FROM CRYSTAL STRUCTURE TO PHASE DIAGRAMS: USE OF ANNNI- AND RELATED MODELS

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Abstract The suitability of different pseudo spin models for a description of materials exhibiting modulated structures is discussed. We propose certain local generalized coordinates as a basis for an expansion of the displacements in BCCD. The theoretical treatment is simplified by a mapping to corresponding pseudo spin models with one or more spin components depending on the number of local normal modes relevant for the phase transitions. Furthermore, critical exponents at the boundary of the para phase as expected from the ANNNI model are compared with experimental results.

INTRODUCTION

There are many materials which transform from a normal (high temperature) phase to a sequence of modulated structures when external parameters like pressure and temperature are varied. These properties are often described by means of suitable models which can be handled by the methods of statistical mechanics. The models should, at the same time, reflect the symmetries of the actual systems.
The following approach offers a method for connecting the crystal structure and the relevant variables in model Hamiltonians. The method is described for Betaine Calcium Chloride Dihydrate (BCCD), but should also be valid for other substances in the space group $\mathbf{D}_{2\mathbf{h}}^{16}$, e.g. $\mathrm{A_2BX_4}$ compounds. The objective of the following deduction is to reduce systematically the high number of model variables.

RELEVANT LOCAL COORDINATES AND CRYSTAL POTENTIAL

Assuming that only a few coordinates are relevant for the phase transitions, one has to introduce appropriately chosen local coordinates. The displacements are expanded as follows: If $\mathfrak{A}_1^{(000)} = [0;\ \frac{1}{2}] \times [0;\ \frac{1}{4}] \times [0;\ 1]$ denotes the asymmetric unit of the space group $\mathbf{Pnma}$, we create "blocks" $\mathfrak{A}_\mathbf{i}^\mathbf{n} = \{\mathrm{id} \mid \mathrm{n}_1\mathbf{e_1} + \mathrm{n}_2\mathbf{e_2} + \mathrm{n}_3\mathbf{e_3}\}\mathfrak{A}_\mathbf{i}^{(\mathbf{000})}$ with $\mathfrak{A}_\mathbf{i}^{(\mathbf{000})} = \mathcal{G}_\mathbf{i}\mathfrak{A}_1^{(000)}$ by appropriate space group operations $\mathcal{G}_\mathbf{i} \in \mathbf{Pnma}$; $\mathbf{i} = 1\ldots8$. These blocks do not overlap although they may have common faces (mirror planes) and they fill the whole space entirely (see figure 1). The displacements $\mathbf{u}(\nu, \mathbf{i}, \mathbf{n})$ of the νth particle associated with block $\mathfrak{A}_\mathbf{i}^\mathbf{n}$ are expanded in terms of appropriately chosen local modes $\bar{\mathbf{u}}_\kappa$, i.e. $\mathbf{u}(\nu, \mathbf{i}, \mathbf{n}) = \sum_{\kappa=1}^{3\mathbf{K}} \lambda_\kappa(\mathbf{i}, \mathbf{n})\bar{\mathbf{u}}_\kappa(\nu, \mathbf{i}, \mathbf{n})$ where $\mathbf{K}$ is the number of particles per block.

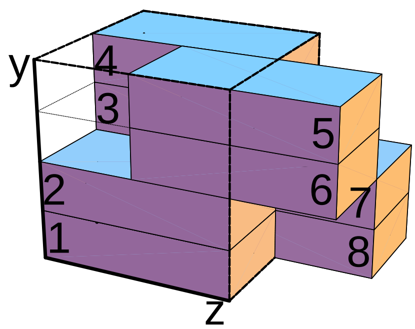

FIGURE 1: Blocks $\mathfrak{A}_\mathbf{i}^{(\mathbf{000})}$, $\mathbf{i} = 1\ldots8$

Focusing interest only on the main contribution, we retain only one $\lambda(\mathbf{i}, \mathbf{n})$ per block $\mathfrak{A}_\mathbf{i}^\mathbf{n}$ and from now on omit the subscript κ. We use local mode displacements satisfying the relations $\bar{\mathbf{u}}(\nu, \mathbf{i}', \mathbf{n}') = \mathbf{R}\bar{\mathbf{u}}(\nu, \mathbf{i}, \mathbf{n})$ for $\mathfrak{A}_{\mathbf{i}'}^{\mathbf{n}'} = \mathcal{G}\mathfrak{A}_\mathbf{i}^\mathbf{n}$ with $\mathcal{G} = \{\mathcal{R} \mid \mathbf{t}\} \in \mathbf{Pnma}$. The $\bar{\mathbf{u}}$ are specific for the material under discussion. Assuming a bilinear two-particle interaction $\mathbf{W}\binom{\nu,\mathbf{i},\mathbf{n}}{\mu,\mathbf{j},\mathbf{m}}$, the interaction energy between blocks $\mathfrak{A}_\mathbf{i}^\mathbf{n} \neq \mathfrak{A}_\mathbf{j}^\mathbf{m}$ is

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

where

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

is the interaction between blocks which depends only on $\mathbf{m}-\mathbf{n}$. Its explicit calculation, e.g. by means of the atom-atom potential method[1], is beyond the scope of our treatment. Now consider a modulation with a wave vector $\mathbf{q} = \mathrm{q}\mathbf{e_3}$. We define Fourier transforms $\widehat{\lambda}_\mathbf{i}(\mathbf{q}) = \sum_\mathrm{z} \lambda_\mathbf{i}^\mathrm{z} \exp \mathrm{iqz}$ (with $\lambda_\mathbf{i}^\mathrm{z}$ as the value of $\lambda(\mathbf{i},(\mathrm{xyz}))$ for definite z) and $\widehat{\mathbf{W}}_{\mathbf{ij}}(\mathbf{q}) = \sum_{\Delta\mathrm{z}} \mathbf{W}_{\mathbf{ij}}^{\Delta\mathrm{z}} \mathrm{e}^{\mathrm{iq}\Delta\mathrm{z}}$ ($\mathbf{W}_{\mathbf{ij}}^{\Delta\mathrm{z}}$: interaction of blocks at distances $\Delta\mathrm{z}$). The group of $\mathbf{q}$ (along the line Λ) is $\mathbf{C}_{2\mathbf{v}}$ (cf. [2]). We therefore only consider the space group operations $\mathcal{G}_2 = \{\sigma_\mathbf{y} \mid 0\frac{1}{2}0\}$, $\mathcal{G}_5 = \{\mathbf{C}_2^\mathrm{z} \mid \frac{1}{2}1\frac{1}{2}\}$ and $\mathcal{G}_6 = \mathcal{G}_5\mathcal{G}_2 = \{\sigma_\mathbf{x} \mid \frac{1}{2}\frac{1}{2}\frac{1}{2}\}$. $\mathcal{G}_2$ interchanges $\lambda_{\mathbf{2k-1}}^\mathrm{z}$ and $\lambda_{\mathbf{2k}}^\mathrm{z}$ for $\mathbf{k} = 1\ldots 4$; $\mathcal{G}_5$ transforms $\lambda_\mathbf{i}^\mathrm{z}$ into $\lambda_{\mathbf{i+4}}^\mathrm{z}$ for $\mathbf{i} = 1\ldots 4$ (i.e. for blocks extending from z to z + 1) and into $\lambda_{\mathbf{i-4}}^{\mathrm{z+1}}$ for $\mathbf{i} = 5\ldots 8$ (i.e. for blocks extending from $\mathrm{z}+\frac{1}{2}$ to $\mathrm{z}+\frac{3}{2}$). This suggests to define new four component variables ξ by $\lambda^\mathrm{z} =: (\xi^\mathrm{l},\xi^{\mathrm{l+1}}) = (\xi_1^\mathrm{l},\ldots,\xi_4^\mathrm{l},\xi_1^{\mathrm{l+1}},\ldots,\xi_4^{\mathrm{l+1}})$; $\mathrm{l} = 2\mathrm{z}$. Restricting the range of the interactions $\mathbf{W}_{\mathbf{ij}}^{\Delta\mathrm{z}}$ to $\Delta\mathrm{z} = 0, \pm 1$ (adjacent blocks in z-direction), the interaction energy of a row of unit cells is

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

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

where the $\mathbf{J}^\mathrm{k}$ are 4×4-submatrices of the 8×8-interaction matrices $\mathbf{W}_{\mathbf{ij}}^{\Delta\mathrm{z}}$.
All ξ_i must be taken into account, because $\mathcal{G}_1,\mathcal{G}_5,\mathcal{G}_6$ interchange $\xi_1\ldots\xi_4$ and the respective displacements therefore do not transform according to any irreducible representation (IR). We introduce new variables $\xi' := \mathbf{Q}\xi$ as linear combinations of ξ, that transform according to certain IRs of $\mathbf{C}_{2\mathbf{v}}$. The displacements $\mathbf{u}'(\nu)$ related to ξ' then transform according to (in general other) IRs depending on the choice of the orthogonal matrix $\mathbf{Q}$ and the transformation behavior of $\bar{\mathbf{u}}(\nu,1,(000))$.

APPLICATION TO BCCD

It is experimentally observed, that the main distortion in BCCD (space group Pnma, 4 formula units per elementary cell, many phases modulated in z-direction depending on pressure and temperature) is along the y-axis. Choosing $\bar{\mathbf{u}}(\nu,1,(000)) = \mathbf{u}(\nu)\mathbf{e_2}$ and selecting appropriate linear combinations ξ' and retaining only ξ'_1 as the relevant variable, the structures determined so far (ferro[3], normal[4], fourfold[5] and incommensurate[6]) can be well approximated by a modulation of that variable (see figure 2). The resulting interaction potential is the same as yielded by a version of the discrete frustrated Φ^4 model[7]. Including also ${\xi'}_2$, which is one order of magnitude smaller, the structure can be described even better. The structural distortion with respect to the normal phase does not strictly transform

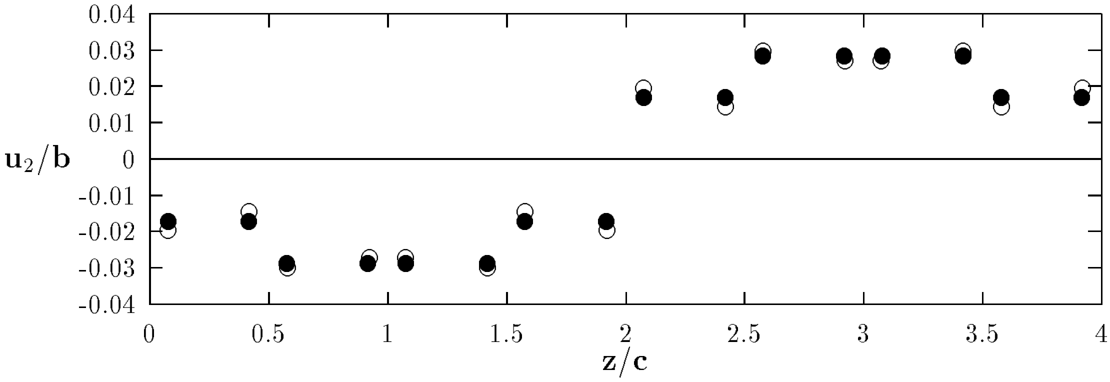

FIGURE 2: Measured ($\circ$) and calculated ($\bullet$) y-deviations of the nitrogen atoms in the fourfold phase of BCCD. Only one variable (ξ_1^{l}) is used. Its modulation is calculated from the ANNNI model. (The displacement amplitude $\bar{\mathrm{u}}_2(\mathrm{N}, 1, (000))$ is taken from experiment).

according to the IR Λ_3 but will also contain minor contributions corresponding to other IRs, which are coupled to the primary Λ_3 mode. Note that the present procedure is different from the consideration of "layer modes"[8] although the resulting physics is essentially the same.

PSEUDO SPIN HAMILTONIANS

The crystal potential $\mathbf{V}$ is a sum of single-variable energies $\mathbf{V}^1(\xi'_1, \dots)$, described, e.g., by double-well potentials, and harmonic two-variable couplings $\mathbf{V}^{\mathrm{int}}$. The ratio of the coupling strength and the height of the single-variable potential barrier determines whether the system is more of the order-disorder or more of the displacive type.
If $\mathbf{V}^1$ has two equivalent pronounced minima for each relevant variable ξ'_{i}, averaging $\xi'_{\mathrm{i}} = \mid \xi'_{\mathrm{i}} \mid \mathrm{sign}\, \xi'_{\mathrm{i}}$ over the wells yields $\overline{\mid \xi'_{\mathrm{i}} \mid} \,\mathrm{sign}\, \xi'_{\mathrm{i}}$ and the interaction between the variables ξ'_{i} and ξ'_{j} at positions l and l$'$ becomes:

$$\xi'^{\mathrm{l}}_{\mathrm{i}} \mathbf{J}^{\mathrm{l}'-\mathrm{l}}_{\mathrm{ij}} \xi'^{\mathrm{l}'}_{\mathrm{j}} \rightsquigarrow \overbrace{\overline{\mid \xi'^{\mathrm{l}}_{\mathrm{i}} \mid} \mathbf{J}^{\mathrm{l}'-\mathrm{l}}_{\mathrm{ij}} \overline{\mid \xi'^{\mathrm{l}'}_{\mathrm{j}} \mid}}^{=:\tilde{\mathbf{J}}^{\mathrm{l}'-\mathrm{l}}_{\mathrm{ij}}} \sigma^{\mathrm{l}}_{\mathrm{i}} \sigma^{\mathrm{l}'}_{\mathrm{j}}$$

$\sigma_{\mathrm{i}} := \mathrm{sign}\, \xi'_{\mathrm{i}} = \pm 1$ indicates whether ξ'_{i} is located in the one or the other minimum and is called pseudo spin for historical reasons. Switching σ_{i} from $+1$ to -1 or vice versa is connected with a collective motion of all related particles as determined by the corresponding local modes $\bar{\mathbf{u}}'$. Depending on the number of relevant local generalized coordinates ξ', one-, two- or more-component spin models can be applied. The pseudo spin should not be confused with usual spins nor is it localized at a definite position in the cell.
An appropriate model for the description of uniaxially modulated structures is the Axial Next Nearest Neighbor Ising (ANNNI) model. Recently we applied its mean field version to BCCD[9] and succeeded in describing e.g. the $\mathbf{p}$-$\mathbf{T}$-phase diagram, displacements of major phases and dependences of the interactions on $\mathbf{p}$ and $\mathbf{T}$. With $\sigma^{\mathrm{l}}_1 = \mathrm{sign}\, \xi'^{\mathrm{l}}_1$ and $\tilde{\mathbf{J}}^0_{11} > 0$, $\tilde{\mathbf{J}}^1_{11} \lesseqgtr 0$, $\tilde{\mathbf{J}}^2_{11} < 0$, the present method corresponds to our previous approach.
Another pseudo spin model is the Double Ising Spin (DIS) model[10] with two spin variables σ_1 and σ_2 representing $\mathrm{sign}\, \xi'_1$ and $\mathrm{sign}\, \xi'_2$. Assuming competing nearest neighbor interactions $\tilde{\mathbf{J}}^1_{12} = -\tilde{\mathbf{J}}^1_{21}$ and neglecting the next nearest neighbor interaction $\tilde{\mathbf{J}}^2$, one can generate similar modulated structures as in the ANNNI model and also reproduce the $\mathbf{p}$-$\mathbf{T}$-phase diagram of BCCD quite well.

CRITICAL BEHAVIOR

The universality hypothesis (stating that the critical behavior is determined by a few basic properties of the system) is a useful means for selecting adequate models. During the last twenty years, critical exponents were determined for many pseudo spin systems.
In the ANNNI model, the transition from para to ferro phase is of 3d Ising type. But there is according to a renormalization group analysis[12, 11] a crossover to $3\mathrm{d} - \mathbf{XY}$ behavior for transitions to the (IC) modulated structures. The critical exponents for BCCD[13] ($\beta = 0.35 \pm 0.01$ and $\zeta = 0.625 \pm 0.025$) are in excellent agreement with those calculated for the universality class of the ANNNI model ($\beta = 0.346$, $\zeta = 0.6241$).

CONCLUSIONS

Local modes defined for asymmetric subcells represent a natural lattice theoretical basis for the formulation of model Hamiltonians for modulated systems. Further symmetry considerations in terms of the group of the modulation vector lead to the selection of admissible local mode combinations. By well defined thermal averaging, the lattice theoretical systems can be projected onto corresponding pseudo spin models. The interaction energies of the latter depend, by their very definition, on temperature and pressure. The inherent symmetry simplifies extensions of the model, e.g. coupling to phonons. The Free Energy can be derived from the Hamiltonian with approximations but without further assumptions. 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. For the fourfold phase, for example, the experimentally determined displacements are well reproduced, even if only the primary local mode is taken into account; an inclusion of one more mode leads to an almost perfect agreement.

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