1. Introduction, Commensurately and Incommensurately Modulated Structures

Present situation

- Extensive experimental and theoretical investigations
  - phase diagrams as functions of pressure, temperature, external fields, stresses, defect concentration
  - critical exponents
- Use of many different models
- Relation between variables in model Hamiltonians and experimentally accessible quantities not well established

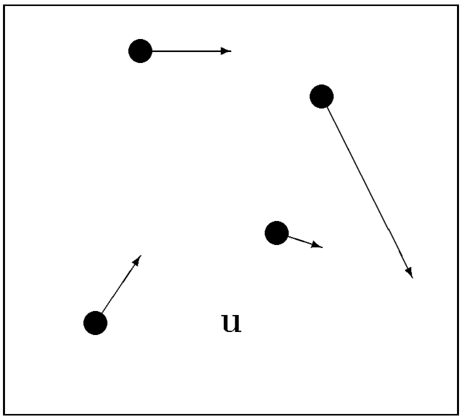
Aim

- Definition of microscopic models based on the relevant characteristics of the underlying solid state systems
- Description and explanation of typical observed properties

Solution

- Development of a symmetry-based approach to phase transitions in materials with D_{2h}^{16} / $Pnma$ space group symmetry $\rightsquigarrow$ relevant local modes
- Introduction of different pseudo spin Hamiltonians based on the relevant local mode coordinates
- Application to specific experimentally investigated materials; example: betaine calcium chloride dihydrate as an outstanding substance

2. Relevant Local Coordinates and Crystal Potential



cell $\mathbf{n}$

Variation of external parameters, phase transition $\rightsquigarrow$ displacements $\mathbf{u}$ of particles from their normal phase positions

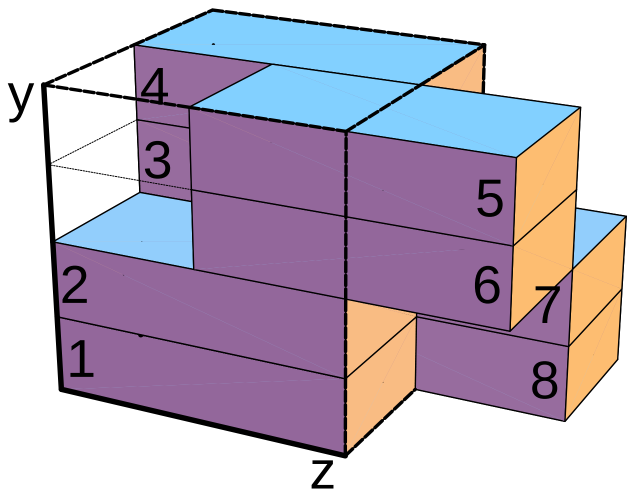
Assumption: Only a few coordinates relevant for the phase transitions

Problem: Introduction of appropriately chosen local coordinates for cell $\mathbf{n}$

"blocks" $\mathfrak{A}_i^{\mathbf{n}}$ (not overlapping):

$$
\begin{aligned}
\mathfrak{A}_1^{(000)} &= [0;\frac{1}{2}] \times [0;\frac{1}{4}] \times [0;1] \quad \text{(asymmetric unit of } Pnma\text{)} \\
\mathfrak{A}_i^{(000)} &= \mathcal{G}_i \mathfrak{A}_1^{(000)} \\
\mathfrak{A}_i^{\mathbf{n}} &= \{\mathrm{id}|n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3\}\mathfrak{A}_i^{(000)}
\end{aligned}
$$

$$
\begin{array}{lll}
\mathcal{G}_1 = \{\mathrm{id}|000\} & \mathcal{G}_5 = \{\mathrm{C}_2^z|\frac{1}{2}1\frac{1}{2}\} & \mathcal{T}_x = \{\mathrm{id}|100\} \\
\mathcal{G}_2 = \{\sigma_y|0\frac{1}{2}0\} & \mathcal{G}_6 = \{\sigma_x|\frac{1}{2}\frac{1}{2}\frac{1}{2}\} & \mathcal{T}_y = \{\mathrm{id}|010\} \\
\mathcal{G}_3 = \{\mathrm{C}_2^y|1\frac{1}{2}1\} & \mathcal{G}_7 = \{\mathrm{C}_2^x|\frac{1}{2}\frac{1}{2}\frac{3}{2}\} & \mathcal{T}_z = \{\mathrm{id}|001\} \\
\mathcal{G}_4 = \{\mathrm{inv}|111\} & \mathcal{G}_8 = \{\sigma_z|\frac{1}{2}0\frac{3}{2}\} &
\end{array}
$$



$Pnma$ generated by $\mathcal{G}_2, \mathcal{G}_5, \mathcal{G}_8, \mathcal{T}_x, \mathcal{T}_y, \mathcal{T}_z$

Series Expansion of displacement of particle ν associated with block $\mathfrak{A}_i^{\mathbf{n}}$ in terms of appropriately chosen *local modes* $\bar{\mathbf{u}}_\kappa(\nu, i, \mathbf{n})$ (specific for material under discussion; K = number of atoms per block):

$$\mathbf{u}(\nu, i, \mathbf{n}) = \sum_{\kappa=1}^{3K} \lambda_\kappa(i, \mathbf{n}) \bar{\mathbf{u}}_\kappa(\nu, i, \mathbf{n})$$

Focus only on *main contributions*: simplest case: *one* $\lambda(i, \mathbf{n})$ per block $\mathfrak{A}_i^{\mathbf{n}}$

Symmetry:
if $\mathcal{G}\mathfrak{A}_i^{\mathbf{n}} = \mathfrak{A}_{i'}^{\mathbf{n}'}$ with $\mathcal{G} = \{\mathcal{R}|\mathbf{t}\} \in Pnma$, then $\mathcal{G}\bar{\mathbf{u}}(\nu, i, \mathbf{n}) = \mathbf{R}\bar{\mathbf{u}}(\nu, i', \mathbf{n}')$
especially $\bar{\mathbf{u}}(\nu, i, \mathbf{n}) = \mathbf{R}_i\bar{\mathbf{u}}(\nu, 1, (000))$ with $\mathcal{G}_i = \{\mathcal{R}_i|\mathbf{t}_i\}$

Interaction energy V between blocks $\mathfrak{A}_i^{\mathbf{n}} \neq \mathfrak{A}_j^{\mathbf{m}}$ (bilinear two-particle interaction):

$$V\begin{pmatrix} i, \mathbf{n} \\ j, \mathbf{m} \end{pmatrix} = \sum_{\nu,\mu=1}^{K} \mathbf{u}^{\mathrm{T}}(\nu, i, \mathbf{n}) \mathbf{W}\begin{pmatrix} \nu, i, \mathbf{n} \\ \mu, j, \mathbf{m} \end{pmatrix} \mathbf{u}(\mu, j, \mathbf{m}) = \lambda(i, \mathbf{n})\lambda(j, \mathbf{m}) W(i, j, \mathbf{m} - \mathbf{n})$$

Uniaxial modulation $\mathrm{q} = q\mathrm{e}_3$ (line Λ in q-space); group of q: C_{2v}

$$\begin{array}{rclrcl} \widehat{\lambda}_i(\mathbf{q}) & = & \sum_z \lambda_i^z \mathrm{e}^{\mathrm{i}qz} & \lambda_i^z & : & \text{value of } \lambda(i, (xyz)) \\ \widehat{W}_{ij}(\mathbf{q}) & = & \sum_z W_{ij}^{\Delta z} \mathrm{e}^{\mathrm{i}q\Delta z} & W_{ij}^{\Delta z} & : & \text{interaction of blocks at distances } \Delta z \end{array}$$

λ_i^z: $i = 1 \dots 4$: blocks extending from z to $z + 1$
$i = 5 \dots 8$: blocks extending from $z + \frac{1}{2}$ to $z + \frac{3}{2}$

Transformation of λ_i^z under group operations:

$\mathcal{G}_2$: exchanges λ_{2k-1}^z and λ_{2k}^z $(k = 1 \dots 4)$
$\mathcal{G}_5$: transforms λ_i^z into λ_{i+4}^z for $(i = 1 \dots 4)$
transforms λ_i^z into λ_{i-4}^{z+1} for $(i = 5 \dots 8)$
$\mathcal{G}_6$ $= \mathcal{G}_5\mathcal{G}_2$

$\rightsquigarrow$ **Introduction of new four component variables** ξ
defined by $\lambda^z =: (\xi^l, \xi^{l+1}) = (\xi_1^l, \dots, \xi_4^l, \xi_1^{l+1}, \dots, \xi_4^{l+1})$

Interaction energy

$$V^{\text{int}} = \frac{1}{2}\sum_{z,z'} \lambda^{z\mathrm{T}} W^{z'-z} \lambda^{z'} =$$

$$\frac{1}{2}\sum_{l} \xi^{l\mathrm{T}} J^0 \xi^l + \xi^{l\mathrm{T}} J^1 \xi^{l+1} + \xi^{l\mathrm{T}} J^{1\mathrm{T}} \xi^{l-1} + \xi^{l\mathrm{T}} J^2 \xi^{l+2} + \xi^{l\mathrm{T}} J^{2\mathrm{T}} \xi^{l-2}$$

$W^{\Delta z}$: Interactions restricted to nearest neighbor blocks in z-direction (8×8-matrices)
J^k: 4×4-submatrices of the matrices $W^{\Delta z}$

$$W^0 = \left(\begin{array}{c|c} J^0 & J^1 \\ \hline J^{1\mathrm{T}} & J^0 \end{array}\right) \qquad W^1 = \left(\begin{array}{c|c} J^2 & 0 \\ \hline J^1 & J^2 \end{array}\right) \qquad W^{(-1)} = W^{1\mathrm{T}}$$

Result:

- Displacements $\mathbf{u}(\nu, i, \mathbf{n})$ as functions of 2×4 different variables per cell (4 per half cell)
- Interaction V^{int} up to next nearest neighbors

3. Symmetry of the Order Parameter

Problem

- All ξ_k must be taken into account, because $\mathcal{G}_2, \mathcal{G}_5, \mathcal{G}_6$ interchange $\xi_1 \ldots \xi_4$
- The respective displacements therefore do not transform according to any irreducible representation (IR) of C_{2v}

Solution

- Use linear combinations ξ' of ξ transforming according to certain IRs

Result

- The displacements $\mathbf{u}'(\nu)$ related to ξ' transform according to (in general other) IRs depending on the choice of the linear combinations and the transformation behavior of $\bar{\mathbf{u}}(\nu, 1, (000))$

IMPORTANT

- The structural distortion with respect to the normal phase does *not* strictly transform according to the IR yielded by the previous derivation but is on the contrary a superposition of elementary distortions transforming according to different IRs under the condition that the primary one has the desired symmetry.
- The present ansatz deals with "block modes" rather than with the conventional "layer modes" (e.g. Z. Y. Chen, M. B. Walker, Phys. Rev. Lett. 65, 1223, 1990; B. Neubert et al., Ferroelectrics 155, 359-364, 1994). These concepts are different although the resulting physics is essentially the same.

4. Application to BCCD

Betain Calcium Chloride Dihydrate (BCCD)

- space group $Pnma$, 4 formula units per elementary cell, many phases modulated in z-direction depending on pressure and temperature

Experimental observation

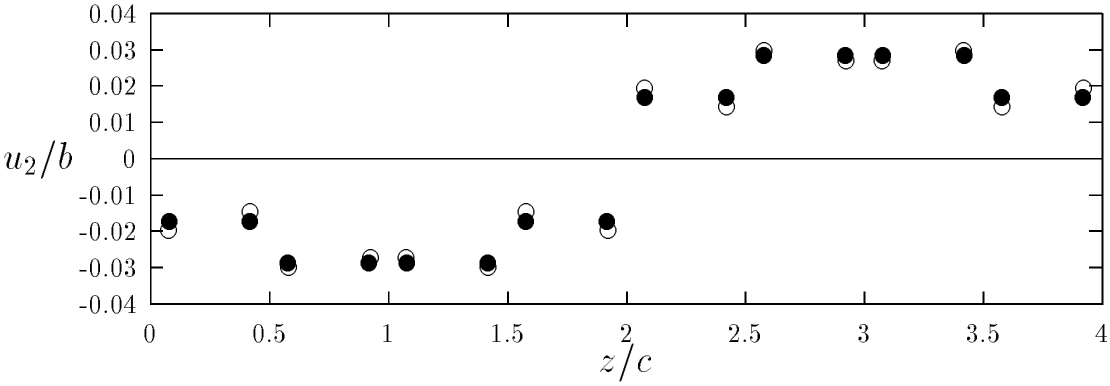
- Main distortion: along y-axis (e.g. D. Dernbach, Dissertation, Saarbrücken 1993; J. M. Ezpeleta et al., Acta Cryst. B48, 261, 1992)
  $\rightsquigarrow$ Choose $\bar{\mathbf{u}}(\nu, 0, (000)) = u(\nu)\mathbf{e_2}$
- Order parameter symmetry: Λ_3 (J. M. Perez-Mato, Solid State Comm. Vol. 67, No. 12, pp. 1145-1150, 1988)

Define

$$\begin{pmatrix} {\xi'}^l_1 \\ {\xi'}^l_2 \\ {\xi'}^l_3 \\ {\xi'}^l_4 \end{pmatrix} = Q \cdot \begin{pmatrix} \xi^l_1 \\ \xi^l_2 \\ \xi^l_3 \\ \xi^l_4 \end{pmatrix} \qquad Q^{-1} = Q^{\mathrm{T}} \text{ appropriate orthogonal matrix}$$

Result

- Taking only a modulation of ${\xi'}_1$ into account and dropping all other modes, the structures determined so far can be approximated quite well. ${\xi'}_1$ is therefore the relevant variable for a model Hamiltonian.
- The respective 3d modes transform according to Λ_3
- Good agreement with observed displacements



Measured (○) and calculated (●) y-displacements of the nitrogen atoms in the fourfold phase of BCCD

5. Use of Different Model Hamiltonians

Most general Hamiltonian

- with two particle interaction

$$\mathcal{H} = \sum_{\nu,i,\mathbf{n}} \frac{\dot{\mathbf{u}}(\nu,i,\mathbf{n})^2}{2m(\nu,i,\mathbf{n})} + \sum_{\nu,i,\mathbf{n}} V^1(\mathbf{u}(\nu,i,\mathbf{n})) + \sum_{\substack{\nu,\,i,\,\mathbf{n}\\ \mu,\,j,\,\mathbf{m}}} V^{\mathrm{int}}\begin{pmatrix}\nu,i,\mathbf{n}\\ \mu,j,\mathbf{m}\end{pmatrix}$$

Introduction of relevant variables

- Selection of dominant modes per block $\mathfrak{A}_i^{\mathbf{n}}$ (simplest case: one mode)
- Construction of linear combinations transforming according to certain IRs

Number of variables

- If we deal with one primary order parameter, one variable describes the main contribution to the structural distortion.
- Taking additional variables into account the structure can be approximated better
- Only the relevant variables enter the model Hamiltonian: all others are dropped by thermal averaging

Type of model

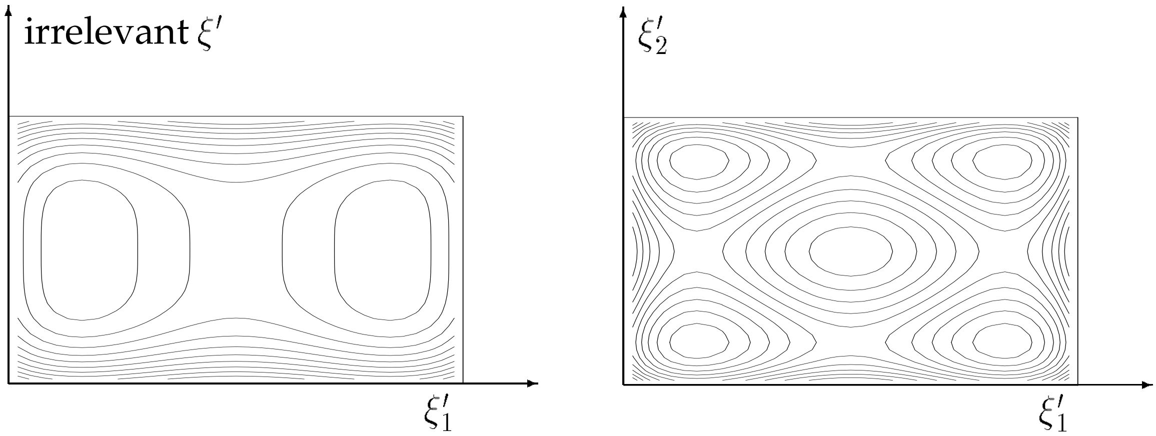
- The crystal potential V is a sum of single-variable energies V^1 for the relevant variables as determined by double-well potentials, and the harmonic couplings V^{int} between different positions.
- The ratio of the coupling strength and the height of the single-variable potential barrier determines whether the transitions are more of the order-disorder or more of the displacive type.
- Taking only one variable into account, the interaction energy is the same as yielded by a version of the discrete frustrated Φ^4 model (e.g. T. Janssen, Ferroelectrics 124, 41, 1991).

6. Pseudo Spin Models

Requirement

- Equivalent pronounced minima for the local potential $V^1(\xi'_1, \ldots)$

two minima four minima



schematic contour plots of the local potential V^1

- Averaging over wells: $\xi' = |\xi'| \,\mathrm{sign}\, \xi' \longrightarrow \overline{|\xi'|} \,\mathrm{sign}\, \xi'$

$$\xi' \longrightarrow \mathrm{sign}\, \xi' =: \sigma = \pm 1$$

σ is called *pseudo spin* for historical reasons

$\sigma = +1$: ξ' located in one minimum
$\sigma = -1$: ξ' located in the other minimum

Properties

- The number of relevant variables ξ' yields the number of pseudo spins σ per cell.
- Switching σ from $+1$ to -1 or vice versa is connected with a *collective motion* of all related particles as determined by the corresponding local modes $\bar{\mathrm{u}}'$.
- The pseudo spin should not be confused with usual spins nor is it localized at a definite position in the cell.

7. Results for the ANNNI Model

Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\sum_l \sigma^l 4J^0\sigma^l + \sigma^l J^1(\sigma^{l+1} + \sigma^{l-1}) + \sigma^l J^2(\sigma^{l+2} + \sigma^{l-2})$$

one relevant variable $\rightsquigarrow$ one pseudo spin σ

$J^0 > 0$ interactions between variables with $\Delta z = 0$

$J^1 \lesseqgtr 0$ interactions between variables with $\Delta z = \pm\frac{1}{2}c$

$J^2 < 0$ interactions between variables with $\Delta z = \pm c$

Mean Field Free Energy

$$F^{\mathrm{MFA}} = -\frac{1}{2}\sum_l 4J^0 S_l^2 + S_l J^1(S_{l+1} + S_{l-1}) + S_l J^2(S_{l+2} + S_{l-2}) + k_B T \cdot \mathrm{A}(S_l)$$

where $S_l = \langle \sigma^l \rangle$ thermal average and $\mathrm{A}(x) = \int_0^x \operatorname{artanh} y \, dy$.

p-T **Phase Diagrams**

- Phase diagrams for model Hamiltonians are 2d surfaces in a higher dimensional parameter space (e.g. $\{J^0, J^1, J^2, T\}$-space)
- What is the 2d surface corresponding to the experimental p-T phase diagram?

The interactions J depend on the inter-particle distances and configurations and therefore on stresses (pressure) and temperature. Making use of material constants, a mapping between the parameter space and experimentally accessible quantities p and T can be established.

Results (B. Neubert et al., loc. cit.)

- Theoretical p-T phase diagrams for BCCD.
  Good description of the succession and of the extension of the phases
- Interactions J^0, J^1, J^2 as functions of the lattice constants
- One should not assume $J^0 = J^1$ (obvious from the definition of the interactions).

8. Critical Behavior

Universality Hypothesis

- The critical behavior of a physical system is determined only by a few features of the underlying Hamiltonian: spatial dimensionality, range and sign and symmetry of interactions, number of components of the order parameter etc.

A comparison of measured and theoretical critical exponents can be used as a means of eliminating inadequate models.

Transition from para phase to modulated phases

- The ANNNI model shows the critical behavior of the $3dXY$ model.
- This is actually observed for BCCD.

BCCD	$\beta = 0.35 \pm 0.01$	$\zeta = 0.625 \pm 0.025$	(K. Holzer et al., Phys. Rev. Lett. 71, 89, 1993)
ANNNI	$\beta = 0.346$	$\zeta = 0.6241$	(T. Garel, P. Pfeuty, J. Phys. C9, L245, 1976; M. Droz, M. D. Coutinho-Filho, Magnetism and Magnetic Materials 1975, p. 465, 1976)

9. Conclusion

- Local modes defined for asymmetric subcells represent a natural lattice theoretical basis for the formulation of model Hamiltonians for modulated systems.
- By well defined thermal averaging the lattice theoretical systems can be projected onto corresponding pseudo spin models
- Advantages of such pseudo spin models:
  - explicit modelling of the discrete atomistic crystal structure by a discrete effective Hamiltonian with only a few parameters
  - inherent symmetry simplifies extensions of the model, e.g. coupling to phonons
- An explicit application of the method to BCCD leads to a good description of the displacements from the normal phase of those modulated structures for which quantitative experimental data have been published so far.
- p-T phase diagrams are calculated making use of material constants. The results describe the experimental situation quite well.