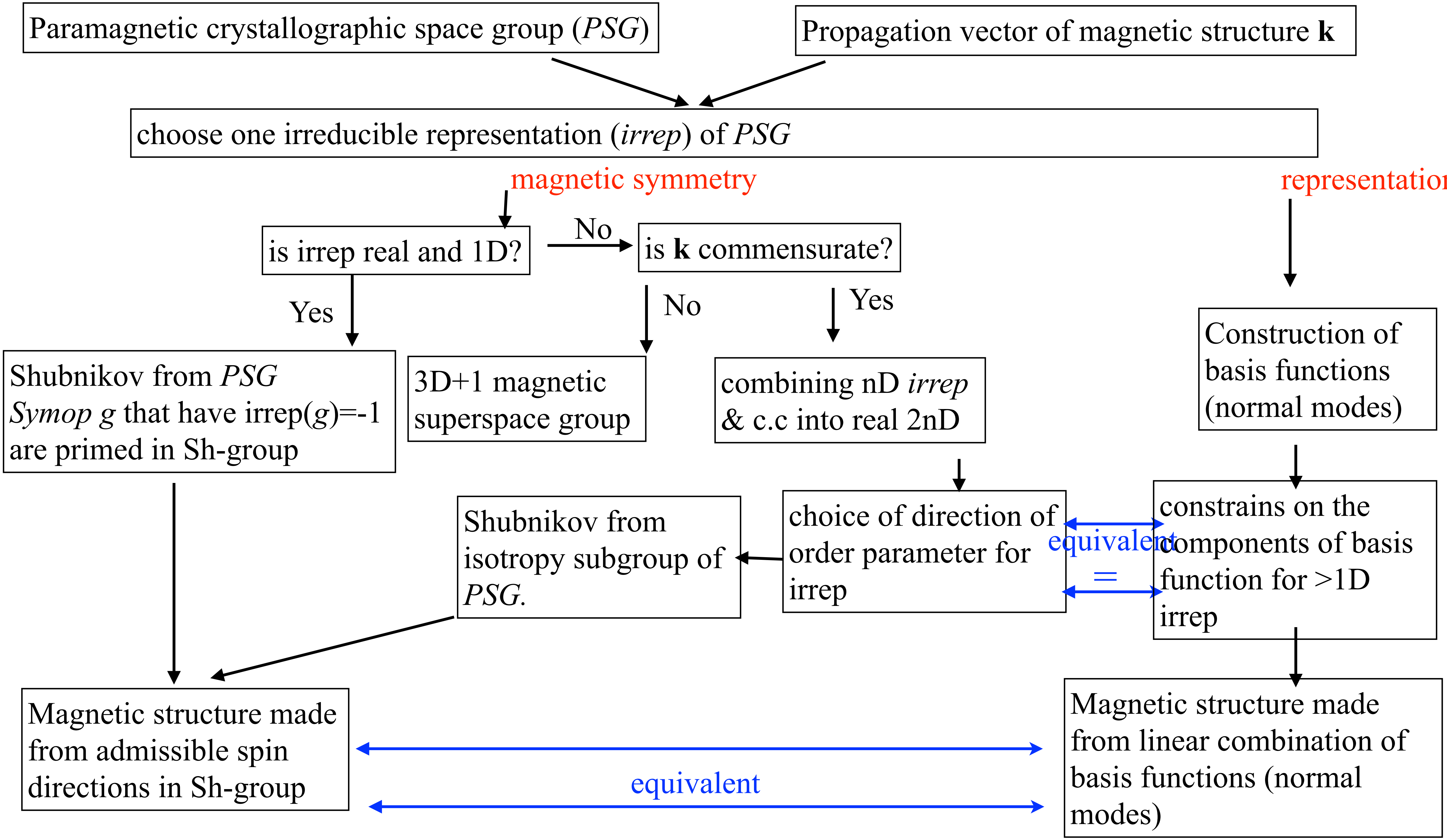
constrains on the components of basis function for >1D irrep

Magnetic structure made from admissible spin directions in Sh-group

equivalent

Magnetic structure made from linear combination of basis functions (normal modes)

Relation of magnetic Shubnikov symmetry and irreducible representation of space group



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choose one irreducible representation (*irrep*) of *PSG*

magnetic symmetry

representatio

is irrep real and 1D?

No

is **k** commensurate?

Yes

No

Yes

Shubnikov from *PSG*
Symop g that have irrep(g)=-1 are primed in Sh-group

3D+1 magnetic superspace group

combining nD *irrep* & c.c into real 2nD

Construction of basis functions (normal modes)

Shubnikov from isotropy subgroup of *PSG*.

choice of direction of order parameter for irrep

equivalent

=

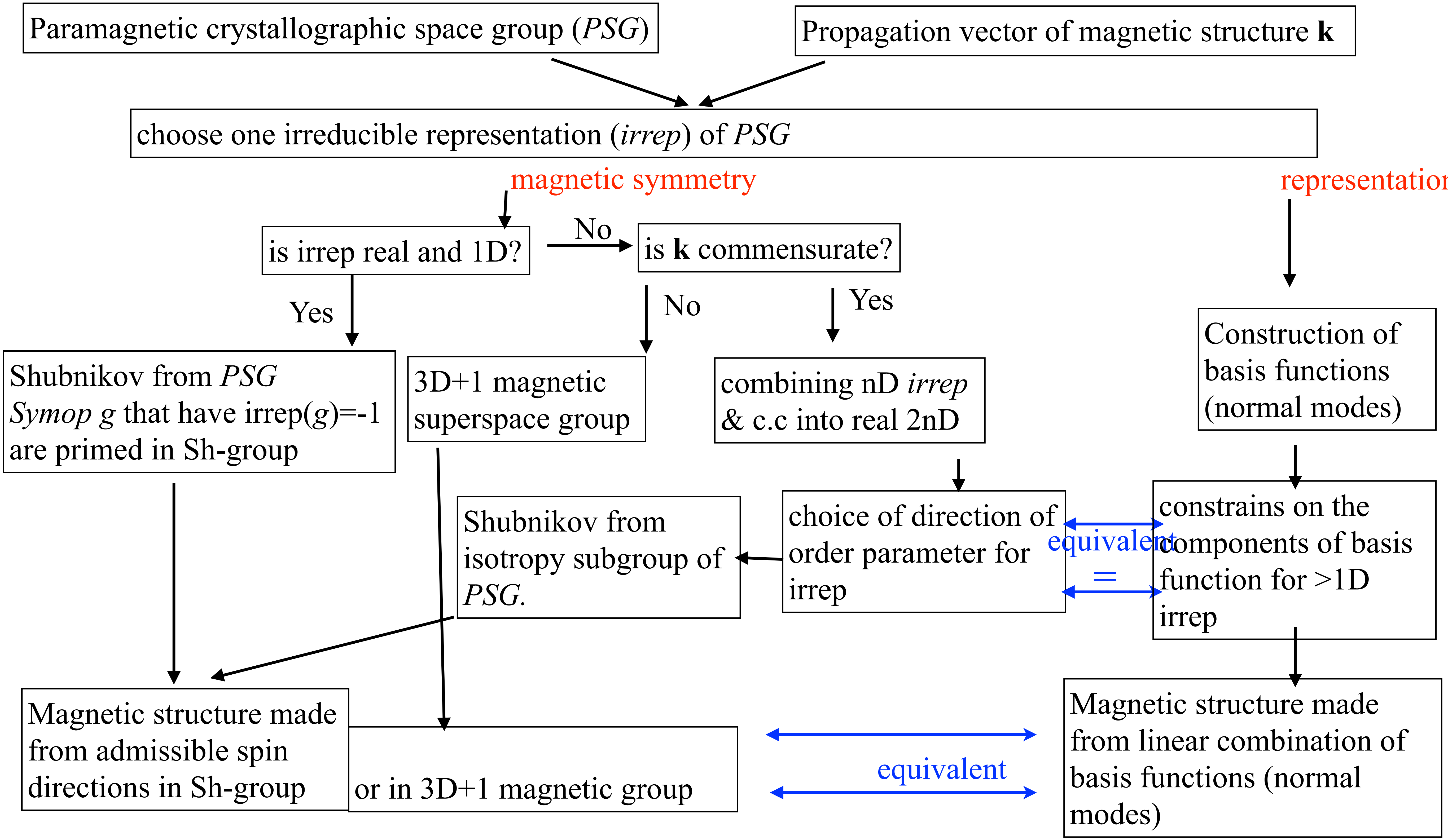
constrains on the components of basis function for >1D irrep

Magnetic structure made from admissible spin directions in Sh-group

equivalent

Magnetic structure made from linear combination of basis functions (normal modes)

Relation of magnetic Shubnikov symmetry and irreducible representation of space group



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is irrep real and 1D?

No

is **k** commensurate?

Yes

No

Yes

Shubnikov from *PSG*
Symop g that have irrep(*g*)=-1 are primed in Sh-group

3D+1 magnetic superspace group

combining nD *irrep* & c.c into real 2nD

Construction of basis functions (normal modes)

Shubnikov from isotropy subgroup of *PSG.*

choice of direction of order parameter for irrep

equivalent

=

constrains on the components of basis function for >1D irrep

Magnetic structure made from admissible spin directions in Sh-group

or in 3D+1 magnetic group

equivalent

Magnetic structure made from linear combination of basis functions (normal modes)