Deformation Modes according to Irreducible Representations

Jürgen K. Gutmann and Horst Böhm

Institut für Geowissenschaften, Johannes-Gutenberg-Universität Mainz, D-55099 Mainz, Germany.

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Introduction

The symmetry of a crystal with ideal structure can be described by one of 230 space groups. The connection between phase transitions and symmetry changes was investigated by L.D.LANDAU [1]: mostly there is a group-subgroup relation between the involved space groups. The loss of symmetry from the high symmetry phase to the low-symmetry phase can be classified by the irreducible representations of the high-symmetry space group. Especially for second order phase transitions it is true under certain conditions that the loss of symmetry elements is effected by a *single* irreducible representation of the high-symmetry space group. This fact provides models for the structure determination of the low-symmetry phase, because it narrows down the number of possible solutions.

Experimental background and motivation

Experimental starting point of the investigations is a phase transition in Co-åkermanite $Ca_2CoSi_2O_7$. This crystal has basic melilite structure. Its space group symmetry is $P\bar{4}2_1m$ at temperatures higher than T_1=498(1) K [2]. The rapidly growing amount of independent parameters, which have to be refined in large superstructures of incommensurate phases, gives rise to the following general question: Does group theory help finding the correct solution, if *one* or only *a few*, but *not all* irreducible representations of a given high-symmetry space group are taken into account?

Results

This poster presents two important contributions for solving incommensurate structures:

- A ***graphically oriented* and therefore *calculation-free* method** for converting irreducible representations of space groups into corresponding atomic distortion fields.
- Irreducible representations of space groups can be classified by wave vectors **k** in the first BRILLOUIN-zone. For an example space group ($P\bar{4}2_1m$), **all irreducible representations, induced by a wave vector k = (*q*,*q*,0)** with $q\in$]0,½[, have been calculated according to the method by G.YA.LYUBARSKII [3], [4]. Here, representation matrices for each space group element are explicitly given for this infinite number of irreducible representations.

By combining these two results it can easily be shown for the chosen example that the obtained displacement field according to irreducible representations are plane waves with wave vector **k**.

Projection operators

Mathematical basis for obtaining atomic distortion fields from irreducible representations are projection operators

$$\mathsf{P}_{ij}^{\alpha} = \frac{D_\alpha}{|G|}\sum_{g\in G}\left[\Gamma_{ij}^{\alpha}(g)\right]^{*}\mathsf{O}(g) \qquad (1)$$

with $1\le i,j\le D_\alpha$, which projections according to the D_α-dimensional irreducible representation Γ^α of the underlying group G. The factor $\left[\Gamma_{ij}^{\alpha}(g)\right]^{*}$ is the complex conjugate of the i,*j*-th matrix element in the representation matrix $\Gamma^\alpha(g)$. The linear operator $\mathsf{O}(g)$ describes the acting of the group element g onto the mathematical objects (e.g. vector-valued functions) which are to be projected. Therefore the mathematical definition of $\mathsf{O}(g)$ crucially depends on the considered objects.

Vector-valued functions $\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x})$

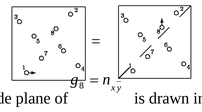
Key for a quick and calculation-free evaluation of equation (1) in the application on space groups are a special kind of vector-valued functions $\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x})$ with a discrete domain of definition $L^\alpha(\mathbf{x}_1)$, which finally allow a graphically oriented determination of displacement fields. Choosing an arbitrary position $\mathbf{x}_1$ in a crystal, the finite set $L^\alpha(\mathbf{x}_1)$ consists of all points $\mathbf{x}_j = g_j\mathbf{x}_1$ of the corresponding site of $\mathbf{x}_1$ within a primitive cell (or supercell respectively depending on Γ^α). Then $\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x})$ is defined by

$$\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x}) = \begin{cases}\mathbf{y} & \text{if } \mathbf{x}=\mathbf{x}_i\\ 0 & \text{else}\end{cases} \qquad (2)$$

To illustrate this definition, a primitive cell in space group $P\bar{4}2_1m$ is considered as an example: If $\mathbf{x}_1$ is chosen as a general point, then the space group elements $g_1=1$, $g_2=2_z$, $g_3=\bar{4}_z$, $g_4=\bar{4}_z^3$, $g_5=2_{1,y}$, $g_6=2_{1,x}$, $g_7=m_{s,xy}$, $g_8=n_{x\bar{y}}$ induce an eight-elementary set $L^\alpha(\mathbf{x}_1)$ which finally allow a graphically oriented determination of displacement fields. Now a symbolic diagram notation is introduced, for instance,

$\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x}) =$  (3)

where $\mathbf{y}=\frac{1}{8}\mathbf{a}_1$ is chosen as displayed. The operation of $\mathsf{O}(g)$ onto $\overset{\rho}{V}_{i,\mathbf{y}}(\mathbf{x})$ is carried out mathematically or graphically, for example, $\mathsf{O}(n_{x\bar{y}})\overset{\rho}{V}_{1,\mathbf{y}}(\mathbf{x}) = \overset{\rho}{V}_{8,m_{x,y}\mathbf{y}}(\mathbf{x})$ becomes

$\mathsf{O}(n_{x\bar{y}})$  (4)

$g_8 = n_{x\bar{y}}$

in diagram notation, where the glide plane of is drawn in.

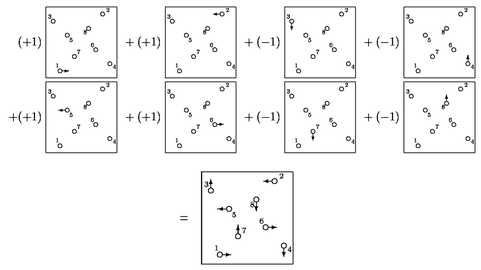
Obtaining atomic displacement fields

The following table lists all irreducible representations of $P\bar{4}2_1m$ which are induced by $\mathbf{k}=(0,0,0)$ and which therefore leave all primitive cells unchanged:

g =	$g_1=1$	$g_2=2_z$	$g_3=\bar{4}_z$	$g_4=\bar{4}_z^3$	$g_5=2_{1,y}$	$g_6=2_{1,x}$	$g_7=m_{s,xy}$	$g_8=n_{x\bar{y}}$
$\Gamma^1(g)$	1	1	1		1		1	
$\Gamma^2(g)$	1	1	-1		1		–1	
$\Gamma^3(g)$	1	1	-1		-1		1	
$\Gamma^4(g)$	1	1	1		-1		–1	
$\Gamma^5(g)$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$

Choosing the non-trivial irreducible representation Γ^2 and $\mathbf{y}=\mathbf{a}_1$, equation (1) can directly be evaluated:

$\mathsf{P}_{11}^{2}\overset{\rho}{V}_{1,\mathbf{a}_1}(\mathbf{x}) \overset{1}{=} \frac{1}{8}\sum_{g\in G}\left[\Gamma_{11}^{2}(g)\right]^{*}\mathsf{O}(g)\overset{\rho}{V}_{1,\mathbf{a}_1}(\mathbf{x}) =$



Obviously, distortion fields according to *non-trivial* irreducible representations can *directly* be obtained from the trivial ones by inverting all displacement arrows according to the local displacement factor $\left[\Gamma_{ij}^{\alpha}(g)\right]$ (respectively by shortening, if $\Gamma_{ij}^{\alpha}(g)\neq\pm1$). This principle is illustrated by the following figures, which display 3 linear independent distortion modes per diagram. The 3 modes in each figure are induced by 3 linear independent initial displacement vectors **y**:

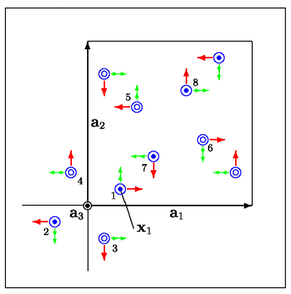


Figure 1: Three linear independent displacement modes from Γ^1.

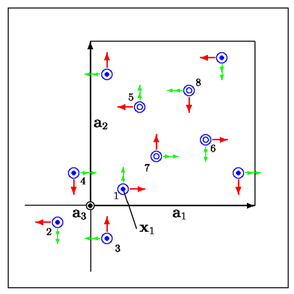


Figure 2: Three linear independent displacement modes from Γ^2.

Irreducible represention from $\mathbf{k}=(\frac{1}{3},\frac{1}{3},0)$ in $P\bar{4}2_1m$

Appplying the method by LYUBARSKII [3] for determining irreducible representations of space groups, two 4-dimensional irreducible representations $\Sigma^{q,1}$ (upper signs) and $\Sigma^{q,2}$ (lower signs) can *analytically* be calculated for any *q*-value in]0,½[:

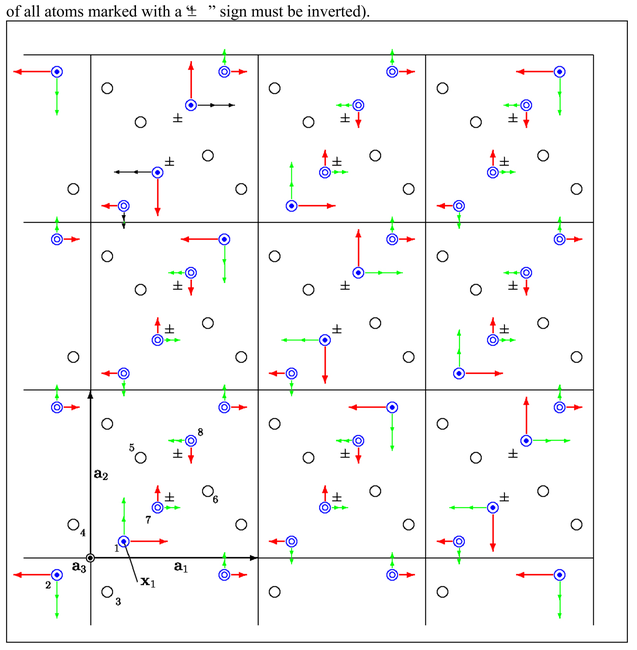
Space group elements have the form $g=t_\mathbf{a}g_0$ with lattice translation part $t_\mathbf{a}=n_1t_y+n_2t_y+n_3t_z$

$\Sigma^{q,\nu}(t_\mathbf{a}) = \begin{pmatrix}B_{n_1+n_2} & \\ & B_{n_1-n_2}\end{pmatrix}$	$\Sigma^{q,\nu}(t_\mathbf{a}2_z) = \begin{pmatrix}B_{n_1+n_2}M & \\ & B_{n_1-n_2}M\end{pmatrix}$
$\Sigma^{q,\nu}(t_\mathbf{a}\bar{4}_z) = \begin{pmatrix} & B_{n_1+n_2}M \\ B_{n_1-n_2} & \end{pmatrix}$	$\Sigma^{q,\nu}(t_\mathbf{a}\bar{4}_z^3) = \begin{pmatrix} & B_{n_1+n_2} \\ B_{n_1-n_2}M & \end{pmatrix}$
$\Sigma^{q,\nu}(t_\mathbf{a}2_{1,y}) = \pm\begin{pmatrix} & B_{n_1+n_2+1}M \\ B_{n_1-n_2}M & \end{pmatrix}$	$\Sigma^{q,\nu}(t_\mathbf{a}2_{1,x}) \pm \begin{pmatrix} & B_{n_1+n_2+1} \\ B_{n_1-n_2} & \end{pmatrix}$
$\Sigma^{q,\nu}(t_\mathbf{a}m_{s,xy}) = \pm\begin{pmatrix}B_{n_1+n_2+1}M & \\ & B_{n_1-n_2}\end{pmatrix}$	$\Sigma^{q,\nu}(t_\mathbf{a}n_{x\bar{y}}) \pm \begin{pmatrix}B_{n_1+n_2+1} & \\ & B_{n_1-n_2}M\end{pmatrix}$

where $B_j=\begin{pmatrix}\cos(2\pi qj) & \sin(2\pi qj)\\ -\sin(2\pi qj) & \cos(2\pi qj)\end{pmatrix}$ and $B_jM=\begin{pmatrix}\cos(2\pi qj) & -\sin(2\pi qj)\\ -\sin(2\pi qj) & -\cos(2\pi qj)\end{pmatrix}$.

Atomic displacement fields from $\mathbf{k}=(\frac{1}{3},\frac{1}{3},0)$ in $P\bar{4}2_1m$

Starting from $\mathbf{k}=(\frac{1}{3},\frac{1}{3},0)$, 72 representation matrices can be determined for each of the two representations $\Sigma^{\frac{1}{3},\nu}$, $\nu=1,2$ which result in 48 linear independent atomic displacement modes per representation within a $3\times3\times1$ supercell. As an example, the following figure displays 3 projections $\mathsf{P}_{11}^{\alpha}\overset{\rho}{V}_{1,\mathbf{y}}(\mathbf{x})$ from $\alpha=\Sigma^{\frac{1}{3},1}$, and 3 from $\alpha=\Sigma^{\frac{1}{3},2}$ (displacement vectors of all atoms marked with a "±" sign must be inverted).



References

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