Models for the description of uniaxially modulated materials

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Models which allow an explicit application to structurally modulated substances are reviewed within the frame of a symmetry-based approach starting from discrete lattice theory. Focus is set on models formulated in terms of local variables assigned to discrete crystallographic units (unit cells or parts of them). Especially considered are symmetry-based pseudo spin models. Methods are discussed which permit the handling of the statistical mechanics of such models, the translation of model calculation results to a form allowing the prediction of experimental data, and the theoretical determination of point defect influences.

Keywords: modulated structures, microscopic models

I. INTRODUCTION

An interesting class of materials exhibits, as a distinguishing feature, phase diagrams with several, in some cases with very many, commensurately and incommensurately modulated phases. At present there exists a large body of experimental data on a multitude of such materials, and various types of models have been proposed as bases for a theoretical description. An assessment of their merits and their shortcomings depends i) on the weight which one attaches to the physical justification of the general form of the model and of the special values of its parameters, ii) on the properties of the real system which are to be explained, and iii) on the degree of agreement between theory and experiment which one requires.

At the present state of research it seems appropriate to survey a large class of these models on the same footing, to discuss how they are connected with the original atomistic or lattice theoretical basis, to find, if possible, a methodological and hierarchical classification scheme into which they can be fitted, and to compare model predictions of properties like phase diagrams, values of physical quantities etc. with each other and with experimental data.

There exist extensive discussions of models exhibiting spatially modulated structures[1, 2]. In the present paper it will be our special concern to discuss how different models are obtained when the basic first principles theory is gradually more and more simplified so that finally theoretical descriptions arise which allow explicit, though only approximate, calculations of physical properties. We will be particularly interested in various models whose common feature is that they describe the macroscopic specimens in terms of local variables assigned to discrete crystallographic units on the atomistic level. We will be especially concerned with a class of such models, which arise if the continuous local variables are projected onto a number of discrete states and, finally, with a description of these states in terms of local pseudo spins with one or several components.

Besides the derivation of model characteristics – e.g. the global structure of phase diagrams, detailed information on the formation of new phases by structure branchings and their accumulation points (which are connected with transitions from first to second order phase transitions) or the exact structure of phase diagrams in the vicinity of multiphase points – we shall also report methods for establishing a connection between theoretical (model) data and experimentally accessible properties of real systems.

An interesting additional aspect of the theoretical treatment is the possibility to incorporate impurities into the theory. On the one hand, this line of the theory is of practical relevance for the understanding of real, imperfect crystals; on the other hand it is of interest to find out if the basic ideas of the modelling procedure carry so far as to allow also the description of impurity effects.

The paper is organized as follows. After a brief reference to the experimental situation and some general remarks on the interrelation of model parameters and measured quantities in section II, short comments on phenomenological theories of modulated structures and on the derivation of pressure-temperature or temperature-electric field phase diagrams from Landau type thermodynamic potentials are made in section III. In section IV, a symmetry-based lattice theoretical description of uniaxially modulated structures is presented which provides a framework for reviewing a number of models in the subsequent sections (models with continuous variables in section V, pseudo spin models in section VI). Section VII describes methods for bridging the gap between the results of model calculations (in terms of model parameters) and experimentally observed properties (in terms of experimental control parameters). These methods do not postulate an ad hoc correspondence but – with further approximations – make use of the lattice theoretical foundation of the models and of macroscopic material properties. The incorporation of point defects into...
the theory is discussed in section VII. In section IX, a summarizing discussion and an outlook to future developments is given.

II. EXAMPLES OF MODULATED SYSTEMS; OBJECTIVES OF THEIR THEORETICAL DESCRIPTION

During the late 70s and 80s a worldwide hunt for materials with cascades of structurally modulated phases led to a large amount of experimental data on numerous compounds. The largest class of such crystals is formed by \( A'A''BX_4 \)-compounds, among which \( \text{Rb}_2\text{ZnCl}_4 \) is a prototypical member. Apart from measurements under different temperatures, pressures and electric fields, homologous series of \( A'A''BX_4 \)-compounds, e.g. the tetrathymethylammonium tetrahalogenometallate (TMA – MX_4) series, allow the investigation of the influence of the chemical composition on the sequence of phase transitions.

An outstanding specific material with an especially large number of commensurately or incommensurately modulated phases is betaine calcium chloride dihydrate (BCCD). Its phase diagram, which has been thoroughly investigated experimentally e.g. with respect to its dependence on temperature, pressure, uniaxial stress, electric fields, or impurities shows many very interesting features. The observed global and local details of the phase diagrams invite a comparison with theoretical predictions to test the performance of various models.

We only briefly mention three further special examples since surveys on structurally modulated materials were given elsewhere (e.g. [16]). These examples are interesting in that they show that in families of isomorphous compounds materials with properties deviating significantly from the majority behavior may be observed: a) All investigated modulated substances of the TMA – MX_4 family have their modulation wave vector \( \mathbf{q} \) along \( \mathbf{a} \) with the exception of \( [\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4 \) with \( \mathbf{q} \) parallel to \( \mathbf{c} \) (similar to its homologue tetramethylphosphonium-CuBr_4). b) \( \text{Rb}_2\text{ZnCl}_4 \) and \( \text{Rb}_2\text{ZnBr}_4 \) on the one hand and \( \text{Cs}_2\text{CdBr}_4 \) and \( \text{Cs}_2\text{HgBr}_4 \) on the other hand show cascades of modulated phases but \( \text{Cs}_2\text{ZnCl}_4 \) and \( \text{Cs}_2\text{ZnBr}_4 \) do not. c) Whereas most of the members of the \( \text{A}_2\text{BX}_4 \) family exhibit phase transitions of purely order-disorder type and hence lack a soft mode, \( \text{K}_2\text{SeO}_4 \) is primarily displacive in its incommensurate transition, but also possesses a significant order-disorder component.

Most of the previously mentioned materials with uniaxial structural modulations were investigated at ambient pressure over large temperature intervals; for some substances, pressure was also varied or the influence of an electric field was studied.

Different approaches offer themselves for a theoretical interpretation of these data: a rather rigorous treatment would start from the basic Hamiltonian formulated as a function of atomic positions, momenta, and externally imposed parameters (e.g. homogenous stresses and electric field components). This Hamiltonian might be deduced e.g. from an ab initio electron theory or from a formulation in terms of empirical interatomic or intermolecular interactions. This treatment would then employ the methods of statistical mechanics to derive for example thermodynamic potentials for equilibrium structures and phase diagrams. These would be obtained as functions of temperature and experimental control parameters and could be directly compared with experimental results. If (due to computational difficulties) the method is not (yet) feasible, one can make use of semiempirical treatments employing suitable models. In the standard procedure for such a model description of modulated systems, physical properties like phase diagrams are derived from effective model Hamiltonians with the help of approximate methods of statistical mechanics. The results are primarily obtained as functions of temperature and model parameters (including e.g. effective intercell interactions and electric field components). For a comparison with experimental data it would be desirable to find physically motivated connections between the effective interactions occurring in the model Hamiltonian and experimentally given parameters like temperature and applied stresses.

Most applications of model calculations to the interpretations of empirical data restrict themselves, however, to a comparison of general topological features of the model phase diagrams with those obtained experimentally or try to establish an ad hoc correspondence. In ref. [16] an explicit mapping from a theoretical temperature-interaction-phase diagram to a pressure-temperature phase diagram was presented which makes use of material properties like thermal expansion, elastic constants etc. The method was used exemplarily for BCCD and is described in subsection VII A.

Phase diagrams were calculated e.g. for the DIFFOUR model, the ANNNI model and its extensions, the DIS model, the AANNDI model, and for Chen and Walker’s model. Usually two-dimensional \textit{planar} parameter space sections were considered.

All models discussed in the sections IX – XI contain variables that correspond explicitly to microscopic crystalline quantities: both local generalized coordinates or pseudo spins describe degrees of freedom of crystallographic (sub)cells. These model variables are coupled by effective interactions, which correspond to certain thermal averages of combinations of original atomic interactions. If it were possible to find a temperature-, stress-, and electric field-dependent mapping of the atomistic couplings onto the model parameters, precise predictions for the occurrence of phase tran-
sitions could be made. Particularly, it would be possible for a special substance to transform a theoretical phase diagram.

Because of their experimental relevance, phase diagrams as functions of temperature and pressure are of special interest. The set of states experimentally accessible by variations of $T$ and $p$ corresponds to a curved two-dimensional surface in the higher-dimensional model parameter space spanned for example by temperature and effective interactions. In general, this surface will not be planar.

### III. PHENOMENOLOGICAL THEORIES

As the phenomenological Landau theory has been the subject of various reviews (see for example [22]) we will focus in the following on different schemes for describing successive transitions between phases characterized by different wave numbers. We will especially discuss two approaches to handle a cascade of commensurate phases.

In order to describe the cascade of phase transitions of a devil’s staircase Sannikov [23] proposed a phenomenological theory in which the sequence of phase transitions is determined by one soft branch of the lattice vibrations. The thermodynamic potential for a transition to a commensurate phase characterized by the wave number $q_l = m/l$ can be written in the form

$$\Phi = \alpha \rho^2 + \beta \rho^4 - \alpha' \rho^{2l} \cos 2l \zeta$$  \hspace{1cm} (1)

where $\rho$ and $\zeta$ are the amplitude and the phase of the normal coordinates. The coefficients $\alpha'$ differ from zero only at the points of the Brillouin zone given by $q = q_l = \frac{2\pi}{l}$ where $m$ and $l$ are integers, i.e. for every $l$ one obtains a different potential $\Phi$ (the wave numbers $q$ will be given in units of $2\pi/\alpha$, $i = 1, 2, 3, \ldots$, $a_i$ being the lattice constants). The limit $l \rightarrow \infty$ corresponding to irrational values of $q$ yields the potential

$$\Phi = \alpha \rho^2 + \beta \rho^4$$

describing the transition to an incommensurate phase.

The coefficient $\alpha$ in eqn. (1) is a continuous function of $q$. The approximation used for this function depends upon the interval of $q$-values considered. If the end points of the interval do not satisfy the Lifshitz condition, $\alpha$ is approximated by the expression

$$\alpha = a + \delta (q - b)^2.$$  

Here $b$ is the wave number of the soft mode responsible for the minimum of the branch $\alpha(q)$. This first case is realized for example in the TMA $\rightarrow$ MCl$_4$ family. If, on the contrary, one of the end points satisfies the Lifshitz condition (e.g. $q = 0$) the proposed form is

$$\alpha = A + \kappa (q^2 - B^2)^2$$

which results from an expansion in $q^2$ around the point $q = 0$. Examples for this case are thiourea [SC(NH$_2$)$_2$] and BCCD [25]. In the following we will focus on the latter case.

Introducing new dimensionless variables $x = \frac{\beta}{\alpha} \rho$ and $y = \frac{1}{\kappa Q^2} \zeta$ and assuming that the value $|\alpha'|$ is the same for all $l$

Sannikov derived a phase diagram in the $x$-$y$-space. $Q$ has the same dimension as $q$ and its value is arbitrary. Under the assumption of a linear $T$-dependence of $A$ and $B$ (and therefore of $x$ and $y$) the phase sequences were obtained for different materials.

In a detailed analysis for BCCD, thermodynamic potentials for various values of $q$ were derived. Using an ad hoc linear transformation from dimensionless model variables to $T$ and $p$ and choosing tentative values for the remaining parameters a rather satisfying fit of theoretical to experimental $T$-$p$ phase diagrams could be obtained [26].

In order to study the influence of external (electric) fields $E_i$ coupling terms between the fields and the two-component order parameter were added to the potential [22]. The transformation properties of the conjugated quantities $P_i = -\partial \phi_i/\partial \phi_j$ (spontaneous polarization) could than be derived and compared to experimental results [27].

A different phenomenological theory was developed especially for the interpretation of the phase transition sequence of BCCD [28]. Noticing that the polarization of the ferroelectric low temperature phase ($q = 0$) corresponds to the primary order parameter, the starting point for this approach is the free energy density (in reduced units)

$$g(x) = t\xi^2 + \frac{1}{4} \xi^4 - \frac{1}{4} \left( \frac{\partial \xi}{\partial x} \right)^2 + \frac{1}{4} \left( \frac{\partial^2 \xi}{\partial x^2} \right)^2 + \mu \xi^2 \left( \frac{\partial \xi}{\partial x} \right)^2.$$
The order parameter is supposed to be site-dependent. The terms $-\frac{1}{4} \left( \frac{\partial \xi}{\partial x} \right)^2$ and $\frac{1}{4} \left( \frac{\partial^2 \xi}{\partial x^2} \right)^2$ describe the occurrence of modulations whereas the term $\mu \xi^2 \left( \frac{\partial \xi}{\partial x} \right)^2$ is responsible for the temperature dependence of the wave vector $q$. In addition umklapp terms were introduced into the expression for the free energy density of the commensurate phases and approximated by a forth degree term in the order parameter amplitude,

$$U_{\text{umklapp}} = -b_{2}l \xi^{2l} \approx -\frac{1}{4} \beta_{\text{eff}}(q) \xi^{4},$$

for a commensurate phase with wave number $q = \frac{m}{L}$.

Using the plane-wave approximation (i.e. $\xi = \xi_0 \cos kx$) and choosing appropriate values for $\beta_{\text{eff}}(q)$, the phase diagram was derived by computing the free energies of the diferent phases as functions of temperature. Introducing coupling terms between the order parameter and an electric field the $E-T$ phase diagram was calculated. In a subsequent paper the sinusoidal scheme was abandoned and the occurrence of a multisoliton regime was considered.

### IV. DERIVATION OF MODELS FROM AN ATOMIC LATTICE THEORETICAL BASIS

**A. Formulation in terms of local modes**

Models based on the discrete structure of the lattice can provide a way to achieve a physical understanding of the processes on the atomic level of the crystal which goes beyond a mere phenomenological description. Such microscopic models can be handled analytically or numerically. In the subsequent sections models which have been closely studied with respect to the application to experimentally investigated substances are discussed. Each model variable – either continuous as in the case of the DIFFOUR models or discrete as in the case of pseudo spin models – usually describes one degree of freedom per lattice site. Previously it was considered a weak spot, especially of pseudo spin models, that the significance (on an atomic scale) of the model (pseudo spin) variables was not well defined. For this reason we summarize a general procedure for the systematic definition of symmetry-based model variables on a lattice theoretical basis. This procedure stresses the atomistic roots of the models, leads to models conforming to lattice symmetry and facilitates the prediction of spontaneous polarizations of modulated phases and of the atomic displacements occurring at structural transitions. It combines the idea of local modes formulated e.g. in ref. with the rigorous symmetry considerations of Landau’s theory (for instance, see ref. ). It leads to a Hamiltonian that serves as a starting point for various approximations leading to different models (e.g. the DIFFOUR models or the DIS model) and thus provides a frame for reviewing very different models from a common point of view.

The key idea of the general procedure for the derivation of a microscopic model Hamiltonian of this procedure is the introduction of variables as generalized coordinates of symmetry-adapted local modes (SALMs). This facilitates the incorporation of both the discreteness of the lattice and the overall symmetry of the crystal. The symmetry properties of the SALMs can either be derived from first-principles calculations or taken from experimental data, i.e. from the observation of the symmetry of the displacements responsible for the phase transitions.

Let the crystal be composed of $N$ unit cells each containing $K$ particles (of which $K'$ are non equivalent) and assume, for definiteness, Born-von Kármán periodic boundary conditions. The crystal structure is then described by a $3KN$-dimensional configuration vector $\mathbf{R}$, where each entry specifies a component of the position of an atom. An arbitrary configuration

$$\mathbf{R} = \mathbf{R}_0 + \delta \mathbf{R}$$

is decomposed into a contribution $\mathbf{R}_0$, which is invariant under all elements $G = \{ \mathbf{R} \mid t \}$ of the high temperature normal phase space group $G_{\mathbf{P}}$, and a symmetry-breaking displacement $\delta \mathbf{R}$, which is zero above the transition temperature $T_{\text{crit}}$ from the normal phase to the lower symmetry phases (unmodulated or commensurately or incommensurately modulated). The displacement $\delta \mathbf{R}$ from a reference structure at given reference values of $T$, $p$, etc. can be written as a superposition

$$\delta \mathbf{R} = \sum_n \delta \mathbf{R}_n,$$

of local contributions $\delta \mathbf{R}_n$. They describe displacements for only those atoms which are associated to unit $n$, having zero entries for all others. These units do not necessarily correspond to the unit cells of the crystal; in the case of the space group $Pnma$ discussed in subsection half cells are chosen as units accounting for the pseudoperiodicity of
such crystals along one of the lattice vectors. $\delta \mathbf{R}_n$ is expanded in terms of local modes. In most cases it is sufficient to retain only a few (e.g. one or two) local modes per unit.

It is useful to choose the local modes such that they reflect the crystal symmetries: the smallest unit in the crystal with respect to symmetry is the asymmetric unit $\mathbf{A}_0$ of the space group $\mathbf{G}$. Symmetry imposes no restrictions on the position of the $K'$ atoms associated to the structural axis. The subcell $\mathbf{A}_n$ defined by

$$\mathbf{A}_n = \mathbf{G} \mathbf{A}_0 \quad \text{and} \quad \mathbf{A}_n^{i} = (\mathbf{E}[n] \mathbf{A}_0^{i},$$

cover the whole crystal. The $B$ space group operations $\mathbf{G}_1^{i}, \ldots, \mathbf{G}_B^{i}$ are coset representatives in a coset decomposition of $\mathbf{G}$ with respect to its invariant subgroup $\mathbf{I}$ of primitive translations. The index $B = [\mathbf{G} : \mathbf{I}]$ equals the order of the point group $\mathbf{G}_0$ of $\mathbf{G}$ and determines the number of subcells $\mathbf{A}_n^{i}$ per cell $n$. The coset representatives have to be chosen such that these $B$ subcells form a contiguous new choice of cell. Any displacement of the $K'$ atoms associated with $\mathbf{A}_n^{i}$ can be expanded in terms of a basis set of $3K'$ subcell modes $\mathbf{v}_n^{ik}$, $\kappa = 1, \ldots, 3K'$. They should satisfy the relation $\mathbf{v}_n^{ik} = \mathbf{g} \mathbf{v}_n^{ik}$ where $\mathbf{g} \in \mathbf{G}$ is the space group operation transforming subcell $\mathbf{A}_n^{i}$ into $\mathbf{A}_n^{i'}$. Thus, the modes in any subcell are entirely determined by the (arbitrary) choice of modes in the asymmetric unit $\mathbf{A}_0$.

A complete - for $K'B > K$ over-complete (see below) - set of $3K'BN$ local modes can be constructed as linear combinations of the subcell modes

$$\mathbf{w}_n^{ik} = \sum_{i=1}^{B} S^{ij} \mathbf{v}_n^{ik}$$

with a $B \times B$ transformation matrix $S$, the form of which is determined by the IRREPs of the point group $\mathbf{G}_0$. For fixed $i \kappa$ each local mode $\mathbf{w}_n^{ik}$ describes the same displacement pattern of atoms in their respective unit, i.e. $\mathbf{w}_n^{ik} = \{ \mathbf{E}[n] \mathbf{w}_n^{ik} \}$. We will call the set $\{\mathbf{w}_n^{ik} : \kappa = 1, \ldots, 3K'\}$ the $i$th set of symmetry-adapted local modes for unit $n$. Any linear combination of displacement vectors in one set of SALMs has the same symmetry properties. Apart from a primitive translation, an arbitrary space group operation only permutes the subcell indices and thus the transformation behavior of the set of $\mathbf{w}_n^{ik}$ is entirely determined by $S$. The actual positions of the atoms in the subcells have not to be known. Only those sets of SALMs can contribute to the structural deformation $\mathbf{U}$ that have the symmetry properties imposed by the IRREP according to which $\mathbf{U}$ transforms.

The existence of atoms on special positions, i.e. on faces, edges and corners of the subcells causes the number $3K'BN$ of local modes to be in general higher than the number $3KN$ of independent displacements. Hence, the coefficients of an expansion of a general displacement in terms of these SALMs have to satisfy consistency relations. The symmetry-breaking displacement $\delta \mathbf{R}_n$ in unit $n$ is decomposed into contributions $\delta \mathbf{R}_n^{i}$ from the $B$ sets of SALMs:

$$\delta \mathbf{R}_n = \delta \mathbf{R}_n^{1} + \delta \mathbf{R}_n^{2} + \delta \mathbf{R}_n^{B} = \sum_{i=1}^{B} \delta \mathbf{R}_n^{i} = \sum_{i=1}^{B} \sum_{\kappa=1}^{3K'} a_{n}^{i \kappa} \mathbf{w}_n^{ik}.$$

Under a continuous change of external parameters the average positions of the atoms are displaced in such a way that a valley of low energy is followed in the high-dimensional configuration space. The symmetry-breaking displacement of any atom in the asymmetric unit $\mathbf{A}_0$ which is connected with the transition is not determined by space group symmetry. It will, in general, be different even for materials exhibiting the same symmetries of the normal and the modulated phases (e.g. A$_2$BX$_4$ compounds). Hence, the contribution $\delta \mathbf{R}_n^{i} = \sum_{\kappa=1}^{3K'} a_{n}^{i \kappa} \mathbf{w}_n^{ik}$ from the $i$th set of SALMs will, in general, lie on a $d_{a} \leq 3K'$-dimensional curved surface or, in its simplest and most frequent case, describe a curved path ($d_{a} = 1$) upon changing temperature or pressure. Either case corresponds to a simultaneous variation of in general all coefficients $a_{n}^{i \kappa}$ in equation (4) as the fixed subcell modes $\mathbf{w}_n^{ik}$ can not simultaneously be adapted to the curved paths described by every $\delta \mathbf{R}_n^{i}$. Thus, instead of using the coefficients from equation (4) as generalized variables for the determination of the displacements in unit $n$, one introduces new local sets of curvilinear coordinates for each set of SALMs by means of a coordinate transformation $a_{n}^{i \kappa} = f_{n}^{i \kappa}(Q_{n}^{11}, \ldots, Q_{n}^{33K'})$, $\kappa = 1, \ldots, 3K'$ such that the contribution

$$\delta \mathbf{R}_n^{i}(Q_{n}^{11}, \ldots, Q_{n}^{33K'}) = \sum_{\kappa=1}^{3K'} f_{n}^{i \kappa}(Q_{n}^{11}, \ldots, Q_{n}^{33K'}) \mathbf{w}_n^{ik}$$

to the symmetry-breaking displacement in unit $n$ [cf. equation (4)] occurs when $Q_{n}^{11}, \ldots, Q_{n}^{33K'}$ increase from zero to some non-zero value whereas all other generalized variables remain at their thermal average of zero. In the simplest
case \( d_a = 1 \), only one relevant variable \( Q_n^{I_1} \) per set of SALMs is needed and thus the value of \( Q_n^{I_1} \) determines a linear combination of displacement vectors from the \( I \)th set of SALMs for unit \( n \) (which has the same transformation behavior as any other linear combination of SALMs from the same set).

On the one hand, the space group symmetries and the direction of the modulation determine the subcell generators \( G^1, \ldots, G^B \) and the matrix \( S \) and thus should be the same for a whole class of materials. On the other hand, the displacements of atoms in the asymmetric unit and thus the coordinate transformations \( f_I^{n} \) are determined by the local potential and thus by the specific material under investigation. This allows a separation of properties specific for a certain class of materials from properties specific for the substance under investigation.

The vector field \( \delta R_n^I(Q_n^{I_1}, \ldots, Q_n^{B,3K'}) \) gives a contribution to the structural transformation in unit \( n \) with definite transformation behavior. In general, \( d_s \) sets of SALMs \((I = 1, \ldots, d_s)\) without loss of generality) are needed for the construction of symmetry modes transforming according to irreps of the group \( G(q) \) of the wave vector. When \( G_n \) has only one-dimensional real irreps and only one order parameter transforming according to one irrep of \( G(q) \) gives the primary contribution to the structural deformation (it is the case in BCCD). One \( d_s = 1 \) certain set of SALMs \((I = 1)\) and the corresponding symmetry-breaking displacement \( \delta R_n^I \) is needed for every unit. The reverse is not true because by different spatial modulations of \( Q_n^{I_1} \) one set of SALMs can be used to construct symmetry modes transforming according to different irreps of \( G(q) \) and different sets of SALMs may contribute to symmetry modes with same transformation behavior (e.g. at a point \( q \neq 0 \) inside the Brillouin zone when \( G(q) \) is a true subgroup of \( G_0 \); examples will be given in subsection IV C). Especially, the set of SALMs corresponding to the totally symmetric representation of \( G_0 \) may be relevant because it may contribute to a structural deformation not transforming according to the totally symmetric representation of \( G_0 \).

In the simplest case of one relevant set of SALMs \((d_s = 1)\) and one degree of freedom in the asymmetric unit \((d_a = 1)\), expansion (2) can be written

\[
\delta R = \sum_n \delta R_n^I(Q_n^{I_1}, 0, \ldots, 0)
\]

and the 3\( KN \)-dimensional lattice theoretical problem is reduced to a system with one generalized local variable \( Q_n^{I_1} \) per unit. In the next paragraph, for simplicity, we will restrict ourselves to this special case, which however can easily be generalized.

The crystal potential is expanded in terms of the local generalized coordinates \( Q_n^{I_1} \). The terms containing only variables with given \( n \) form the local potential \( \Phi^{loc}(Q_n^{1,1}, \ldots, Q_n^{B,3K'}) \) for unit \( n \). The general Hamiltonian of the system can then be written

\[
\mathcal{H} = \sum_n \left[ \sum_{I,K} (P_n^{I,I})^2 + \Phi^{loc}(Q_n^{I_1}, \ldots, Q_n^{B,3K'}) \right] + \Phi^{int}(\ldots, Q_n^{I_1}, \ldots, Q_m^{I_1}, \ldots)
\]

where \( P_n^{I,I} \) is a momentum canonically conjugate to \( Q_n^{I_1} \). Averaging out all irrelevant variables yields an effective Hamiltonian

\[
\overline{\mathcal{H}} = \text{tr}(\rho\mathcal{H}) = \sum_n \left[ (P_n^{I_1})^2 + \overline{\Phi}^{loc}(Q_n^{I_1}) \right] + \overline{\Phi}^{int}(\ldots, Q_n^{I_1}, \ldots, Q_m^{I_1}, \ldots).
\]

(The trace is taken only for the variables to be averaged out: \( I \neq 1, \kappa \neq 1 \).)

In the case of two relevant sets of SALMs per unit \((d_s = 2, I = 1, 2)\), one gets the two-variable version

\[
\overline{\mathcal{H}} = \sum_n \left[ (P_n^{I_1})^2 + \overline{\Phi}^{loc}(Q_n^{I_1}, Q_n^{21}) \right]
\]

\[
+ \overline{\Phi}^{int}(\ldots, Q_n^{11}, Q_n^{21}, \ldots, Q_m^{I_1}, Q_m^{I_2}, \ldots).
\]

The same form with the superscript \((21)\) replaced by \((12)\) is obtained in the case of one relevant set of SALMs per unit \((d_a = 1, I = 1)\) but two relevant generalized coordinates \((d_a = 2)\) per asymmetric subcell. We will omit the superscript referring to \( \kappa = 1 \) for brevity in the case \( d_a = 1 \) of one generalized variable for each set of SALMs.

### B. Relation to other models

The models discussed in the subsequent sections can be viewed as special cases of the Hamiltonian (3) or its two-variable versions. The total number of relevant variables per unit is \( d_a \cdot d_s \). The local potential \( \overline{\Phi}^{loc} \) and the
interaction potential $\Phi^{\text{int}}$ are effective potentials which, by their very definition, depend directly on elastic stresses (which determine the lattice constants) and on temperature due to the thermal averaging over the irrelevant variables. The potentials are usually expanded up to forth or second order respectively and only a subset of interactions between nearest, next nearest and third next nearest neighbors is kept.

As in Landau theory, space group operations can be considered to act on the generalized variables instead on the modes $W_n$. Hence, symmetry considerations give conditions for the dependence of the potential on the generalized variables, which have for example been taken into account when formulating the AANNDI or the DIS model. Moreover, the local potential may have equivalent minima: assume that there is one global minimum of the local potential for a certain configurational set of generalized local coordinates; then every space group operation which transforms a unit into itself but changes the configuration of the respective coordinates may generate another equivalent minimum.

A further simplification may be introduced by projecting the remaining continuous generalized local variables onto two-valued pseudo spin variables as the signs of the former. This leads to different pseudo spin models: we discussed either the ANNNI model in the case of one relevant mode per half cell or the DIS model in the case of two relevant variables earlier.

The Hamiltonian $\{3\}$ corresponds to a version of the DIFFOUR model with one degree of freedom per lattice site or to the ANNNI model. The more general case where two local modes with different transformation behavior ($d_s = 2$) are incorporated corresponds to Chen and Walker’s model or to the DIS model. Assuming two relevant displacement vector fields for the asymmetric unit ($d_s = 2$), i.e. two generalized variables $Q_{11}$ and $Q_{12}$ for the relevant set of SALMs, one arrives at a model corresponding to the version of the DIFFOUR model with two degrees of freedom per lattice site discussed in ref.3 (e.g. $Q_{11}$ and $Q_{12}$ correspond to variables describing the displacements of the betaine and calcium chloride groups of BCCD respectively). For the description of BCCD with space group $\mathcal{G}_0 = Pnma$, the units correspond to half cells. The latter two cases yield Hamiltonians with two different variables for each of such units.

It is noteworthy that the Hamiltonian $\{3\}$ contains only one symmetry-breaking contribution per unit. As discussed above, the totally symmetric IRREP of $\mathcal{G}_0$, which also contributes to the deviation of the displacements from the structure of the para phase at the original reference values of $T$, $p$, etc., is always present but has been absorbed into the atom positions of a new reference state. The latter can be viewed as giving a background contribution to the structural deformation of the crystal which is present throughout the whole range of temperature and pressure.

C. Exemplary study of the procedure for materials with space group $Pnma$

Among the 66 crystals with structurally incommensurate phases listed by Cummins, the 22 materials belonging to the space group $\mathcal{G}_0 = D_{2h}^{16}$ (in their normal phase) form the largest class. The materials in the $A_2BX_4$ (K$_2$SeO$_4$) family (apart from a small group of tungstates and molybdates), betaine calcium chloride dihydrate (BCCD), ammonium oxalate hemihydrate (AHO) and thiourea all exhibit the symmetries described by that space group. Depending on the particular choice of axes, various Hermann-Mauguin symbols have been attributed to these substances. For a more detailed discussion see ref.4. In the present study, we choose the assignment $Pnma$ and restrict ourselves to modulations along $c$. Special attention is payed to the pseudoperiodicity. The reader should not get confused by the formalism as in the present case units correspond to half cells but the labeling with cell subscripts $n$ is kept for simplicity.

The asymmetric unit $\mathcal{A}_0 = [0; \frac{1}{2}] \times [0; \frac{1}{2}] \times [0 ; 1]$ of the space group $Pnma$ is a parallelepiped (‘block’) containing all $K'$ nonequivalent atoms from which the whole crystal can be filled by the $B = 8$ space group operations

$$G^1 = \{E|000\}, \quad G^2 = \{\sigma_y|0\frac{1}{2}0\}, \quad G^3 = \{C_2^x|1\frac{1}{2}\}, \quad G^4 = \{I|111\}$$

$$G^5 = \{C_2^z|\frac{1}{2}\frac{1}{2}\}, \quad G^6 = \{\sigma_z|\frac{1}{2}\frac{1}{2}\}, \quad G^7 = \{C_2^y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}, \quad G^8 = \{\sigma_z|\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$$

and primitive translations $\{E|n_1e_1 + n_2e_2 + n_3e_3\}$. The eight blocks (see figure 3) generated from the asymmetric unit by the operations $G^1, \ldots, G^8$ are considered to form a new choice of cell at $n = (000)$. An arbitrary block is labeled by the index $i$ of the space group operation and the vector $n$ of the primitive translation it was generated by. Blocks 1, 2, 3, 4 extend from $z = n_3$ to $n_3 + 1$ (first half of cell), blocks 5, 6, 7, 8 from $z = n_3 + 1/2$ to $n_3 + 3/2$ (second half of cell) along the $c$-axis.

Local modes $W_n^{\text{loc}}$ are constructed from the subcell displacement vectors $\mathbf{V}_n^{\text{loc}}$ by means of the $8 \times 8$-matrix (cf. eqn. 3).
Although constructed for the whole (new) unit cell, these local modes describe displacements for either the first (\(I = 1, 2, 3, 4\)) or the second half (\(I = 5, 6, 7, 8\)) of the cell when viewed along the \(c\)-direction in accordance with the definition of the blocks. Thus half cells (quadruples of blocks) are the units used to introduce the local potential. Nevertheless, we do not relabel the half cells but distinguish between front and back half cells by means of the subscript \(n\) and the superscript \(I\).

In Landau theory, \(\delta R\) is decomposed into symmetry modes \(\mathbf{e}_{s}^{k_{s}\alpha\lambda}\) of the crystal transforming according to irreducible representations (IRREPs) \(\Gamma^{k_{s}}\) of \(\mathfrak{g}_{0}\):

\[
\delta R = \sum_{\text{star}} \sum_{k} \sum_{\alpha} \sum_{\lambda} \left( \dim \Gamma^{k_{s}} \right) c_{s}^{k_{s}\alpha\lambda} \mathbf{e}_{s}^{k_{s}\alpha\lambda},
\]

where the first sum runs over all distinct stars, \(\alpha\) labels the different IRREPs connected with star \(k\), \(\lambda\) accounts for the fact that the IRREP \(\Gamma^{k_{s}}\) can appear more than once and the sum over \(s\) extends over all basis function of the IRREP \(\Gamma^{k_{s}}\). Contributions from the totally symmetric IRREP of \(\mathfrak{g}_{0}\) are included in \(R_{0}\) and excluded in equation \([\bar{\Phi}]\) by the definition of \(\delta R\). Below \(T_{\text{crit}}\) at least one IRREP gives a non-zero contribution to equation \([\bar{\Phi}]\) and the respective symmetry-breaking displacement determines the structure of the newly formed phase. In the microscopic theory presented in this section, the symmetry modes \(c_{s}^{k_{s}\alpha\lambda}\) are formed by superposition of the local mode vector fields \(\delta R_{n}^{I}\). The generalized variables \(Q_{n}^{I}\) are spatially modulated order parameters.

It follows from the transformation behavior of the local modes under arbitrary elements of the space group \(\mathfrak{g}_{0}\) that it is possible to construct symmetry modes transforming according to the IRREPs \(\Lambda_{2}\) or \(\Lambda_{3}\) (but not \(\Lambda_{1}\) or \(\Lambda_{4}\)) if one takes into account local modes with superscripts \(I = 3, 4, 7, 8\) and transforming according to \(\Lambda_{5}\) or \(\Lambda_{4}\) (but not \(\Lambda_{2}\) or \(\Lambda_{3}\)) if one takes into account \(I = 1, 2, 5, 6\) \((0 < q < \frac{1}{2}, q = q^{*})\), labeling of IRREPs as in ref. [25]. For BCCD, which exhibits a soft phonon branch of \(\Lambda_{3}\)-symmetry, the primary contribution is produced by the SALMs \(\{\mathbf{W}_{n}^{3k}\}, \{\mathbf{W}_{n}^{7k}\}\). Additional secondary contributions (transforming according to the IRREPs \(\Lambda_{3}\) and \(\Lambda_{2}\) which were observed in the fourfold phase) are accounted for by a second set of SALMs for each unit (half cell) (\(\{\mathbf{W}_{n}^{4k}\}\) and \(\{\mathbf{W}_{n}^{8k}\}\) respectively). For the description of the relevant main contribution to structural deformations in BCCD, it is sufficient in both cases to keep one generalized variable for each set of SALMs, i.e. one has either two \((Q_{n}^{3}, Q_{n}^{7})\) or four generalized variables \((Q_{n}^{3}, Q_{n}^{7}, Q_{n}^{4}, Q_{n}^{8})\) per cell.

### D. The introduction of the pseudo spin formalism

The effective potential \(\bar{\Psi}\) is a sum of local half cell potentials \(\mathbf{F}_{\text{loc}}^{n}\) and harmonic two-variable couplings. To describe a system with \(2r\) equivalent minima of \(\mathbf{F}_{\text{loc}}^{n}\), one keeps \(r\) relevant generalized coordinates \(Q_{1n}^{r}, \ldots, Q_{rn}^{r}\) per unit. The positions of the equivalent minima differ only in the signs of the \(r\) corresponding variables. In general, there are \(B\) equivalent minima per unit at the most. The ratio of the coupling strength and the height of the local potential barrier determines whether the system is more of the order-disorder or more of the displacive type.

A pseudo spin formulation is derived in the following way: The interactions are expanded up to second order terms in the variables

\[
Q_{n}^{p} = |Q_{n}^{p}| \text{sign } Q_{n}^{p} =: |Q_{n}^{p}| \sigma_{n}^{p}.
\]

These are replaced by the averages \(\langle Q_{n}^{p} | \sigma_{n}^{p}\rangle\) over single wells (taken separately for each \(|Q_{n}^{p}|\)). Here

\[
\sigma_{n}^{p} := \text{sign } Q_{n}^{p}
\]

is just a shorthand notation for the sign of \(Q_{n}^{p}\). The interaction between the variables \(Q_{n}^{p}\) and \(Q_{m}^{q}\) becomes

\[
\mathbf{F}_{nm}^{pq} \cdot |Q_{n}^{r}| \cdot |Q_{m}^{q}| \cdot \sigma_{n}^{p} \sigma_{m}^{q} =: J_{nm}^{pq} \sigma_{n}^{p} \sigma_{m}^{q}.
\]
with pseudo spin interactions \( J_{nm}^{pq} = \overline{W}_{nnm}^{pq} \cdot |Q_n^p| \cdot |Q_n^q| \). Since they are defined as thermal averages the latter depend quite naturally on temperature and stresses. The procedure yields the following pseudo spin Hamiltonian:

\[
\mathcal{H} = \frac{1}{2} \sum_{nnm} \sum_{pq} J_{nm}^{pq} \sigma_n^p \sigma_m^q. \quad (8)
\]

A switch of \( \sigma_n^p \) from +1 to −1 or vice versa is connected with a collective motion of all particles in the unit according to the corresponding SALM \( \overline{W}_{nnm}^{pq} \) which is associated with a transition from one well to another. Because \( \sigma \) assumes only the values +1 or −1, it is called pseudo spin. It should not be confused with usual spins nor is it localized at a definite position in the unit. An association of pseudo spins with local normal coordinates for the description of soft modes was described in ref. 18.

In this way, the distribution of the variables \( Q_n^p \) over the wells in the unit is described by of the operators \( \sigma_n^p \). The formulation takes the actual average displacements and the thermal fluctuations in the neighborhood of a given equilibrium position into account. A more detailed analysis extending previous treatments to uniaxially modulated materials and incorporating both order-disorder and displacive phenomena will be reported in a future publication.

It should be mentioned that part of the SALM model was inspired by an idea presented in a paper describing the distortions of four crystallographically equivalent ammonium tetrahedra in ammonium hydrogen oxalate hemihydrate by four pseudo spins. This model exhibited the possibility of incorporating symmetry considerations into pseudo spin Hamiltonians, although the interactions were not properly defined.

V. MODELS WITH CONTINUOUS VARIABLES

Many models proposed so far by various authors for the description of materials with modulated structures can be connected with the atomistic basis along the lines discussed in section III. In the present section we shall refer to some models with continuous local variables.

A. The Frenkel-Kontorova and DIFFOUR models

In the Frenkel-Kontorova model\(^{24,43}\) a linear chain of atoms with harmonic nearest neighbor couplings in an external periodic potential incommensurate with the underlying lattice is considered. The incommensurability of the external potential (period \( b \)) with the lattice distance \( a \) in the potential

\[
V = \frac{\alpha}{2} \sum_\ell \left[ (x_{\ell+1} - x_\ell - a)^2 + \Phi \cdot (1 - \cos(2\pi x_\ell/b)) \right]
\]

of the Frenkel-Kontorova model produces the frustrations necessary for the appearance of (in)commensurate structures. In the continuum limit of this model (also known as Frank-van der Merwe model\(^{43}\)) the equations of motion lead to the sine-Gordon equation of which the solutions correspond to a soliton lattice.

In the beginning of the 80s, Janssen and Tjon proposed a model\(^{45}\) that they later called \( \Phi \) model following a similar model in field theory. Ref.\(^{44}\) provides an extensive discussion. The DIFFOUR model is intended as a simple one-dimensional model featuring most of the typical properties found in modulated crystal phases. Its essential ingredient is the competition between short-range interactions. In its simplest version it introduces a linear chain with anharmonic nearest neighbor and harmonic next nearest and third nearest neighbor interactions. The frustration mechanism is the competition of the next and third nearest neighbor interactions. The reduced potential of the translation invariant version is given by

\[
V_{\text{red}} = \sum_\ell \left[ \frac{\alpha}{2} (u_\ell - u_{\ell-1})^2 + \frac{\beta}{2} (u_\ell - u_{\ell-2})^2 + \frac{\delta}{2} (u_\ell - u_{\ell-3})^2 + \frac{1}{4} (u_\ell - u_{\ell-1})^4 \right],
\]

where \( u_\ell \) denotes the displacement of the \( \ell \)th particle in the chain. \( u_\ell \) is scaled such that \( V_{\text{red}} \) contains only the necessary model parameters \( \alpha, \beta \) and \( \delta \). Substituting \( x_\ell := u_\ell - u_{\ell-1} \) yields the not-translation invariant version:

\[
V_{\text{red}} = \sum_\ell \left[ \frac{A}{2} x_\ell^2 + \frac{1}{4} x_\ell^4 + B x_\ell x_{\ell-1} + D x_\ell x_{\ell-2} \right].
\]

This is the potential of an effective Hamiltonian with a local 2-4-potential and nearest and next nearest neighbor interactions which can be considered as the result of thermal averaging over the non-relevant variables, while the
quantity \( x_\ell \) is interpreted as the relevant degree of freedom for position \( \ell \) in the chain. The coefficients the depend quite naturally on temperature and other control parameters. The stable structures fulfilling \( \partial V_{\text{red}}/\partial x_\ell = 0 \) and having the smallest free energies represent the ground state configurations. A temperature can be introduced either by identifying the potentials as the respective thermodynamic potentials (e.g., free energies) and assuming that the parameters of the model are temperature-dependent or by starting from a Hamiltonian with the above potential and treating (a three-dimensional version of) the model in mean field approximation.

An extension of this model to two degrees of freedom per position leads to a DIFFOUR model for the description of the phonon spectrum of BCCD.

B. Chen and Walker’s model

Contrary to the approach of the DIFFOUR models starting from a general formulation and adapting the coefficients to specific substances later, Chen and Walker use information about the crystal structure and the symmetries of excitations in uniaxially modulated materials whose high temperature phase exhibits the symmetries of the space group \( D_{2h}^{16} \) from the beginning. Their model was adapted to the class of \( A_2BX_4 \) compounds and to BCCD. The crystal is decomposed in equidistant layers with a layer spacing of half the lattice constant along the direction of modulation. Displacements of the atoms in layer \( \ell \) are given by:

\[
v_\ell e_\ell(\Gamma_2) + w_\ell e_\ell(\Gamma_3),
\]

where \( e_\ell(\Gamma_2) \) and \( e_\ell(\Gamma_3) \) are layer modes belonging to the irreducible representations \( \Gamma_2 \) and \( \Gamma_3 \) of the two-dimensional group \( C_{2v} \), respectively, from which three-dimensional symmetry modes transforming like the observed soft mode can be constructed. Neglecting other layer modes, a Landau-type reduced free energy

\[
F = \sum_\ell \left[ \frac{1}{2} a v_\ell^2 + \frac{1}{4} v_\ell^4 + \frac{1}{2} a' w_\ell^2 + \frac{1}{4} w_\ell^4 + b v_\ell^2 w_\ell^2 \right] + \frac{1}{2} \sum_\ell (J v_\ell v_{\ell+1} + J' w_\ell w_{\ell+1}) + \frac{1}{2} \sum_{\ell} (v_\ell w_{\ell+1} - v_{\ell+1} w_\ell)
\]

invariant under the transformations of the normal phase space group \( D_{2h}^{16} \) with temperature-dependent parameters is introduced. Besides a local energy term, only nearest neighbor layer interactions are considered. The competition between the interactions \( J \) and \( J' \) on the one hand and the antisymmetric interaction term \( v_\ell w_{\ell+1} - v_{\ell+1} w_\ell \) on the other hand leads to frustrations and hence to the occurrence of commensurately and incommensurately modulated structures.

Phase diagrams are calculated as planar two-dimensional sections through the higher-dimensional \((a, a', b, J, J')\)-parameter space: the specific structure of the layer variables \( \{v_\ell, w_\ell\} \) minimizing \( F \) determines the stable phase at every point of the parameter space. The respective space group can be determined from a given profile of amplitudes making use of the definition of \( e_\ell(\Gamma_2) \) and \( e_\ell(\Gamma_3) \). Up to three different space groups can be found for a given wave number of the modulation. A path is drawn in the parameter space of the theoretical phase diagram in such a way as to obtain the same sequence of phases as determined experimentally as a function of \( T \) (for \( p = 0 \)) for BCCD. The expressions for the spontaneous polarization as expansion in terms of the layer variables can be used to determine the sequence of phases under an external electric field. Observing that the soft mode in BCCD is an acoustic mode further layer mode coupled to the two optic modes and belonging to the irreducible representation \( \Gamma_3 \) is introduced in the free energy. Phonon branches calculated from the latter show a softening of the lowest-lying acoustic mode for an appropriate choice of the eight reduced parameters.

DIFFOUR model and ANNNI model (subsection VI.A) on the one hand and Chen and Walker’s model and DIS model (subsection VI.C) on the other hand are closely related since in each case the pseudo spin model can be considered as the Ising limit of the model with continuous variables.

VI. PSEUDO SPIN MODELS

A. The ANNNI model and its extensions
1. The model

The Axial Next Nearest Neighbor Ising (ANNNI) model\textsuperscript{1} was the subject of different excellent review articles.\textsuperscript{2,3,4} In the following we will focus on the three-dimensional version and present the main results as well as some techniques used to examine the properties of this model. In the ANNNI model only one pseudo spin per unit \((ijk)\) is considered. The Hamiltonian (without an external field) is given by

\[
\mathcal{H} = -J_0 \sum_{ijk} \sigma_{ijk} (\sigma_{(i+1)jk} + \sigma_{i(j+1)k}) - J_1 \sum_{ijk} \sigma_{ijk} \sigma_{ij(k+1)} - J_2 \sum_{ijk} \sigma_{ijk} \sigma_{ij(k+2)}. \tag{9}
\]

\(J_0 > 0\) is the ferro-type in-plane interaction between nearest neighbors whereas \(J_1\) and \(J_2\) are the couplings between nearest and next nearest neighbors in direction of the modulations respectively. Frustration effects and therefore modulations arise for \(J_2 < 0\) and either sign of \(J_1\). Due to the invariance of the Hamiltonian \((9)\) under a simultaneous transformation \(J_1 \rightarrow -J_1\) and \(\sigma_{ijk} \rightarrow (-1)^k \sigma_{ijk}\), it is only necessary to examine the case \(J_1 > 0\). Using reduced units, the ground state is given by the ferro phase for \(\kappa < \frac{1}{3}\) and the \((2)\)-phase for \(\kappa > \frac{1}{2}\) with \(\kappa = -\frac{q}{p}\). For the \((2)\)-phase the spin structure repeats itself after four layers and is given by \(+ + - -\), i.e. two layers where all the pseudo spins have the value +1 followed by two layers with −1 pseudo spins. The two ground phases are separated by a multiphase point (MP) where an infinity of phases is degenerate.

The A3NNI (Axial Third Nearest Neighbor Ising) mode\textsuperscript{5} differs from the usual ANNNI model by considering a third neighbor interaction in \(c\)-direction. This extension leads to a two-dimensional ground state phase diagram where some of the phases are separated by multiphase lines (ML). The two phases \((12)\) and \((3)\) occupy now a finite stability region at \(T = 0\). Starting point for the ELII (Effectively Long-range Interaction Ising) model\textsuperscript{6,7} is the coupling between two degrees of freedom (one degree of freedom is considered to be an Ising spin) which leads to indirect effective long-range oscillating interactions \(J_r = \sum_q J_q e^{iqr}\) between the pseudo spins, \(r\) being the number of layers separating the interacting pseudo spins.

2. The mean field approximation

In the mean field approximation (MFA)\textsuperscript{8,9} it is assumed that every spin interacts only with a mean field produced by the thermal averages of all spins interacting with it. This is equivalent to neglecting spin fluctuations or approximating the density operator by a product of single spin density operators. The free energy of the ANNNI model derived in this approximation (apart from constant factors)

\[
F = \sum_k \left[-2J_0 S_k^2 - J_1 S_k S_{k+1} - J_2 S_k S_{k+2} + k_B T \left((1 + S_k) \ln (1 + S_k) + (1 - S_k) \ln (1 - S_k)\right)\right]
\]

is a function of the the mean field value \(S_k = \langle \sigma_{ijk} \rangle\) of the \(k\)-th layer. Minimizing the free energy leads to the equilibrium equations

\[
S_k = \tanh \left[4J_0 S_k + J_1 (S_{k-1} + S_{k+1}) + J_2 (S_{k-2} + S_{k+2})\right]. \tag{10}
\]

The critical line

\[
k_B T_{\text{crit}}(\kappa) = \begin{cases} 
4J_0 + 2(1 - \kappa)J_1 & \kappa \leq \frac{1}{4} \\
4J_0 + (2\kappa + \frac{1}{4\kappa})J_1 & \kappa \geq \frac{1}{4} 
\end{cases}
\]

which separates the disordered para phase from the ordered phases and the critical wave vector

\[
q_{\text{crit}} = \begin{cases} 
0 & \kappa \leq \frac{1}{4} \\
\arccos \frac{1}{2\kappa} & \kappa \geq \frac{1}{4} 
\end{cases} \tag{11}
\]

are obtained by linearizing the equilibrium equations \((10)\). At the Lifshitz point \((\kappa = \frac{1}{4})\) the para phase, the ferro phase and the modulated phases meet. Figure \((3)\) (from ref \(14\)) shows a typical mean field phase diagram with the
main commensurate phases derived for the case $J_0 = J_1$. Mean field phase diagrams of the A3NNI and of the ELII model have also been published.

Duxbury and Selke verified for the ANNNI model the existence of structure combination branching processes responsible for the creation of new phases at finite temperatures. In this process two neighboring stable phases ($A$) and ($B$) produce a new phase ($AB$) at a definite branching point. At higher temperatures this process repeats itself leading for example to the appearance of the phases ($A^nB$) at different branching points. The order of the phase transition changes at the accumulation points of the branching processes from first to second order. The coordinates of the accumulation point of the ($23^m$) phases were determined by numerical extrapolation. Using a fixed point expansion the positions of accumulation points were calculated numerically and analytically for very different series of phases. This fixed point expansion will be the subject of the next section. MFA seemed to indicate the existence of partially disordered and asymmetric phases for weak in-layer coupling $J_0$ (i.e. $J_0 \leq 0.3J_1$). In order to further examine this behavior Nakanishi used the mean field transfer matrix method (MFTM) where the interactions in c-direction are treated exactly, while the interactions in the layers are approximated by mean fields. The problem is reduced to one dimension with the free energy

$$F = \sum_k \left[ -\frac{1}{2} J_0 S_k^2 + h_k S_k \right] - k_B T \ln Z$$

where the partition function $Z = \text{Tr} \exp \left[ \beta \sum_k \left( J_1 \sigma_k \sigma_{k+1} + J_2 \sigma_k \sigma_{k+2} + h_k \sigma_k \right) \right]$ can be calculated by use of transfer matrices. $h_k$ is the mean field of the $k$-th layer. Minimizing the free energy with respect to the calculated thermal average $S_k$ leads to a system of nonlinear equations which have to be solved selfconsistently. As a result Nakanishi showed that the free energies of the partially disordered and the asymmetric states are always higher than the free energy of the symmetric state and concluded that the former states were an artifact of the MFA. Monte Carlo calculations supported this claim.

3. The fixed point expansion

The fixed point expansion method was developed for the calculation of profiles, free energies and interaction energies of discommensurations in the frame of the ANNNI model. The mean field equilibrium equations are reformulated as a four-dimensional mapping $P^{k+1} = \text{h}(P^k)$ for the vectors $P^k = (S_{k-2}, S_{k-1}, S_k, S_{k+1})$. The pseudo spin profile $P^{\gamma k}$ of a phase $\gamma$ with the periodicity $N$ verifies the relation $P^{\gamma k} = P^{\gamma k+N} = Z (P^{\gamma k})$ and corresponds, thus, to an iterated fixed point of the mapping.

Since a discommensuration is a localized defect the changes in the pseudo spin profile are the largest in the immediate vicinity of this defect. This region is treated numerically by means of the original (not linearized) equilibrium equations. The large number of pseudo spins whose numerical treatment would be cumbersome is conveniently handled by an expansion in the asymptotic region, however, about the fixed point leading to the linearized mapping $\Delta^{k+1} = H^k \Delta^k$ for the deviations $\Delta^k = P^{\gamma k} - P^k$. The matrices $H^k$ are symplectic matrices, whose special properties allow a largely analytic derivation of the profiles, the free energies and the interactions of such defects. Of special importance is the (symplectic) product $G^k = \prod_{\mu=1}^n H^{\mu+n-\mu}$ where the period $n$ of the matrices $H^k$ (i.e. $H^{k+n} = H^k$) is $n = N$ or $n = \frac{N}{2}$ depending on the symmetry of the profile $P^{\gamma k}$.

The asymptotic behavior of the deviations is determined in terms of the product matrix $G^k$ in the form $\Delta^{k+n} = G^k \Delta^k$ and therefore by the eigenvalues $\lambda_\nu$ of $G^k$. Figure shows the different fixed point types resulting from the positions of the four eigenvalues in the complex plane. The approach to the fixed point is thus monotonic for fixed point type 2 ($2'$) and oscillatory for type 3 (see ref. for a detailed discussion of the fixed point types).

Analytical results for the free energy $\Sigma$ of one discommensuration or the interaction energy $W_2$ of two discommensurations (which depends on the distance $d$ between the two discommensurations) can be derived. If the fixed point type is 2 ($2'$) the interaction $W_2(d)$ between two discommensurations is a monotonic function of $d$. For the fixed point type 3 the interaction is oscillatory.

The fixed point expansion is very useful for the determination of the order of the transitions and for a (numerical and analytical) calculation of the positions of accumulation points. Suppose two neighboring stable commensurate phases $\gamma$ and $\gamma'$ are separated by a transition line. The phase $\gamma'$ can be viewed as resulting from a periodic arrangement of $Z$ adequate discommensurations in the phase $\gamma$ separated by $d_1, \ldots, d_Z$ ($d_{\nu+Z} = d_\nu$) layers. The difference of the free energies per layer is
\[ F = F^{\gamma} - F^{\gamma'} = Z\Sigma + W(d_1, \ldots, d_Z) \approx Z\Sigma + \sum_{\nu=1}^{Z} W_2(d_{\nu}) \]

where we use the fact that usually, due to the rapid exponential decay of \(W_2(d)\), only nearest neighbor discommensuration interactions are to be considered. The phase transition between the phases \(\gamma\) and \(\gamma'\) takes place when \(F\) is equal to zero. If, at the transition, the interaction is monotonic [fixed point type 2 (2')] the transition is of second order and occurs where \(\Sigma\) is zero, the distance \(d\) of neighboring spontaneously formed discommensurations being infinite. If, on the contrary, the interaction is oscillatory (fixed point type 3) the transition is of first order and takes place for positive \(\Sigma\). The distance of neighboring discommensurations is then finite.

For a phase \(\gamma\) three different lines meet at the accumulation point: the phase boundary, the line separating the fixed point types 3 and 2 (2'), and the line separating the fixed point types 3 and 2 (2'). This enabled Tentrup, Jenal, and Siems to find numerically the accumulation points of the series \((2^{k}3)^{3}\), \((2^{k})^{3}\) and \((2^{k+1}3^{2})^{3}\). A low temperature mean field analysis allowed to derive analytical approximations\cite{74,75} which render the coordinates of the accumulation points well.

4. The low temperature series expansion

In their seminal work Fisher and Selke\cite{76,77} derived the low temperature behavior of the ANNNI model by analyzing an exact series expansion of the free energy. Herefore, they used the concept of structure variables \(l_\mu\), thus characterizing each possible ground state by an unique set of these variables. The variable \(l_\mu\) is defined by \(l_\mu = \frac{L_\mu}{T}\) where \(L_\mu\) is the number of band sequences of type \(\mu\) in a given structure in a lattice of \(L\) layers. The free energy can then be written in the form

\[ F = \sum_{\mu} a_\mu l_\mu \]

where the sum is over all possible band sequences. The parameters \(a_\mu\) are expanded in the form

\[ a_\mu = \sum_{k} a_\mu^{(k)} \]

the contributions \(a_\mu^{(k)}\) resulting from the \(k\)th order term in the series expansion of the free energy. In the \(k\)th order term of the free energy enter all terms where the values of \(k\) spins differ from their ground state value. In their analysis of the different orders of the free energy Fisher and Selke concluded\cite{76,77} that the infinity of phases with the phase symbol \((2^{k}3)^{3}\) are stable at low temperatures. Later Fisher and Szpilka refined this expansion using a transfer-matrix method\cite{78}. They showed that among the periodic phases \((2^{k}3)^{3}\) only those with \(1 \leq k \leq k_{\text{max}}\) appear at any fixed small temperature. Since \(k_{\text{max}}\) diverges as \(T \to 0\) all phases of the form \((2^{k}3)^{3}\) indeed spring from the MP. Similarly they concluded that the mixed phases \((2^{k}32^{k+13})\) appear for \(k^{(1)}(T) \leq k \leq k^{(2)}(T)\). Since \(\frac{k^{(1)}}{k_{\text{max}}} \to 0\) and \(\frac{k^{(2)}}{k_{\text{max}}} \to 1\) in the limit \(T \to 0\) phases \((2^{k}32^{k+13})\) appear arbitrarily close to the MP.

This low temperature series expansion technique has also been applied to other models exhibiting modulations, for example to the A3NNI model\cite{79}, the three-state chiral clock model\cite{80}, the generalized \(p\)-state chiral clock mode\cite{81}, a six-state clock model with next nearest neighbor interactions\cite{82}, or the DIS (Double Ising Spin) model\cite{83}. This latter model will be the subject of subsection VI C.

5. The high temperature series expansion

In the high temperature series expansion\cite{84,85} the wavevector dependent susceptibility

\[ \chi(q) = \sum_{j} \langle \sigma_{0}\sigma_{j} \rangle e^{2\pi i q z_{j}} \]

is considered, where the sum is over all correlations and \(z_{j}\) is the number of lattice spacings in \(c\)-direction. Writing the correlation function

\[ \langle \sigma_{0}\sigma_{j} \rangle = \frac{\text{Tr} \left(e^{-\beta H} \sigma_{0}\sigma_{j}\right)}{\text{Tr} \left(e^{-\beta H}\right)} \]
as an high temperature expansion one can construct a series for any wavenumber. As a result the Lifshitz point (for the case $J_0 = J_1$) was found to occur for $\kappa = 0.27$. The critical wavenumber and the critical temperature as function of $\kappa$ were also calculated. In ref. [8], the critical exponents for the different regions along the para phase boundary (i.e., for the para phase-ferro phase transition, the para phase-modulated region transition, as well as for the multicritical Lifshitz point) were calculated for the ANNNI model formulated on a sc or fcc lattice using a series expansion. It was found, in agreement with the results of renormalization group theory [5][6][7][8], that the critical exponents of the phase transition from the para phase to the modulated region are given by the exponents of the 3d-XY model, whereas the critical behavior of the transition from the para to the ferro phase is that of the 3d-Ising model.

B. The AANNDI model

The Axial Antisymmetric Nearest Neighbor Double Ising (AANNDI) model [9] has originally been formulated [10] as an order-disorder mechanism of phase transitions for the compounds of the $A'A''BX_4$-family. Two pseudo spins were introduced, describing the orientational states of a BX tetrahedron. The four discrete orientational states are labeled by $\sigma^A = \pm 1$ (apex up or down) and $\tau^A = \pm 1$ (turn to the right or left). Remarking that the pseudospins $\tau^A$, $\sigma^A$ and the product $\tau^A\sigma^A$ transform according to three different onedimensional representations of the local symmetry group, the general Hamiltonian

$$\mathcal{H} = J' \sum_{nn \text{ in}} \sigma^A_i \sigma^A_j + K' \sum_{nn \text{ in}} \tau^A_i \tau^A_j + L' \sum_{nn \text{ in}} \sigma^A_i \tau^A_j \tau^A_j + J \sum_{nn \text{ out}} \sigma^A_i \sigma^A_j$$

$$+ K \sum_{\text{nn in}} \tau^A_i \tau^A_j + L \sum_{\text{nn in}} \sigma^A_i \tau^A_i \tau^A_j + \frac{1}{2} M' \sum_{\text{nn in}} \sigma^A_i \sigma^A_j (\tau^A_i - \tau^A_j)$$

$$+ \frac{1}{2} M \sum_{\text{nn out}} \tau^A_i \tau^A_j (\sigma_i - \sigma_j)$$

(12)

was derived by retaining only symmetry-allowed nearest neighbor couplings between $\tau^A$, $\sigma^A$ and $\tau^A\sigma^A$. The sums nn in and nn out are over nearest neighbors in the planes and perpendicular to the planes respectively. The AANNDI model is derived from eqn. (12) by retaining the terms

$$\mathcal{H} = J \sum_{l} \sigma^A_l \sigma^A_{l+1} + K \sum_{l} \tau^A_l \tau^A_{l+1} + \frac{1}{2} M \sum_{l} \tau^A_l \tau^A_{l+1} (\sigma^A_l - \sigma^A_{l+1})$$

(13)

where $l$ labels the different layers. In-plane couplings assuring ferro or antiferro orderings in the planes are assumed but not taken explicitly into account. The Hamiltonian (13) is therefore only a onedimensional one which is examined in mean-field approximation [6]. In this analysis the product $\omega^A = \tau^A \sigma^A$ was taken to be independent of $\tau^A$ and $\sigma^A$ thus leading to a mean-field free energy depending on the three layer order parameters $\langle \tau^A \rangle$, $\langle \sigma^A \rangle$ and $\langle \omega^A \rangle$. A closer look reveals that in the equilibrium equations $\langle \sigma^A \rangle$ decouples from the other order parameters. Therefore the term proportional to $J$ can be neglected [9]. It should be noticed that, retaining the antisymmetrical interactions in the planes (cf. eqn. (12)), one obtains the PANNDI (Planar Antisymmetrical Nearest Neighbor Ising) model suitable for the investigation of twodimensional modulations in $A'A''BX_4$-compounds.

C. The Double Ising Spin (DIS) model

The Double Ising Spin or DIS model has been proposed by us [11][12] as a simple model for the investigation of uniaxially modulated materials with the para phase symmetry group $D_{2h}^{16}$. Its Hamiltonian can be derived from the general Hamiltonian (12) by introducing the two spins $\tau \equiv \tau^A$ and $\sigma \equiv \sigma^A \tau^A$. Retaining only symmetric in-layer couplings (as we are not interested in twodimensional modulations) we finally obtain the DIS Hamiltonian

$$\mathcal{H} = K \sum_{ijk} \tau_{ijk} \tau_{ijk(k+1)} + L \sum_{ijk} \sigma_{ijk} \sigma_{ijk(k+1)} + \frac{M}{2} \sum_{ijk} \left( \sigma_{ijk} \tau_{ijk(k+1)} - \tau_{ijk} \sigma_{ijk(k+1)} \right)$$

$$+ J \sum_{ijk} \tau_{ijk} \left( \tau_{i(j+1)j} + \tau_{i(j+1)k} \right) + J' \sum_{ijk} \sigma_{ijk} \left( \sigma_{(i+1)jk} + \sigma_{i(j+1)k} \right)$$

(14)
Comparing it to the AANNDI Hamiltonian (13) reveals that the unimportant term $J$ has been dropped whereas the term $L$ is considered. Furthermore in-layer couplings are explicitly taken into consideration giving way to a three-dimensional model. In the mean-field treatment we have only two order parameters per layer ($\langle r \rangle$ and $\langle \sigma \rangle$) compared to the three order parameters of the AANNDI model.

Frustration and therefore modulations arise in c-direction because of the antagonistic effects of the symmetric nearest neighbor interactions $K$ and $L$ on the one hand and the antisymmetric interaction $M$ on the other hand. The in-layer couplings $J$ and $J'$ are ferro couplings.

In the ground state phase diagram (figure 3) five different phases with a twodimensional stability region are separated by multiphase lines at which infinitely many different phases are degenerate. In the following we will only consider the multiphase lines $K - L = -M$ (line 1) and $K + L = -M$ (line 2). The lines 3 and 4 are obtained from the lines 1 and 2 by the symmetry of the Hamiltonian.

The global temperature-interaction phase diagram is examined in the mean-field approximation. One obtains very different twodimensional sections of the phase diagram depending on whether, at $T = 0$, the line 1 (figure 3) or the line 2 (figure 3) is intersected. In the first case the modulated phases are only encountered at rather high temperatures, in the second case all examined phases reach to low temperatures and seem to converge to the multiphase point. Only some of the commensurate phases are shown, the high-commensurate and the incommensurate phases filling up the shaded areas.

Using the fixed point expansion (cf. subsection VI A 3) we examined the processes leading to the appearance of new phases. In the case 1 the existence of structure combination branching processes and of accumulation points of these branchings has been verified, i.e. new phases are created by the same processes as in the ANNNI model. In the case 2 no branching points nor accumulation points have been found. The phase creation process is therefore different from the process in the ANNNI model.

In order to further clarify this different behavior we performed a low temperature series expansion of the free energy following the ideas by Fisher and Selke for the investigation of the ANNNI model (i.e. of a model with one-component spins). This expansion reveals that in case 1 only four of the infinity of phases degenerate at the MP are stable at low temperatures. All other modulated phases are created by branching processes at higher temperatures. For case 2 it follows from the low temperature expansion that an infinity of different phases spring from the MP. At higher (but still small) temperatures some of the high-commensurate phases disappear. A close inspection of the matrices and vectors entering the computation of the free energy reveals that in the limit $T \to 0$ the DIS model exhibits a complete devil’s staircase for case 2.

The critical properties of the model can be derived by writing the Hamiltonian (14) in matrix form. A special local transformation then leads to a Hamiltonian where the interaction terms are given by scalar products between vectors entering the computation of the free energy. This expansion reveals that in case 1 only four of the infinity of phases degenerate at the MP are stable at low temperatures. All other modulated phases are created by branching processes at higher temperatures. For the case $K < 0$ and $L < 0$ the partition function of this Hamiltonian can then be transformed to the partition function of an effective Ginzburg-Landau-Wilson-Hamiltonian for which one can show that it has the critical behavior of the 3d-XY model.

A connection with experimental results obtained for actual crystals is established by applying the method described in section VII to the DIS model. For BCCD, for example, this leads to a description which is at least as good as the description by the ANNNI model, the latter being a special case of the former.

### D. Interrelations of various pseudo spin models

A general $r$-spin model containing $r$ spins per cell $\sigma_1^r, \ldots, \sigma_r^r$ can also be described as a $q = 2^r$-state model. The state variable $p_n = 1, \ldots, 2^r$ and the spin variables $a_n = (\sigma_1^r, \ldots, \sigma_r^r)$ are, for example, connected by the equation:

$$p_n = 1 + \frac{1}{2} \sum_{i=1}^{r} (\sigma_i^r + 1) 2^{i-1}.$$ 

Special cases of $r$-spin models are, e.g., $2^r$-state Potts models.

Pseudo spin systems in the narrower sense are described by Hamiltonians of the form

$$H = \sum_{n,m} \Lambda_{nm}^r \sigma_n^r \sigma_m^r.$$ 

For uniaxially modulated systems with nearest neighbor interactions in the planes perpendicular to the direction of the modulations this Hamiltonian may be rewritten as

$$H = \sum_{(n,m)} V_{nm}^{ij} \sigma_n^i \sigma_m^j + \sum_{n,m} W_{nm}^{ij} \sigma_n^i \sigma_m^j.$$
The matrix \( V \) denotes couplings perpendicular to the modulation direction, the sum running over all nearest neighbor pairs \((n,m)\) in the planes, whereas \( W \) denotes couplings along the direction of the modulations.

In the previous sections we discussed three different pseudo spin models: the ANNNI model (section \( VI.A \)), the AANNDI model (section \( VI.B \)) and the DIS model (section \( VI.C \)). Whereas the ANNNI model is an one-spin model, the DIS and the AANNDI model are, in their original formulation, two-spin models. However, in the treatment of the AANNDI model Kurzyński considered three independent order parameters \( \langle \tau^A \rangle, \langle \sigma^A \rangle \) and \( \langle \omega^A \rangle \), i.e. the AANNDI model is treated as a model with the three pseudo spins \( \tau^A, \sigma^A \) and \( \omega^A \). The DIS model is, on the contrary, treated as a model with two pseudo spins \( \tau \) and \( \sigma \) per cell.

Both the AANNDI and the DIS model can be derived from the general Hamiltonian \( (12) \).

The DIS model represents a model which is somewhat more general than the ANNNI model but nevertheless so simple, that it allows the derivation of explicit results (dependent on a few well defined local interactions) which can be compared to experimental data. This powerful model contains some other much discussed models as special cases:

Since a general \( r \)-Ising spin model (i.e. a model, where \( r \) spins describe the state of every unit) can also be considered to be a \( 2^r \)-state model \( \left( \text{i.e. a variable} \ p = 1, \ldots, 2^r \ \text{describes the state of every unit} \right) \), it follows that the DIS model can be formulated as a four-state model. For the special case \( K = L < 0 \) and \( J = J' < 0 \) the DIS Hamiltonian can be rewritten in the form \( (12) \)

\[
\mathcal{H} = -\zeta_0 \sum_{<n,m>}^\perp \cos \left( \frac{\pi}{2} (p_n - p_m) \right) - \zeta \sum_{<n,m>}^\parallel \cos \left( \frac{\pi}{2} (p_n - p_m + \Delta) \right),
\]

where we introduced the variables

\[
\zeta_0 := -2J, \quad \zeta := \sqrt{M^2 + 4K^2} \quad \text{and} \quad \Delta := -\frac{2}{\pi} \arctan \left( \frac{M}{2K} \right).
\]

This is exactly the Hamiltonian of the four-state chiral clock \( (CC_4) \) model \( \square \). It follows from the exact expansion of the free energy for the special case \( K = L < 0 \) of the DIS model that in the limit \( T \to 0 \) the \( CC_4 \) model exhibits a complete devil’s staircase. This is in marked contrast to an earlier statement \( \square \) that only specific phases spring from the MP. A detailed analysis of this rather complicated calculation reveals \( \square \) that in the earlier investigation the treatment of the in-layer interactions was erroneous, thus leading to wrong expressions for the free energies. In fact, recent Monte Carlo simulations \( \square \) of the \( CC_4 \) model show the existence of modulated phases not predicted by ref. \( \square \) but in accordance with our results.

It can further be shown \( \square \) that a special case of the DIS model (two pseudo spins per cell with nearest neighbor interactions) can be mapped exactly onto the ANNNI model (one pseudo spin per cell with nearest and next nearest neighbor interactions). At the first sight this is surprising, since with respect to the range of direct interactions the ANNNI model is more general. For the special case considered no direct couplings between neighboring \( \sigma \)-spins are retained, i.e. \( L = 0 \) and \( J' = 0 \) in eqn. \( (13) \). The \( \sigma \)-spins then mediate an indirect next nearest neighbor coupling between the \( \tau \)-spins. The resulting relation between the coupling parameters of the two models is temperature-dependent. Its explicit analytic form is \( 14 \)

\[
J_0 = -J,
J_1 = -K,
J_2 = -\frac{1}{2\beta} \ln \cosh (\beta M).
\]

### VII. CONNECTION OF MODEL CALCULATIONS WITH EXPERIMENTALLY DETERMINED PROPERTIES OF ACTUAL MATERIALS

#### A. Theoretical derivation of phase diagrams in terms of experimental control parameters

All the reviewed theoretical models for the description of uniaxially modulated materials have in common that the displayed phase diagrams are twodimensional sections of a higher dimensional space spanned by the model parameters (for example reduced temperature, reduced interactions etc.). The experimental phase diagrams, however, are spanned by external quantities like temperature, pressure or applied fields. It is thus necessary to find a mapping between the experimental quantities and the theoretical parameters in order to compare the experimental and theoretical phase diagrams. In the following we will present a procedure for transforming a two-dimensional theoretical phase
diagram from model parameters to the temperature-pressure variables. This mapping has originally been formulated for
the ANNNI and the DIS models in order to describe BCCD. Since the experimental wave numbers \( q \) are given as
multiples of \( 2\pi/c \), the assignment of units to half cells yields (for the ANNNI model) \( q = \nu/(Z_1 + Z_2 + \ldots + Z_\nu) \) for
the relation between the phase symbol \( \langle Z_1 Z_2 \ldots Z_\nu \rangle \) and \( q \). We will now present a more general approach transforming
arbitrary theoretical phase diagrams into temperature-pressure phase diagrams.

The method requires the knowledge of the thermal expansion coefficients, the elastic constants, and information on
the critical line \( T_{\text{crit}}(p_{\text{crit}}) \) separating the normal phase from the lower-symmetry phases in the \( T-p \) diagram. From
the determination of the critical wavenumber for different pressures \( k_{\text{crit}} \) a fit \( q_{\text{crit}}(p_{\text{crit}}) \) can be found.

Let the two quantities spanning the considered two-dimensional theoretical diagram be \( \kappa \) and \( \theta \). In the ANNNI
model, for example, \( \kappa \) is given by \( \kappa = -\frac{\partial k}{\partial T} \) whereas \( \theta \) is the reduced temperature \( \theta = \frac{k_BT}{\kappa} \). The critical line \( \theta_{\text{crit}}(\kappa) \) and
the critical wavenumber \( q_{\text{crit}}(\kappa) \) result from an analytical calculation (ANNNI, AANNDI, DIS model) or from a
numerical fit (DIFFOUR, Chen and Walker’s model).

In the first step the critical line \( \theta_{\text{crit}}(\kappa_{\text{crit}}) \) is transformed into a critical \( T-p \)-line. For a given \( \kappa = \kappa_0 \) the critical
values \( q_{\text{crit}}(\kappa_0) \) and \( \theta_{\text{crit}}(\kappa_0) \) are obtained. On the other hand, as the wavenumber \( q_{\text{crit}} \) is now known, the values
\( p_{\text{crit}}(q_{\text{crit}}) \) and \( T_{\text{crit}}(p_{\text{crit}}(q_{\text{crit}})) \) for the critical pressure can be derived, thus leading to a theoretical \( T-p \) critical line.

In the next step we consider an arbitrary point \( (\kappa, \theta) \). The temperature coordinate is obtained by the simple
transformation rule \( k_BT = \frac{k_BT_{\text{crit}}}{\kappa_{\text{crit}}} \theta \). Depending on the models this rule may be replaced by a more sophisticated
approach. For simplicity, we assume that the model interactions depend only via the mean lattice constant on temperature and pressure, i.e. \( J_k = J_k(\pi(T, p)) \). Under this assumption the interactions are constant along lines
where \( \pi \) is constant. Lines with constant \( \pi \) are especially lines with constant volume. Expanding the volume about its
value for a given temperature \( T_0 \) and pressure \( p_0 \) leads to the equation

\[
V(T, p) = V(T_0, p_0) + \frac{\partial V}{\partial T}(T_0, p_0) \cdot (T - T_0) + \frac{\partial V}{\partial p}(T_0, p_0) \cdot (p - p_0) \\
+ \frac{1}{2} \frac{\partial^2 V}{\partial T^2}(T_0, p_0) \cdot (T - T_0)^2 + \frac{1}{2} \frac{\partial^2 V}{\partial p^2}(T_0, p_0) \cdot (p - p_0)^2 \\
+ \frac{\partial^2 V}{\partial T \partial p}(T_0, p_0) \cdot (T - T_0) \cdot (p - p_0) \\
or

\[
v = \frac{V(T, p) - V(T_0, p_0)}{V(T_0, p_0)} \\
= 3\pi \cdot (T - T_0) - k \cdot (p - p_0) + \frac{3}{2} \frac{\partial \pi}{\partial T} \cdot (T - T_0)^2 \\
- \frac{1}{2} \frac{\partial k}{\partial p} \cdot (p - p_0)^2 - \frac{\partial k}{\partial T} \cdot (T - T_0) \cdot (p - p_0)
\]

(15)

where we introduced the thermal expansion coefficient \( \pi = \frac{1}{V} \frac{\partial V}{\partial T} \) and the compressibility \( k = -\frac{1}{V} \frac{\partial V}{\partial p} \). The value of \( v \) is determined by the intersection point of the line of constant volume with the para phase boundary, i.e. \( v = \frac{V(T_{\text{crit}}, p_{\text{crit}}) - V(T_0, p_0)}{V(T_0, p_0)} \). Inserting the temperature \( T \) in eqn. (15) finally leads to the respective pressure.

Figure 7 shows the theoretical temperature-pressure phase diagram derived from the ANNNI model for the de-
scription of BCCD. This diagram shows the same topology as the experimental diagram, similar extensions of the
modulated branchings, and the observed branchings. The phase diagram for the DIS model is transformed in a similar
way as the ANNNI-phase diagram.

The observed increase of transition temperatures with uniaxial compressional strains \( -\varepsilon_{ii} \) corroborates the assump-
tion that the interactions depend on \( p \) and \( T \) only via the lattice constants.

This approach especially allows the determination of the effective couplings \( J_k \) as a function of the lattice parameters.
They can also be derived from the shape \( \omega(q) \) of a softening phonon branch. A linear chain with up to \( N \)th nearest
neighbor couplings with dispersion relation

\[
|k\omega(q)|^2 = \sum_{k=1}^{N} J_k \cdot (1 - \cos kq)
\]

is considered as analogon to the crystal. A least-squares fit of this relation to the soft phonon branch for various
temperatures \( T \) above the transition to the modulated phases yields the dependence \( J_k(T) \).
For uniaxial modulations, the mean values of atomic displacements do not vary in planes perpendicular to the axis of modulation, which is c in the case of BCCD. Hence, the generalized variables have (at the thermal average) values \( Q_n^\ell = Q_\ell(3) \) and \( Q_n^T = Q_\ell(4) \) and \( Q_n^4 = Q_\ell(4) \) where \( \ell = 2n_3 \) and \( \ell + 1 = 2n_3 + 1 \) label consecutive layers (dotted vertical lines in figure 8), formed from quadruples of blocks belonging to cells at positions \((n_1 n_2 n_3)\). The displacements related to the \( \ell \)-layer variables \( Q_\ell(3) \) and \( Q_\ell(4) \) are called the \( \ell \)-layer modes. The notation is adapted to the fact that these layers can be considered equivalent as the space group operation \( \mathcal{G}^5 = \{C_{3\bar{1}5}\} \) generates a pseudoperiodicity of half a lattice constant along the c-axis by transforming one layer into the next. This construction yields \( \ell \)-layer variables as in Chen and Walker’s model (cf. subsection V B). Specific differences arise for modulations along b, whereas the \( \sigma \)-displacements produced by the second layer mode are in opposite direction. Depending on how one combines the nitrogen atoms and the layers, whether both modes are considered equivalent or only one (the layer mode related to \( Q_\ell(3) \) in our nomenclature). Hence, we tried a structure prediction for the displacements of the nitrogen atoms in the fourfold phase of BCCD either in terms of the layer modes of Chen and Walker’s model or in terms of relevant cell modes. If, following Chen and Walker, two consecutive nitrogen atoms are assigned to the planes given by full vertical lines in figure 8, their displacements are quite different and two modes are needed for a reasonable description. If, however, the nitrogen atoms are assigned to the planes given by dotted lines, as proposed in the present paper, their displacements are very similar and one (relevant) mode gives already a very good description as shown in figure 8. An application of the DIS model to BCCD, which corresponds to taking into account a second set of SALMs as opposed to the ANNNI model with one set of SALMs, yields even better agreement of calculated and measured structures.

If both the ANNNI model and the DIS model are treated in mean field approximation, there is no need in distinguishing pseudo spins derived from amplitudes of cell modes for front or back half cells: in an application of the ANNNI model to BCCD the pseudo spin \( \sigma \) is derived from \( Q^3, Q^7 \). In the DIS model the pseudo spin \( \tau \) is derived from \( Q^7, Q^3 \) whereas the pseudo spin \( \sigma \) is derived from \( Q^3, Q^7 \). Since the pseudo spins \( \sigma \) (for the ANNNI model) or \( \sigma \) and \( \tau \) (for the DIS model) stand for the amplitudes of certain local modes, their transformation behavior under space group operations can be determined and relations between the couplings can be found. It can be shown that the antisymmetric coupling \( M \) between the two pseudo spin subsystems of the DIS model is not introduced ad hoc but follows necessarily from symmetry.

Making use of the transformation behavior of the generalized variables, expressions for the spontaneous polarization of the crystal in terms of the amplitudes \( Q_\ell(3) \) and \( Q_\ell(4) \) can be derived. Since the components of the spontaneous polarization vector \( P_S \) must transform like any vectorial quantity under the operations of the space group \( Pnma \), only such terms are allowable in an expansion of \( P_S \) in terms of relevant mode amplitudes that are in accordance with symmetry. Expanding \( P_S \) up to second order in \( Q_\ell(3) \) and \( Q_\ell(4) \) and keeping only terms involving same or adjacent layers, the following expressions can be derived:

\[
P_S = \sum_\ell (-1)^\ell [P_x Q_\ell(3) Q_{\ell+1}(3) + P_x Q_\ell(4) Q_{\ell+1}(4) + P_x Q_\ell(3) Q_{\ell+1}(4)] + \ldots
\]

\[
P_S = \sum_\ell (-1)^\ell P_y Q_\ell(3) + \ldots,
\]

\[
P_S = \sum_\ell P_z Q_\ell(3) Q_\ell(4) + \ldots.
\]

\( P_x^1, P_x^2, P_y^1 \) and \( P_z^1 \) are constants specific for BCCD. A sequence of equal \( Q_\ell \) leads to alternating signs of \( x \)- and \( y \)-displacements in consecutive layers as the respective layer modes are transformed one into another by the screw axis \( \mathcal{G}^5 \). This is as a consequence of the proposed definition of the local modes. Thus, in the case of BCCD, a correspondence of pseudo spin averages \( S_\ell \) to \( Q_\ell(3) \) with alternating signs was performed in our previous work. The corresponding expressions for the DIS model with

\[
Q_\ell(3) \rightarrow (-1)^\ell t_\ell,
\]

\[
Q_\ell(4) \rightarrow (-1)^\ell s_\ell.
\]
read

\[ \begin{align*} 
P_{S,x} &= \sum_{\ell} (-1)^{\ell} \left[ \hat{P}_{1t}^{4} t_{t+1} + \hat{P}_{2s}^{2} s_{t+1} + \hat{P}_{3}^{3} s_{t} t_{\ell} + \hat{P}_{x}^{4} (t_{t} s_{t+1} - s_{t} t_{\ell+1}) \right], \\
P_{S,y} &= \sum_{\ell} \hat{P}_{y}^{4} t_{\ell}, \\
P_{S,z} &= \sum_{\ell} \hat{P}_{z}^{4} t_{\ell} s_{t}. \end{align*} \]

(16)

For the values of pressure and temperature applied in measurements in BCCD\[\text{[54]}\], the following spontaneous polarizations are obtained depending on the wavenumber: \( m_{a} = \text{odd} \)

\( P_{S,x} \); \( m_{a} = \text{even} \), \( P_{S,y} \); \( m_{a} = \text{odd} \), no spontaneous polarization. This is in perfect agreement with the spontaneous polarizations obtained from the DIS model for the corresponding model parameters and the assumption that a symmetry mode of \( T_{3} \)-symmetry gives the primary contribution to the structural deformation. If only one mode per half cell is retained (\( Q^{3}, Q^{3} \)), the expressions for \( P_{S,x} \), \( P_{S,y} \) and \( P_{S,z} \) are given by the terms in eqn. (16) depending only on \( t_{\ell} \), in complete accordance with the terms we proposed in ref. \[\text{[54]}\]. Recently new dielectric investigations on BCCD revealed the so-called \( T_{3} \)-anomaly \[\text{[54]}\] in the regions of the commensurate \( \frac{1}{2} \)- and \( \frac{1}{2} \)-phases exhibiting the characteristics of a commensurate-commensurate phase transition where the wave number is unchanged. The same phenomenon occurs in structures derived from the DIS model; a detailed discussion will be given elsewhere \[\text{[54]}\].

**VIII. THE INFLUENCE OF POINT DEFECTS**

In subsection \( \text{VII A} \) it was shown that – even if there is not yet an ab initio type of theory – it is possible to establish a quantitative connection between experimentally determined \( T, p \)-phase diagrams and theoretical diagrams formulated originally in terms of model parameters. In the case of an ANNNI model description, the latter are the couplings \( J_{i} \), defined, as explained above, by thermal averaging over local modes. A simplifying step in this procedure was the plausible assumption that these model parameters depend on \( T \) and \( p \) mainly via the total strains or via the lattice constants. By making use of macroscopic material properties like thermal expansion, elastic coefficients etc., this lattice constant dependence of the couplings \( J_{i} \) was explicitly derived. The similarity of the theoretical and the experimental phase diagrams support this procedure. The success of this approach made it promising to interpret defect influences, e.g. on phase diagrams, along the same lines. For the general treatment we shall extend the basic assumption somewhat, allowing for a dependence of the effective interactions not only on \( T \) and dilatation but on \( T \) and general strain components. We shall first formulate this extended version, then include defect contributions to the strains, and finally give some explicit results on defect influences. The method is exemplified for the ANNNI model; it can, however, easily be transposed to other models.

Let the phase diagram be formulated in the space of the experimental control parameters temperature \( T \) and components \( \sigma_{E}^{ij} \) of the tensor \( \sigma_{E} \) describing a homogenous external (applied) stress field. The aim of the method to be described is to obtain an approximate theoretical statement as to which one of the many modulated phases occurring in the model will be stable at a point \( (T, \sigma_{E}) \) in parameter space.

If results of ab initio electron theory or of atomistic interaction potential theory followed by a thermal averaging procedure were at hand, these would yield the effective interactions \( J_{i}(T, \sigma_{E}) \) and the stable phase could directly be read \( (T, \sigma_{E}) \) from the theoretical ANNNI phase diagram in \( (T, J_{0}, J_{1}, J_{2}) \)-space for any set of control parameters.

If the dependence \( J_{i}(T, \sigma_{E}) \) is not known from basic theory, the following procedure, which makes use of macroscopic properties and characteristics of the para phase boundary (PPB) yields approximate results: let the empirically determined PPB and the modulation vectors on the PPB be given by \( T = T(\sigma_{E}) \) and \( q = q(\sigma_{E}) \) and assume the effective model parameters \( J_{i} \) to depend on \( T \) and \( \sigma_{E} \) (only) via certain linear combinations of the stress tensor components \( \varepsilon_{ij} \):

\[ J_{i} = J_{i}(P_{mn}^{(i)} \varepsilon_{mn}) =: J_{i}(\Omega^{(i)}) \]

(summation over repeated subscripts). The coefficients \( P_{mn}^{(i)} \) are chosen in a plausible way taking the lattice structure into account. The displacements are counted from the para phase positions at some temperature \( T_{0} \) above but close to the PPB, zero applied stresses \( \sigma_{E} \) and no defects. For crystals free of defects the total strains are, in linear approximation, the sum of elastic and thermal expansion contributions:

\[ \varepsilon_{mn} = S_{mnkj} \sigma_{E}^{kj} + \alpha_{mn}(T - T_{0}) \]

(17)
and
\[ \Omega^{(i)} = R^{(r)}_{mn} S_{mn kj} \sigma^E_{kj} + R^{(r)}_{mn} \alpha_{mn}(T - T_0) =: \Lambda^{(i)}_{kj} \sigma^E_{kj} + B^{(i)}(T - T_0). \] (18)

For this step, values of the macroscopic elastic moduli and thermal expansion coefficients are required. Relation (18) may be (and was) improved by taking higher order terms and coefficients into account. For any point (defined e.g. by the external stress \( \sigma^E \)) on the PPB, the corresponding set of model parameters \( J_i \) may be determined by observing that in the ANNNI model the modulation vector on the PPB depends only on the interaction ratio \( \kappa = -J_2/J_1 \) [cf. eqn. (14)]:
\[ q_{\text{crit}}(\kappa) = \frac{1}{2\pi} \arccos \frac{1}{4\kappa} \quad \text{for} \quad \kappa > 0.25. \]

Thus \( \kappa \) is known for any point on the PPB. Now the model PPB is given by
\[ kT_{\text{crit}} = 4J_0 + (2\kappa + \frac{1}{4\kappa})J_1 =: 4J_0 + f(\kappa)J_1. \]

\( J_0 \) and \( J_1 \) can be determined from the (experimentally determined) dependence of \( T_{\text{crit}} \) on \( f(\kappa) \) for variations of \( \sigma^E \) which leave
\[ \Omega^{(i)} = \Lambda^{(i)}_{kj} \sigma^E_{kj} + B^{(i)}(T_{\text{crit}}(\sigma^E) - T_0), \quad i = 0, 1 \]
and thus also \( J_0 \) and \( J_1 \) invariant. Once \( \kappa, J_0, J_1 \) are determined, \( J_2 \) is obtained from \( \kappa \) and \( J_1 \). In this way one obtains corresponding values of \( J_i \) and \( \Omega^{(i)} \), that is a numerical representation of the function \( J_i(\Omega^{(i)}) \). One can thus assign to any point \((T, \sigma^E)\) (also to points off the PPB) the corresponding values \( J_i \). Reference to the ANNNI \((T, J_0, J_1, J_2)\)-phase diagram then yields the phase stable at \((T, \sigma^E)\).

For defect crystals the contributions \( \varepsilon^D \) of the point defects to the local strains have to be included in eqn. (17). The deformation due to a point defect (see e.g. ref. 7) is described by its force dipole tensor \( P_{kj} \). With the material's elastic Green's function \( G_{kj}(r, r') \), which is expected to be, in good approximation, the same for different modulated phases, the strain field at \( r \) produced by (equal) defects at positions \( r' \) is
\[ \varepsilon^D_{mn}(r) = \sum \nu G_{mj,kn}(r, r')P_{kj} \]
and that produced by an uncorrelated distribution of defects with local defect density \( \rho^D(r) \) is
\[ \varepsilon^D_{mn}(r, \rho^D) = \int G_{mj,kn}(r, r')P_{kj} dV' \] (19)
with \( f_{k'} := \partial f/\partial x_{k'} \). In extension of the procedure described above, the local model parameters, e.g. the ANNNI couplings \( J_i(r) \) are then assumed to depend on the local strains \( \varepsilon \) and via these not only on temperature and external stresses \( \sigma^E \) (e.g. on pressure), but by eqn. (14) also on the defect distribution \( \rho^D(r) \):
\[ J_i(r) = J_i(\varepsilon(r)) = J_i \left\{ \{ S_{mn kj} \sigma^E_{kj} + \alpha_{mn}(T - T_0) + \varepsilon^D_{mn}(r, \rho^D) \} \right\}. \]

Dividing the defect strain into its average and a position dependent contribution one has
\[ \varepsilon^D(r) = \bar{\varepsilon}^D(\rho^D) + \left( \varepsilon^D(r, \rho^D) - \bar{\varepsilon}^D(\rho^D) \right). \]

The influence of the average strain corresponds to an extra term \( \sigma^D_{kj} = C_{kj pq} \varepsilon^D_{pq} \), which has to be added to the external strain \( \sigma^E_{kj} \). From the experimentally observed average deformation \( \bar{\varepsilon} \) connected with a defect concentration \( \rho^D \), the dipole tensor can be determined. One has
\[ P_{kj} = C_{kj mn} \bar{\varepsilon}_{mn} / \rho^D. \]

\(^1\)In addition, the interactions (between two units) will be changed quite apart from the defect induced strain simply due to the fact that in one of the two units there is a substitutional or an interstitial atom. This effect is not considered here.
If our basic assumption is correct that the model parameters \( J \) depend on temperature and external stresses mainly via the total strain field including elastic and thermal contributions and if the main defect contribution is a function of the average defect induced strain \( \varepsilon^D(p) \), then the dominant impurity effect on the phase diagram should be an alteration obtained by replacing the external stresses \( \sigma_{kj}^E \) by \( \sigma_{kj}^E + \rho^D \sigma_{kj} = \sigma_{kj}^E + C_{kjm\gamma} \varepsilon_{mn} \). This relation was checked for brominated BCCD under hydrostatic pressure for which phase diagrams were experimentally determined for various Br-concentrations. Already the rough approximation of the variables \( \Omega(i) \) by the dilatation \( \varepsilon_{mn}/3 \), i.e. the average relative volume change, leads (with experimentally determined material constants \( R_{mn} \)) to a good agreement with experimental data: For Br-concentrations of 1.8%; 7.3%; 20% the calculated pressure shifts are -20 MPa; -81 MPa; -222 MPa as compared to experimentally observed shifts of -18 MPa; -61 MPa; -238 MPa respectively.

The influence of spatial variations of the defect strains was investigated for a situation with simple model characteristics, control parameters and defect arrangements: the coefficients \( R \) in \( \Omega(i) \) were chosen to define the dilatation part of the strains \( (R_{mn} = \delta_{mn}) \), the external stress is a hydrostatic pressure \( (\sigma_{ij}^E = -p \delta_{ij}) \), and the defect distribution is such as to produce a dilatation strain field \( \varepsilon^D := \varepsilon^D_{ii} \) which varies only in one direction (perpendicular to the modulation axis), with a position \( (x) \) dependence described by a saw tooth function. The nearest neighbor interactions \( J_0 \) and \( J_1 \) were set equal to each other. Depending on the amplitude of the spatial variation of defect concentration or strain, this scenario leads to a coexistence of several phases for given values of temperature and pressure. A small section of the phase diagram is considered and the general procedure described above for calculating the phase diagram is modified correspondingly: the strain field and the free energy densities \( f^\gamma \) of the phases \( \gamma \) are expanded about values of temperature, pressure and position corresponding now to a point in the middle of that section at a local position in the middle of a saw tooth:

\[
f^\gamma \{ J_i[\Omega(T,p,\varepsilon^D(x))], T \} = f^\gamma_0 + A^\gamma_1 \Delta T + A^\gamma_2 \Delta p + A^\gamma_3 \Delta x
\]

with \( f^\gamma_0 = f^\gamma(T^0,p^0,x^0) \) and

\[
A^\gamma_1 := \frac{\partial f^\gamma}{\partial J_i} \frac{\partial J_i}{\partial \Omega} \frac{\partial \Omega}{\partial T} + \frac{\partial f^\gamma}{\partial J_i} \frac{\partial J_i}{\partial \Omega} \frac{\partial \Omega}{\partial p} + \frac{\partial f^\gamma}{\partial J_i} \frac{\partial J_i}{\partial \Omega} \frac{\partial \Omega}{\partial x}; \quad A^\gamma_2 := \frac{\partial f^\gamma}{\partial J_i} \frac{\partial J_i}{\partial \Omega} \frac{\partial \Omega}{\partial p}; \quad A^\gamma_3 := \frac{\partial f^\gamma}{\partial J_i} \frac{\partial J_i}{\partial \Omega} \frac{\partial \Omega}{\partial \varepsilon^D} \frac{\partial \varepsilon^D}{\partial x}.
\]

With the position \( x^\gamma \) of the boundary between phases \( \gamma - 1 \) and \( \gamma \), and with \( \gamma = 0 \) the first and \( \gamma = m \) the last phase to occur, the total free energy is

\[
F(p,T,\{x^\gamma\}) = \sum_{\gamma=0}^{m} \int_{x^{\gamma-1}}^{x^\gamma} f^\gamma dx. \tag{20}
\]

Minimizing \( F \) with respect to the boundary positions \( x^\gamma \) yields the local extensions of the different phases as function of \( T \) and \( p \).

Explicit calculations were performed for the phase diagram show in figure. The temperature (or pressure) dependence of physical quantities which are different in different phases (i.e. which depend on the modulation wave number \( q \)) will vary in a typical way with the defect concentration gradient. As a representative of such quantities we consider \( q \) itself. Its average is obtained from the values \( x^\gamma \), and the wave numbers \( q^\gamma \).

Results of such calculations are shown in figure. For crystals with a spatially constant defect density, \( \overline{q}(T) \) is characterized by a series of plateaus corresponding to one modulated phase each with discontinuous transitions between them (figure). Upon introducing a spatial (saw-tooth-like) variation of the defect density, the plateaus become gradually narrower and the transitions become continuous. This is shown in figure where the amplitude of the defect density variation increases in equal steps from figure (amplitude zero) to figure. The transitions intervals now correspond to the coexistence of two or more phases whose boundaries are continuously shifted with temperature. For sufficiently high concentration gradients some plateaus disappear completely, indicating that the stability range of the corresponding phase is so small that there is no temperature for which \( \gamma \) is the only stable phase in the whole specimen.

**IX. DISCUSSION AND OUTLOOK**

The theoretical description of materials exhibiting modulated phases may be subdivided into four main points:

1) Eventually the description should be based on an ab initio electron theory (e.g. ref), or, if that is too difficult to handle with the necessary accuracy for the rather large number of atoms per unit cell, on calculations using empirical atomic interactions (e.g. ref). A suitable procedure would be to determine total energies for the para
phase configuration and for a number of appropriately chosen deformations. The respective results should allow the
selection of adequate simplified models, the formulation of the respective effective Hamiltonians, and a determination
of the model parameters. These models should then be handled as described under points 2), 3), 4). So far there are
scarcely any results of this kind. Calculations along these lines, however, would allow to go, for a not too complicated
system, all the way from an atomistic theory to explicit statements on phase diagrams, polarizations etc. In such a
treatment approximations are of course necessary and should be made (in the original atomistic theory as well as in
the consecutive model calculations); but one should avoid ad hoc assumptions (fits) as far as possible.

2) The second part of the description is the formulation and investigation of the properties of model systems with
one or a few relevant local variables like e.g. the DIFFOUR model. Especially if this is the first step (i.e. if one cannot
deduce these models explicitly from one of the ab initio theories of point 1), all symmetry information should be
taken into consideration in the formulation of the models. The main task is the statistical mechanics treatment which
should start from the respective (effective) Hamiltonian and should yield information on phase diagrams, orders
of the transitions, polarizations etc. The calculations may be and have been performed either in a more or less
analytic way by using schemes of approximation like e.g. the mean field or the self consistent phonon method. Or,
ameritatively, numerical approaches (molecular dynamics simulations) were used. So far, calculations for such models
were performed mainly for very simplified geometries like linear chains.

3) A further step in the simplification process is the projection of models with a (small) number of continuous local
variables onto models with discrete states, or, finally, onto pseudo spin models. Depending on the number of relevant
original local modes one obtains pseudo spins with one or more components per crystallographic unit. Substantial
advantages of this type of description are, that the powerful apparatus of Monte Carlo simulations can be applied and
that analytic approximations exist which allow the explicit calculation of many interesting physical properties. This
part of the theory is well developed. This holds especially for mean field treatments which in some instances where
compared with more pretentious methods and shown to yield a good description.

4) Finally there is the problem of translating the results of model calculations obtained as functions of the model
parameters into data which can be quantitatively compared to experimental data, i.e. which are expressed as functions
of experimentally given quantities like pressure or stresses (besides temperature). In section VII it was shown how this
can be done. By making use of macroscopic material constants, a physically motivated mapping from one parameter
set to the other can be performed. For the material considered (BCCD) the results show a satisfactory agreement
with experimental data.

In the last years considerable effort has been addressed to the approaches described in section VI, that is to the
formulation of various p-state and pseudo spin models and to their statistical mechanics. Methods applied were MFA
calculations, exact series expansions for selected regions in parameter space, and Monte Carlo simulations. Combining
these approaches, a reliable theoretical determination of most of the interesting thermodynamic properties of such
models is possible.

A transformation of these model properties into a form directly comparable to experimental data can be performed
by the procedure described in subsection VII A or by a similar scheme. An interesting by-product of this method is
information on the dependence of the model parameters on the experimentally given state variables and especially
on the lattice distortions. Combined with a consideration of experimentally determined atomic positions in some of
the more stable phases, this should further the understanding of the local dynamics responsible for the transition
sequences.

Of special interest, finally, would be the determination of model parameters – for not too complicated materials –
from an atomistic theory. It should be possible, with the nowadays available computing power, to carry through the
necessary calculations. Investigations of this type would clarify the details of the relevant atomistic mechanisms and
e.g. help to understand why the phase diagrams of members of the same homologous family of materials may differ
drastically.

X. ACKNOWLEDGEMENTS

Interesting discussions with Prof. D. Sannikov and financial support from the Deutsche Forschungsgemeinschaft (Si
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FIG. 1. The blocks $\mathfrak{A}_i$, $i = 1 \ldots 8$ belonging to the unit cell (depicted as wireframe) at the origin $O$.

FIG. 2. Mean field phase diagram of the ANNNI model with $J_0 = J_1$.

FIG. 3. The different fixed point types. Shown are the positions of the four eigenvalues of the matrix $G^k$ in the complex plane.

FIG. 4. Ground state of the DIS model. The pair of upper/lower signs per column of the symbols represent the signs of the $\tau$- and $\sigma$-spin averages in consecutive layers: I is the fully ferroelectric phase, II the fully antiferroelectric phase, whereas III and IV are mixed phases in which one spin type orders ferroelectrically, the other antiferroelectrically. The structure of the phase V repeats itself after 4 layers. The vertices are given by $(L, M) = (1,0), (0,1), (-1,0)$ and $(0,-1)$.

FIG. 5. Global phase diagram of the DIS model with $\kappa_\pm = -0.1$ and $\frac{L}{M} = \frac{J_0}{J_1} = -0.25$. Only few modulated phases are shown. $\theta = \frac{k_B T}{J_1}$ is the reduced temperature, $\kappa_\pm = \frac{K \pm L}{M}$, and $K, L, M$ are the different couplings in direction of the modulations.

FIG. 6. Global phase diagram of the DIS model with $\lambda = \frac{L}{M} = 0.1$ and $\frac{L}{M} = \frac{J_0}{J_1} = -0.25$.

FIG. 7. $(p, T)$-phase diagram for BCCD calculated from the ANNNI model. Dashed lines: boundaries to higher commensurate or incommensurate phases.

FIG. 8. Measured (o) and calculated (●) $y$-displacements of the nitrogen atoms in the fourfold phase of BCCD. The modulation profile was calculated from the ANNNI model, i.e. with one variable per unit (crystallographic half cell). Solid and dotted lines: centers of layers in Chen and Walker’s model and in the SALM model respectively; consecutive nitrogen atoms are assigned to the layer between them.

FIG. 9. Section of the ANNNI model phase diagram exhibiting some of the more stable phases for which the results shown in figure 10 were obtained. This section is part of the region occupied by the phases observed in BCCD.

FIG. 10. Averaged modulation wave number $q$ vs. $\Theta = kT/J_1$. Plateaus correspond to phases (56) (1), (56)$^2$(556) (2), (56556) (3), (56(556)$^2$) (4) and (556) (5). $\rho_D^a$ and $a_x$ are increasing from a) ($a = \text{const}$) to f) in equal steps. In all six cases the sum of applied pressure and chemical shift at $x_0$ is kept constant (e.g. by keeping $\rho_D^a(x_0)$ and $a(x_0)$ fixed).
B. Neubert, M. Pleimling, R. Siems: FIGURE 2
B. Neubert, M. Pleimling, R. Siems: FIGURE 3
B. Neubert, M. Pleimling, R. Siems: FIGURE 5

\[ \kappa_- = -0.1 \]
\[ \lambda = 0.1 \]

\[ \theta \]

\[ 0.0 \quad 1.0 \quad 2.0 \quad 3.0 \quad 4.0 \quad 5.0 \quad 6.0 \]

\[ 1/10 \quad 1/8 \quad 1/6 \quad 3/16 \quad 1/5 \quad 1/4 \]
B. Neubert, M. Pleimling, R. Siems: FIGURE 8
B. Neubert, M. Pleimling, R. Siems: FIGURE 10