Microscopic theories of order-disorder structural phase transitions in crystals

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The status of the microscopic theories is reviewed for the following types of order-disorder structural phase transitions in crystals: a) phase transitions in crystals with hydrogen bonds; b) orientational phase transitions in ionic-covalent crystals; c) orientational phase transitions in molecular crystals; d) order-disorder phase transitions in ordered interstitial and substitutional alloys. Attention is focused primarily on the static properties, i.e., the nature of the ordering, the phase-transition thermodynamics, and the distinctive features of these phase transitions in comparison with other phase transitions, particularly magnetic ones. The methods employed in the theoretical description of order-disorder structural phase transitions are examined—the Hamiltonians used, approximate methods for calculating the statistical properties (with allowance for correlation effects), exactly solvable models, etc. The existing theories of the phase transitions in various real crystals, including problems and results, are critically discussed for phase transitions of types a) and b).

PACS numbers: 64.60.Cn, 61.50.Ks

CONTENTS

1. INTRODUCTION

Structural phase transitions receive a great deal of attention in solid-state physics. There is an enormous literature on the subject, including many review articles (e.g., Refs. 1–11). However, the theoretical exposition in these reviews, as a rule, deals mainly with the phenomenological description, in the spirit of either the classical Landau theory and its variations[1–4,10,11] or the modern fluctuational theory (see, e.g., Ref. 6). The microscopic theory of structural phase transitions is presented in these reviews only very briefly[6] or else in an extremely specialized way, in application to particular systems.[7–9] These remarks pertain particularly to structural phase transitions of the order-disorder type, since for structural phase transitions of the displacive type the theories based on the concepts of a critical "soft mode" in the phonon spectrum and a small anharmonicity have been worked out and described in the literature in greater detail.[8,6] At the same time there have been no broad surveys of the microscopic theories of order-disorder structural phase transitions, and information on this subject can be found only in the original papers. The inaccessibility and scattered nature of the information may be one of the reasons that some investigators[6] regard the state of the microscopic theory of structural phase transitions as "unsatisfactory."

At the same time, the past decade has witnessed a very broad research activity, both experimental and theoretical, on the microscopic nature of order-disorder structural phase transitions in very different types of crystals—ferroelectrics and antiferroelectrics, molecular cyrstals, metallic alloys, and other systems. This research has yielded a large store of factual information on the features and properties of the various types of order-disorder structural phase transitions, pointing to the presence of a variety of general features and theoretical problems common to these phase transitions. In the present review article we attempt to generalize and compare the available material, discuss how the features of the ordering and the thermodynamics depend on the microscopic nature of the interactions, and examine the problems and methods which pertain to the theoretical description of order-disorder structural phase transitons.

We shall discuss only "properly" structural order-disorder phase transitions—those due to the ordering of atoms
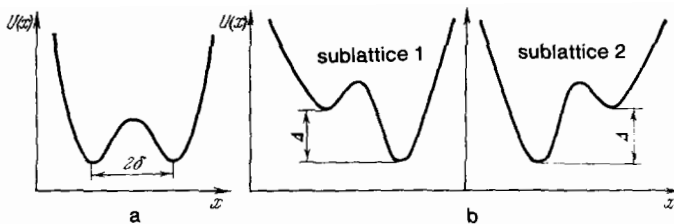
FIG. 1. The shape of the symmetric (a) and asymmetric (b) double-minimum potentials $U(x)$ for groups undergoing ordering in crystals with order-disorder structural phase transitions.

or groups of atoms in crystalline potentials with several minima, of the type shown in Fig. 1. Structural phase transitions due to the ordering in the spin or electronic subsystems—magnetostructural, Jahn-Teller, etc.—will not be considered. Thus, we shall discuss order-disorder phase transitions of the following basic types:

A) Phase transitions in crystals with double-well hydrogen bonds, due to the ordering of the H ions in the bonds.

B) Orientational phase transitions due to the ordering of atom groups in ionic-covalent crystals.

C) Orientational phase transitions in molecular crystals.

D) Order-disorder phase transitions in ordered alloys and interstitial systems.

The theoretical descriptions of all these phase transitions have a number of general features and common problems, which are discussed in this and the next section. However, in considering specific phase transitions in Secs. 3 and 4 we shall, for reasons of space, discuss only phase transitions of types A and B, i.e., phase transitions in nonmolecular and nonmetallic crystals. Orientational phase transitions in molecular crystals have a number of features which stem primarily from the "nearly free' orientational motion in the disordered phase, and the properties and problems of these phase transitions must be reviewed separately. Further, it would hardly be worthwhile to discuss order-disorder structural phase transitions in specific metallic alloys in this short review, as there is an extensive special literature on the subject (see, e.g., Refs. 7 and 156 and the literature cited therein).

We shall consider mainly the static (i.e., structural and thermodynamic) aspects of the order-disorder structural phase transitions. For most transitions of this kind dynamical anomalies are manifested only in a critical slowing down of the relaxation phenomena near the phase transition and are usually described adequately by phenomenological models of the Debye type.[6,8] However, the microscopic theories of these anomalies have received little development (except for the case of certain molecular crystals, where dynamical anomalies due to the phase transition are discussed in terms of a growing influence of the anharmonicity near the phase transition). We shall also barely touch upon critical fluctuation effects (which are treated in many theoretical papers but, as a rule, are only weakly expressed in real order-disorder structural phase transitions; see Ref. 6 and below), and questions of the general theory of phase transitions, exactly solvable models, etc. will be mentioned only in connection with applications to specific systems.

Before turning to the detailed discussion, let us mention certain general characterisitc features of order-disorder structural phase transitions which distinguish them from magnetic transitions, for example. These features stem mainly from the fact that the atomic displacements at an order-disorder structural phase transition are usually not small. Therefore, in these phase transitions an important role is often played by the large short-range repulsive forces and/or the considerably long-range forces of electrostatic or deformations (i.e., due to straining of the lattice) origin, with interaction constants significantly larger than the transition temperature T_c. For this reason there are sharp differences between these interactions and the short-range exchange interactions in magnets with exchange integrals $J \sim T_c$. These differences show up in different ways for phase transitions of the various types A–D listed above.

1. In order-disorder structural phase transitions in crystals with hydrogen bonds (type A phase transitions) there are usually strong correlations in the arrangement of protons on adjacent bonds; these correlations correspond to a forbidding of the so-called "charged" configurations (the "ice rule" of Pauling[12,13]), leading to abrupt anomalies in the thermodynamics of these phase transitions (see Sec. 3).

2. Ordering transitions in interstitial alloys (phase transitions of type D) also manifest marked short-range correlations which amount to the blocking of positions adjacent to each of the interstitial atoms (preventing other interstitial atoms from locating there) and, in addition, diplay effects of strong long-range forces due to the very large values of the deformational interactions in close-packed crystals.[7]

3. For orientational phase transitions of types B and C, the large anisotropy of the high-multiple (quadrupole, octupole, etc.) electrostatic interactions and the consequent presence of competing interactions of opposite signs, in combination with the "long-range" effects (the sizable interactions of non-nearest neighbors), lead to an abundance of complex orderings with a substantial increase in the lattice periods and sometimes to the appearance of incommensurate phases.

4. In highly symmetric (e.g., cubic) lattices there is usually a large number (12, 8, 6, etc.) of equivalent minima of the crystalline potential for different orientations or positions of the interstitial atom for phase transitions of types B, C, or D. As is shown in Sec. 4, this often leads to a succession of "step-like" phase transitions with different orderings as the temperature is lowered.

5. In complex crystals the aforementioned long-range effects often cause the minima of the crystalline potential to be asymmetric, as in Fig. 1b. The phase-transition thermodynamics and the phase diagrams in these cases also tend to be extremely peculiar (see Secs. 3 and 4).

As we shall see, the factors mentioned above also cause the large majority of order-disorder structural phase transitions to be of first order, with order-parameter discontinuities approaching the saturation values. For this reason (and also because of the importance of the long-range electrostatic or elastic interactions, the strong short-range correlations mentioned above, and other effects) critical fluctuation effects, which are quite apparent at phase transitions in mag-

nets, are usually of little consequence in order-disorder structural phase transitions.[6]

On account of all these features and others as well, the methods used in the theoretical description of many order-disorder structural phase transitions are also different from those in the magnetic case. One of the goals of this review is to systematize the results which have been obtained in this area.

In this short review we cannot discuss in detail the historical questions pertaining to research on order-disorder structural phase transitions. Therefore, we have primarily included in the list of references only those papers which seem the most up-to-date and useful for familiarizing the reader with the topics discussed. In giving experimental data on these phase transitions we also cite mainly just the more recent papers; citations of earlier literature can be found in these papers.

2. METHODS OF MICROSCOPIC DESCRIPTION OF ORDER-DISORDER TYPE STRUCTURAL PHASE TRANSITIONS

In the theoretical description of particular structural phase transitions, one can distinguish the following basic steps:

a) formulation of a suitable microscopic model;

b) calculation of the statistical properties and phase-transition thermodynamics in this model;

c) calculations or estimates of the interaction constants and other model parameters.

For phase transitions of the various types A–D listed above, the interactions responsible for the transitions and the extent of their previous study differ widely. Formulation of an adequate model also requires specific information on the crystal structure and how it changes at the phase transition. But in spite of the differences in the physical mechanisms and structures, the general form of the mathematical models and Hamiltonians used to describe the order-disorder structural phase transitions are often similar. The differences lie chiefly in the physical nature of the interactions and the relative values of the interaction constants. Let us discuss the form of these models and Hamiltonians and examine the methods of calculating the thermodynamic properties in these models.

a) Hamiltonians used for describing systems with order-disorder structural phase transitions.

The simplest models of an order-disorder structural phase transition correspond to the case in which the vibrational amplitudes of all the atoms (or of oriented atomic groups, which for the sake of brevity will not be mentioned further) about each of the minima of the crystalline potential $U(x)$ are small. Then one can in a first approximation neglect the vibrations and assign a position of the atom near the i-th minimum $r_i = r + \delta_i$ in the cell centered at r with the aid of a projection operator $c_i(r)$, which is equal to unity if the atom is located in the given minimum and to zero otherwise. If there are only two minima for each of the ordering atoms (as in Figs. 1 and 2), then instead of the operators c_i one usually introduces a pseudospin operator $\sigma^z = \pm 1$ related to the projection operators by $c_{1,2} = (1 \pm \sigma^z)/2$. Then the configu-

rational part of the Hamiltonian, i.e., the part dependent on c_i or σ_i^z, can be written in the form (see, e.g., Refs. 7 and 8)

$$H = -\tfrac{1}{2} \sum_{rr'ij} V_{ij}(\mathbf{R}) c_i(\mathbf{r}) c_j(\mathbf{r}') - \sum_{ri} \Delta_i c_i(\mathbf{r}), \quad (1)$$

or

$$H = -\frac{1}{2} \sum_{rr'ij} V_{ij}(\mathbf{R}) \sigma_i^z(\mathbf{r}) \sigma_j^z(\mathbf{r}') - \sum_{ri} \Delta_i \sigma_i^z(\mathbf{r}); \quad (2)$$

here $\mathbf{R} = \mathbf{r} - \mathbf{r}'$, the interaction of the atoms is assumed binary, and Δ_i characterize the asymmetry of the potential minima (which can also be caused by an external electric field). In the absence of asymmetry one has $\Delta_i = 0$. The indices i and j in formula (2) allow for the possible presence of several sublattices undergoing orders (as in Fig. 1b, which corresponds to the model for the phase transition in Rochelle salt,[4,8] discussed in Sec. 4b).

Transitions $\Delta \mathbf{r}_{ij} = \delta_i - \delta_j$ of the atom undergoing ordering between minima of the potential U induce displacements $\mathbf{u}$ of the remaining atoms of the lattice. When these induced displacements and the oscillations $\mathbf{x}$ of the atom undergoing ordering about each of the minima are taken into account in the harmonic approximation (i.e., the approximation linear in δ_i and $\mathbf{u}$ or $\mathbf{x}$), additional terms—the so-called "pseudospin-phonon coupling" terms, which are bilinear in $\mathbf{u}$ or $\mathbf{x}$ and $c(\mathbf{r})$ or $\sigma^z(\mathbf{r})$—appear in (1) and (2). In the calculation of the thermodynamic properties these terms lead only to a renormalization $V_{ij} \rightarrow \tilde{V}_{ij}$ of the constants in (1) and (2), so that in addition to the "direct" interaction of the atoms undergoing ordering, $\tilde{V}_{ij}$ also describes the indirect or "deformational" interaction through the exchange of phonon.[4,7,8]

When anharmonic effects, i.e., terms of higher order in δ and $\mathbf{u}$ or $\mathbf{x}$ (and also direct many-body forces), are taken into account, the effective Hamiltonians (1) and (2) acquire additional terms involving products of three and four of the operators $c_i(\mathbf{r})$ or $\sigma^z(\mathbf{r})$ (see Ref. 14). These terms have usually been ignored in concrete calculations. They can, however, be important, as in the case when one is attempting a quantitative description of the short-range interaction of the interstitial atoms in interstitial alloys, since the anharmonicity of the displacements $\mathbf{u}$ can be appreciable here. If one is using a binary interaction model, this can lead to an effective "concentration dependence" of the constants $\tilde{V}_{ij}$.

In certain hydrogen-bonded crystals, e.g., ferroelectrics of the KDB type (KDP is potassium dihydrogen phosphate, KH_3PO_4), the quantum mechanical penetrability of the barrier in Fig. 1 is apparently high enough that the tunneling of the proton between the minima of $U(\mathbf{x})$ must be taken into account.[4,15] Here, however, in describing the phase transition it is sufficient to take into account only the two lowest quantum states of the proton in the bond—the symmetric $\psi_s(\mathbf{x})$ and antisymmetric $\psi_a(\mathbf{x})$ states—since the energies of the higher states are estimated[16,17] to be more than an order of magnitude higher than the temperature T_c. If one describes the states of the proton in the i-th bond using the representation $\psi_\pm^i = (\psi_a^i \pm \psi_s^i)2^{-1/2}$ and makes allowance for the fact that the displacements x of the protons from the center of the bond $\mathbf{r}$ are small compared to the distance R

between the centers of different bonds, then in place of (2) the Hamiltonian becomes[14,8]

$$H = -\frac{1}{2} \sum_{\mathbf{rr'} ij} V_{ij}(\mathbf{R}) \sigma_i^z(\mathbf{r}) \sigma_j(\mathbf{r'}) - \sum_i [\Delta_i \sigma_i^z(\mathbf{r}) - \hbar\Omega_i \sigma_i^x(\mathbf{r})];$$

(3a)

here

$$V_{ij}(\mathbf{R}) = \sum_{\alpha, \beta=1}^{3} x_{sa}^{\alpha} x_{sa}^{\beta} \frac{\partial^2 \bar{w}_{ij}(\mathbf{R})}{\partial R_\alpha \partial R_\beta},$$

(3b)

$w_{ij}(\mathbf{R})$ is the interaction potential of the protons of the bonds $(\mathbf{r},i)$ and $(\mathbf{r'},j)$, $\Omega_i = (\varepsilon_a^i - \varepsilon_s^i)/2\hbar$ has the meaning of the tunneling frequency, and σ^z and σ^x are the Pauli matrices. Hamiltonian (3) has also been applied to the description of certain orientational phase transitions, in particular, the transition in Rochelle salt,[4] where the ordering entities are apparently O–H groups.[2]

The small-anharmonicity approximation used in the derivation of (1) and (2), which is equivalent to the assumption of a small probability of hopping between the minima of the potential $U(\mathbf{x})$, is valid for interstitial and substitutional alloys (where different values of $c_i(\mathbf{r})$ or $\sigma^z(\mathbf{r})$ correspond to finding atoms of different kinds[7,18] at site $\mathbf{r}$), for the majority of phase transitions that have been studied in hydrogen-bonded crystals, and also for orientational phase transitions in ionic-covalent crystals. In a number of molecular and ionic-molecular crystals, however, the orientational interaction is small compared to T_c. Therefore, the amplitude and anharmonicity of the orientational oscillations (librations) are not small, and so the expansions of H about the minima of $U(\mathbf{x})$ in (1) and (2) can converge extremely slowly. For describing phase transitions of this kind one uses "continuous" orientational Hamiltonians of the form[19-21]

$$\hat{H} = \sum_{\mathbf{r}} \hat{T}(\omega_\mathbf{r}) + \mathcal{U}, \quad \mathcal{U} = -\sum_{\mathbf{r}} U(\omega_\mathbf{r}) - \frac{1}{2}\sum_{\mathbf{rr'}} V_\mathbf{R}(\omega_\mathbf{r}, \omega_{\mathbf{r'}}).$$

(4)

Here the centers of mass of the molecules are assumed to be fixed at the lattice sites $\mathbf{r}$, $\omega_\mathbf{r}$ is a set of angles describing the orientation of the molecules (e.g., Euler angles), $\hat{T}(\omega)$ is the rotational kinetic energy operator for a rigid molecule (rotator), and the potential energy $\mathcal{U}$ consists of the sum of the crystalline field potential U and the interaction potential $V_\mathbf{R}$. In actual calculations $U(\omega)$ and $V_\mathbf{R}(\omega,\omega')$ are usually series-expanded in a set of basis functions $u_{lv}(\omega)$ corresponding to the symmetry of the molecules (spherical harmonics $Y_{lm}(\omega)$ for linear molecules,[19] the so-called tetrahedral-rotator functions[20] for tetrahedral molecules such as CH_4, and so forth):

$$\mathcal{U} = -\sum_{\mathbf{r}lv} \Delta_{lv} u_{lv}(\omega_\mathbf{r})$$

$$-\frac{1}{2}\sum_{\mathbf{rr'}ll'} f_{ll'} \sum_{vv'} C_{vv'}^\mathbf{R}(l, l') u_{lv}(\omega_\mathbf{r}) u_{l'v'}(\omega_{\mathbf{r'}}),$$

(5)

and only the lowest or several lowest values of the angular momenta l and l' retained in the sums, in accordance with the symmetry of the crystal structure and of the interactions (see, e.g., Ref. 21).

The coupling of the librations with the displacements $\mathbf{u}$ of the centers of mass of the molecules has generally not been taken into account in calculations for phase transitions of this sort. If quantum effects are not important in the description of the phase transition (as is the case for the majority of orientational phase transitions), then allowance for this coupling in the linear (in $\mathbf{u}$) approximation again [as in (1) and (2)] leads only to a renormalization of the constants $V_\mathbf{R}$ in (4) (see, e.g., Refs. 22–24).

b. Methods of calculating the thermodynamic properties

The Hamiltonians H in (1)–(5) are analogous in form to those used to describe phase transitions in magnets. Therefore, for calculations with these Hamiltonians basically the same approximation methods are used as in the magnetic case (these are discussed, for example, in several reviews[25-27]). As we have mentioned, however, structural order-disorder phase transitions have peculiar ordering patterns and correlation properties which often necessitate certain modifications in the calculational methods as well. Let us discuss the approximation methods used in calculating the thermodynamics of order–disorder structural phase transitions.

1) Mean field approximation (MFA). The simplest and most widely used description of the phase transitions in very different systems is the mean (or molecular) field approximation (see, e.g., Refs. 8, 18, and 26). In this method the interaction of each particle (spin) with the rest is described with the aid of a mean field determined from self-consistency conditions. As we know, this approximation does not take into account any correlation in the position (orientation) of the particles due to either long-range critical fluctuations near the phase transition point (which, as we mentioned, are usually not very pronounced in real order-disorder structural phase transitions) or to short-range effects such as the forbidding of charged configurations in hydrogen-bonded systems or the blocking effect in interstitial alloys. If the short-range correlations are not too strong, as, for example, in the simple "ferromagnetic" models of (1) and (2) with $V_{ij} > 0$, $\Delta_i = $ const, then the MFA gives a reasonably good qualitative description of the phase transition. For example, for a nearest-neighbor interaction one can calculate T_c and other characteristics of the phase transition with an accuracy of 15–20%, and as the interactions become longer-ranged this accuracy improves.[8] At the same time, the interactions $V_{ij}(\mathbf{R})$ in the MFA are described by only a small number of constants. For example, if all the atoms in (2) are equivalent, so that the indices i and j can be dropped, and $\Delta_i = Ep_e$, where E is the external field and p_e is the effective dipole moment, then the MFA expressions for the ferroelectric order parameter $\sigma = \langle\sigma_z\rangle$ and free energy per atom F contain only the average interaction V:

$$F = \frac{1}{2}V\sigma^2 - T\ln 2\,\mathrm{ch}\,\alpha, \quad \sigma = \mathrm{th}\,\alpha, \quad \alpha = \beta\,(V\sigma + Ep_e), \quad (6a)$$

$$V = \sum_\mathbf{R} V(\mathbf{R}); \quad (6b)$$

where[1] $\beta = 1/T$. Therefore, the MFA is conveniently ap-

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[1] Throughout this review the temperature T is given in energy units, i.e., the Boltzmann constant k_B is dropped; accordingly, the entropy $S = -\partial F/\partial T$ is dimensionless here. For example, the dimensionless entropy per molecule is obtained by dividing the dimensional entropy S_d by the constant R: $S = S_d/R$.

plied to systems with poorly understood interactions in order to verify qualitative ideas about the nature of the phase transition. In particular, this method has been used to study the features (discussed in Sec. 4) of phase transitions which involve ordering in asymmetric[28,8] and many-well potentials. The use of this simple approximation is also a necessary first step in considering the complex orderings characteristic of order-disorder structural phase transitions. For example, it has enabled investigators to predict the structures of the ordered phases of solid hydrogen,[19] methane,[20] certain alloys,[7] etc. Finally, let us mention a method that has proved effective for describing superstructural order-disorder phase transitions in alloys and many other systems: the so-called method of concentration waves, a modified MFA developed by Khachaturyan.[7] This method is based on an expansion of the occupation probability $n_i(\mathbf{r}) = \langle c_i(\mathbf{r}) \rangle$ [with $c_i(\mathbf{r})$ from (1)] of each of the sublattices in a Fourier series in the wave vectors $\mathbf{k}_s$ corresponding to the stars of the superstructures formed, with detailed allowance for the symmetry of the lattice. The application of this method to the description of phase transitions in systems with many-well potentials (polyorientational systems) is discussed in Sec. 4.

2) Methods of taking correlations into account. Cluster approximations. The methods used to make approximate allowance for correlations in order-disorder structural phase transitions can be divided into the following main groups.

a) Formal expansions of the thermodynamic potentials in powers of the correlational interactions-the Kirkwood method and its variations (see, e.g., Sec. 19 of Ref. 7), expansions in the reciprocal of the range of the interaction,[29] etc.

b) Methods of decoupling the equations for the correlation (Green's) functions[27,30,31]

c) Various sorts of cluster approximations—quasichemical, "constant coupling," and cluster variational methods—Bethe, Kikuchi, etc.[26,32,33]

The methods of group a) are the most systematic from a formal standpoint. For realistic interactions, however, they involve extremely awkward manipulations, and, in addition, the convergence of the expansions used in these methods deteriorates near T_c. These approximations are seldom used to describe real order-disorder structural phase transitions. For example, the only applications of the Kirkwood method that we know of are for models of alloys with nearest-neighbor interactions[18] and for phase transitions in solid hydrogen.[34]

The methods of group b) have been applied for general qualitative discussion of the dynamical features near structural phase transitions[35,8] and for description of the "soft mode" in KDP-type crystals, which is treated as a coupled oscillation of the heavy atoms of the lattice (K, P, and O) and the protons tunneling between the two potential wells.[36,37] However, as far as the thermodynamics is concerned, the decoupling method[36] correponds to the MFA, which, as we shall see, cannot be used for any quantitative description of KDP. These methods have been applied in more detail to molecular crystals, where they have been used to study the relationship between the dynamical and thermodynamic

anomalies at orientational phase transitions (see, e.g., Refs. 30 and 31).

The general idea of the cluster approximations c) is to consider a certain group of particles (a cluster) in such a way that the interactions of the particles within the cluster are described exactly, i.e., as in the initial Hamiltonian, while their interaction with the environment is treated approximately, with the aid of an effective field determined from self-consistency conditions or by minimization of the free energy. In the case of magnets, cluster approximations are seldom used, since their application to quantum systems (whose Hamiltonians contain noncommuting operators) encounters certain difficulties, such as the prediction of fictitious "anti-Curie points"[33,38] at which the ordering vanishes at some $T < T_c$. In order-disorder structural phase transitions, however, quantum effects are usually small, while on the other hand the short-range correlations discussed earlier, which are due to competing interactions or to the forbidding of certain configurations of adjacent particles, are often important. In these cases the MFA becomes completely inapplicable, while the cluster approximation, on the contrary, becomes most adequate. The cluster approximation has been used successfully to study a number of phase transitions in crystals with hydrogen bonds,[33,15,39–41] orientational phase transitions in the case of competing interactions,[42,43] and order-disorder phase transitions in alloys[44,18] and interstitial systems,[45] and we shall discuss this approximation in more detail. We note in this regard that although the various versions of the cluster approximation give mutually consistent results for the simplest models, the calculational methods which they use are very different[25,26] and are sometimes unnecessarily complicated. Here we shall discuss the version of the cluster approximation described in Ref. 8, as this is the most convenient form for applications and generalizations. It is this version that was used in Refs. 15 and 38–42 and, unless otherwise stipulated, is what we mean in this paper by the term cluster approximation.

Let us first illustrate the method on the example of a ferroelectric phase transition in a simple Ising lattice (2) with a nearest-neighbor interaction $V_{ij} = J > 0$ and $\Delta_i = Ep_e$ (see Ref. 8 for details). Singling out a group (cluster) of s adjacent spins, we write the density matrix ρ_s in the form

$$\rho_s(\sigma_1^z, \sigma_2^z, \cdots, \sigma_s^z) = \frac{\exp(-\beta H_s)}{\mathrm{Sp}\exp(-\beta H_s)};$$ (7)

here H_s is the effective Hamiltonian of the cluster, consisting of the interactions H_{in} between the spins within the cluster, the interaction H_{ex} between the spins of the cluster and the surrounding spins, and the interaction H_E with the external field. It is assumed in the cluster approximation that the interactions H_{in} remain the same as in the initial Hamiltonian (2), [i.e., do not incorporate their renormalization by indirect interactions through the outside spins], while the effect of the environment on the cluster spins is described by an effective field φ_{ex}. If all the spins of the cluster are equivalent (as, for example, in a 2-spin cluster, square 4-spin cluster, or cubic 8-spin cluster in a simple cubic Ising lattice), then the expression for H_s in the cluster approximation is of the form

$$H_s = H_{\text{In}} + H_{\text{ex}} + H_{E} = - \sum_{i>j=1}^{s} J\sigma_i^z\sigma_j^z - \sum_{i=1}^{s} \sigma_i^z (\varphi_{\text{ex}} + Ep_{\text{e}}).$$

$$(8)$$

The single-particle density matrix ρ_1 for each of the spins can be written in the form

$$\rho_1(\sigma^z) = \frac{\exp(-\beta H_1)}{\text{Sp}\exp(-\beta H_1)}, \quad H_1 = -\sigma^z(\varphi + Ep_{\text{e}}), \qquad (9)$$

where the field φ, like φ_{ex} in (8), describes the influence exerted on the spin by its environment. To establish the connection between the fields φ and φ_{ex}, we use the obvious idea that the contributions to these fields from each of the bonds combine additively. Then, if each of the spins of a cluster having a total of n bonds has m bonds within the cluster, one has $\varphi_{\text{ex}} = (1 - m/n)\varphi$. An equation for finding φ can be obtained from the self-consistancy conditions $\rho_1 = Sp_{2,3,\ldots,s}\rho_s$, or

$$\langle\sigma^z\rangle = \text{Sp}\,\sigma^z\rho_1(\sigma^z) = \text{Sp}\,\sigma_1^z\rho_s(\sigma_1^z, \sigma_2^z, \ldots, \sigma_s^z). \qquad (10)$$

The average energy per spin, $\mathscr{E}$, is obtained by averaging the initial expression (2), taking (7)–(9) and the relation between φ_{ex} and φ into account:

$$\mathscr{E} = \frac{n}{ms}\langle H_s\rangle - \left(\frac{n}{m} - 1\right)\langle H_1\rangle, \qquad (11)$$

where $\langle H_k\rangle = \text{Sp}H_k\rho_k$. Finally, the free energy F is related to $\mathscr{E}$ as $\mathscr{E} = -\partial(\beta F)/\partial\beta$. A solution of this equation is the function

$$\beta F = -\frac{n}{ms}\ln Z_s + \left(\frac{n}{m} - 1\right)\ln Z_1, \qquad (12)$$

where $Z_k = \text{Sp}\exp(-\beta H_k)$. In fact, the partial derivative of (12) with respect to β gives (11), while the derivative with respect to φ vanishes by virtue of (10). It is thus seen that the self-consistency condition (10) is equivalent to the condition that the free energy be minimum as a function of φ: $\partial F/\partial\varphi = 0$. The integration constant in (12) is chosen such that for $T\to\infty$ the entropy $S = -\partial F/\partial T$ goes to its "free" value ln2. Explicit expressions for Z_s and Z_1 in (12) are easily found by direct summation over all spin states.[8]

For the case under discussion, a simple Ising lattice with nearest-neighbor interaction, the results of the simplest cluster approximations—the binary-cluster, Bethe,[25–26] and quasichemical[25,18] approximations—agree with one another and differ from the exact values [of T_c or $S_c = S(T_c)$, for example] by 10–15%. The accuracy of the cluster approximation improves rather slowly[8] with increasing cluster size s. In addition, the choice of the cluster should correspond naturally with the geometry of the problem.[8] For example, for describing orderings of the Cu_3Au type in a face-centered cubic lattice, the choice of a binary cluster ($s = 2$) even leads to the erroneous result that there is no phase transition, while the choice of a tetrahedral cluster ($s = 4$) already gives a noticeable improvement over the MFA results.[44,18]

More-complicated versions of the cluster approximation (the Kikuchi approximation, etc.) which systematically take into account clusters of different sizes and the couplings between them give results for T_c to an accuracy of 3–7%, but they are extremely awkward[26] and have evidently not been
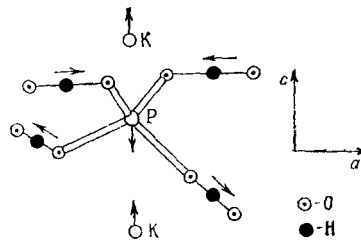

FIG. 2. Schematic diagram of the displacements of the H, K, and P ions at the phase transition in a KDP crystal (KH_2PO_4).

applied to describe a real structural phase transition. The critical exponents[6] near T_c in all versions of the cluster approximation remain the same as in the MFA. Thus, for simple Ising models the cluster approximation gives only a certain quantitative refinement of the mean field results. The situation is different when strong short-range correlations are present in the system, as we illustrate below for the case of KDP.

3) Application of the cluster approximation to the phase transition in KDP. The structure of the KDP crystal is described, for example, in Refs. 1–5 and 8. The tetrahedral PO_4 groups are coupled in a three-dimensional network of hydrogen bonds which lie almost perpendicular to the tetragonal axis c; the displacements of the ions at the phase transition are shown schematically in Fig. 2. For simplicity, let us neglect the effects of the displacements of the heavy ions K, P, and O and the tunneling of the proton between the two potential wells in the hydrogen bond (discussed in Sec. 3). At first we shall take into account the interactions of the protons on nearest-neighbor bonds only. If, as in Sec. 2a, the two equilibrium positions of the proton on the bond are related to the operator σ^z in such a way that values $\sigma^z = +1$ correspond to the ground state shown in Fig. 2, then the phase transition problem again reduces to a model of the form (2). Here, however, there are strong correlations among the orientations of the four spins adjacent to each PO_4 group. In fact, of the 16 possible confirmations of these spins shown in Fig. 3a, six are neutral, eight are singly charged, and 2 are doubly charged, i.e., correspond to finding two, three or one,
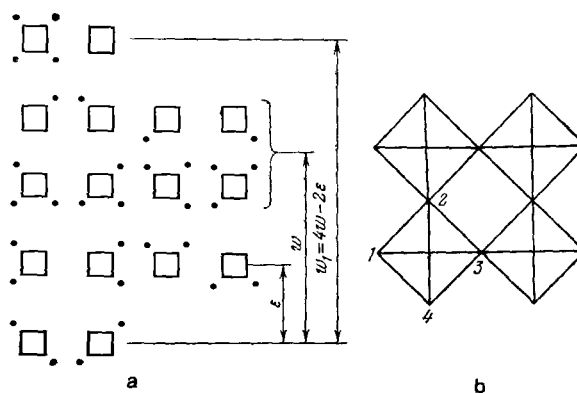

FIG. 3. a) Diagram showing the different proton configurations around the PO_4 groups in KDP and their energies; b) projections of the system of lines representing the interaction of nearest protons in KDP onto a plane perpendicular to the c axis.

and four or zero protons near the PO_4 group. Of the 6 neutral configurations, two (the configuration indicated in Fig. 2 and the configuration obtained from the one shown by reversing the directions of the arrows) have minimum energy and the remaining four (which are degenerate on account of the crystal symmetry) have an excitation energy ε. As we shall show, the phase transition temperature T_c is $\sim \varepsilon$. The energies w of the charged configurations are much larger than ε (by a factor of 8–10),[15] so the population of these configurations [$\sim \exp(-\beta w)$] near T_c is extremely low.

As usual, let us associate with each spin σ_i^z of model (2) a site in an auxiliary lattice, and with each interaction V_{ij} a line joining the sites. Then the projection of the system of these bonds onto a plane perpendicular to the c axis has the form shown in Fig. 3b. Numbering the spins as indicated in the figure, expressing the constants V_{ij} in terms of the parameters ε and w introduced above, and making allowance for the symmetry of the lattice, we find[8,32]:

$$V_{12} = V_{23} = V_{34} = V_{41} = \frac{1}{2}w - \frac{1}{4}\varepsilon, \qquad V_{13} = V_{24} = \frac{1}{2}\varepsilon - \frac{1}{2}w.$$ (13)

It is seen that the suppression of the charged configurations, i.e., the inequality $w \gg \varepsilon \sim T_c$ corresponds in the language of model (2) to the presence of strong competing interactions of different signs. In particular, for $w \to \infty$ the charged configurations are strictly forbidden (i.e., the system obeys the ice rule,[12] which corresponds to the Slater[13] model for KDP and is discussed in Sec. 3). Clearly, the MFA is entirely unsuitable for describing such a situation. For example, according to (13), at $w \to \infty$ the "average interaction" V in (6b) and the MFA value of T_c which is proportional to this quantity go to infinity instead of to the correct value $T_c \sim \varepsilon$. The character of the temperature curves near T_c is also incorrectly described in the MFA at large values of w/ε (see Ref. 8 and below).

In accordance with what we have said about the cluster approximation, we choose as the cluster the set of 4 spins adjacent to a PO_4 group. Reasoning as we did in the derivation of (7)–(12), we obtain for the free energy F per KDP molecule [i.e., per two "spins" in (2)] the expression[8,32,33]

$$\beta F = -\ln Z_4 + 2\ln Z_1,$$ (14)

where

$$Z_4 = 2e^{\beta w}(\operatorname{ch} 2\beta\psi + K + 4L \operatorname{ch} \beta\psi), \quad Z_1 = 2\operatorname{ch}\beta u,$$
$$\psi = \varphi + 2Ep_e, \quad u = \varphi + Ep_e,$$ (15)
$$K = 2e^{-\beta\varepsilon} + e^{-\beta w_2}, \quad L = e^{-\beta w},$$

and $w_2 = 4w - 2\varepsilon$ is the excitation energy of the doubly charged configurations. The effective field φ is determined from the condition $\partial F/\partial \varphi = 0$. In the absence of an external field E, this equation can be solved analytically, yielding the following expression[32,8] for the order parameters $\sigma = \langle \sigma^z \rangle$ at $T < T_c$:

$$\sigma = \frac{\sqrt{(1 - K - 2L)(1 - K + 2L)}}{1 - K},$$ (16)

while the phase transition point T_c is determined from the equation

$$K(T_c) + 2L(T_c) = 1.$$ (17)

Non-nearest-neighbor interactions can be taken into account in the cluster approximation by the mean field method (which is apparently rather accurate in view of the relative weakness of these interactions and the large number of particles participating in them).[8,29] We separate out these interactions in the initial Hamiltonian (2) and, after writing in the usual way[8,29] $\sigma^z(\mathbf{r}) = \sigma + \Delta\sigma^z(\mathbf{r})$, where σ is the average value of the spin, we neglect in these terms the interaction of the fluctuations $\Delta\sigma^z$. Then, in place of (14), F assumes the form[8,46]

$$F = -T \ln Z_4 + 2T \ln Z_1 + \gamma\sigma^2,$$ (18)

where Z_4 and Z_1 differ from (15) only in that Ep_e is replaced by $Ep_e + \gamma\sigma$, while γ is given by (6b) with the summation over $\mathbf{R}$ carried out only over non-nearest-neighbors. The values of φ and σ are found from the self-consistency conditions or by minimizing F with respect to φ and σ.

The thermodynamic consequences of relations (14)–(18) (and the influence of effects which have been left out) are discussed in Sec. 3. Here we note only that, according to (17), $T_c \to \varepsilon/\ln 2$ as $w \to \infty$. In addition, it is seen from (16) that with increasing w, i.e., with decreasing L, the order parameter σ below T_c grows progressively more steeply, and in the limit $w \to \infty$ (i.e., in the Slater model), σ changes abruptly at T_c from zero to its saturation value $\sigma_s = 1$. As will be seen from the following discussion, these (and other) results of the cluster approximation turn out to be exact for the Slater model, and they illustrate the possibility of sharp differences from the case of simple Ising models and the possibility of "nonuniversality" of the thermodynamic behavior at phase transitions in systems with competing interactions, as well as pointing out the adequacy of the cluster approximation and the inapplicability of the MFA for investigating phase transitions of this kind.

c) Exactly solvable models

For realistic models of order-disorder structural phase transitions it is, as a rule, impossible to calculate exactly the statistical properties with Hamiltonians (1)–(5), and one uses the approximation methods described above. For estimating the accuracy of these methods it is of great interest to examine exactly solvable models, especially those which reflect the essential features of real systems. These models also give useful qualitative information on the relationship of the character of the phase transition to the features of both the structures and interactions, particularly for the previously discussed cases with competing interactions, by illustrating the uniqueness and diversity of the orderings and thermodynamic behaviors in these cases. Finally, some of the exactly solvable models are rather close to real (quasi-two-dimensional) systems and can be of aid in understanding the features of phase transitions in crystals of this kind. We shall consider the exactly solvable models for order-disorder structural phase transitions only in connection with the questions discussed above. As a rule, these models are two-dimensional and belong to one of two main types: Ising lattices and vertex models with the ice rule.

1) Ising models with competing interactions. As we know, any two-dimensional Ising model which does not con-
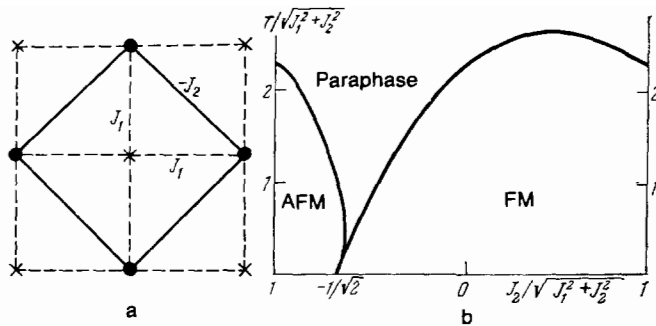
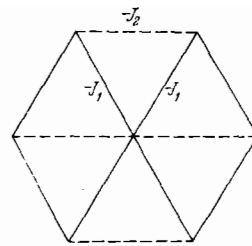FIG. 4. a) Schematic of the interactions ("bonds") in the model of Ref. 48; b) the $T(J_1, J_2)$ phase diagrams in this model.

FIG. 5. Schematic diagram of the bonds in the asymmetric triangular Ising model considered in Ref. 49.

tain crossing bonds is solvable,[47] and many such models have been described in the literature (see, e.g., Refs. 48–51 and the literature cited therein). In the absence of special relationships among the constants (e.g., when all the interactions are ferromagnetic), the phase-transition thrmodynamics do not differ qualitatively from the case of the simple square Ising lattice[47] and are described satisfactorily by any of the approximation methods in Sec. 2b. It is not clear, however, whether these simple models correspond to any real order-disorder structural phase transitions, since the character of the interactions and orderings in the crystals studied to date has generally been much more complex.[1–13] As we have noted, however, systems with competing, almost compensating, interactions of different signs (sometimes called "frustrated" systems[51]) are more typical for order-disorder structural phase transitions. Therefore, we shall mention some of the results[38–50] obtained for models of this type.

In a study of an Ising lattice with the bond scheme shown in Fig. 4a, it was found[48] that the phase diagram showing the dependence of T_c on the interaction constants J_1 and J_2 has the unusual shape shown in Fig. 4b. For values in the range[2] $-|J_1| < J_2 < -0.9068|J_1|$ the system undergoes three phase transitions, passing successively through an upper and lower Néel point and a Curie point as the temperature T is lowered. This illustrates the thermodynamic liability of systems with competing interactions and the possible existence of intermediate phases (observed for a number of order-disorder structural phase transitions) in these systems.

Another system having peculiar thermodynamics is the triangular antiferromagnetic Ising lattice (Fig. 5) with nearly compensating interactions, i.e., with $\delta = J_1 - J_2 \ll J_1 \equiv J$. Here one also has $T_c \sim \delta \ll J$, and with accuracy to exponentially small terms $\sim \exp(-\beta J)$ the character of the phase transition is the same as in the aforementioned two-dimensional Slater model: At the phase transition point the order parameter $\sigma(T_c) = \sigma_s$ jumps abruptly to its saturation value $\sigma_s = 1$ and the specific heat $C(T)$ above T_c grows as $(T - T_c)^{-1/2}$, whereas the usual Ising behavior is $\sigma \sim (T_c - T)^{1/8}$ and $C(T) \sim \ln|T - T_c|$. This again illustrates the fact that nonuniversal features can appear in the thermodynamics and that large values of $\sigma_c \sim \sigma_s$ (observed in many order-disorder structural phase transitions) are possible in

systems with competing interactions. In such systems, peculiarities also appear in the correlations of the particles near T_c. At certain values of T these systems display "disorder" points—nonanalyticities of the correlation functions along certain directions of the crystal, although no anomalies appear in the thermodynamics at these temperatures.[49,50] An approximate description of all these systems cannot be obtained in the MFA, while the cluster approximation gives a reasonably good description of the thermodynamics with an accuracy of the order of 10–20%.[50]

Finally, let us mention one more model with competing interactions—the axial Ising model with non-nearest-neighbor interactions (ANNNI).[52] Although it cannot be solved exactly, this model has been carefully studied in recent years in connection with phase transitions in modulated commensurate or incommensurate phases (which are also observed in order-disorder structural phase transitions; see Sec. 4). This model, which was proposed for antiferromagnets, consists of a three-dimensional Ising lattice with a ferromagnetic interaction of the nearest neighbors in the plane perpendicular to the c axis, while along the c axis it has a ferromagnetic interaction J_1 with the nearest neighbor and an antiferromagnetic interaction $(-\varkappa J_1)$ with the next-nearest neighbor, It has been found that in a certain region of the parameter $\varkappa$ the phase diagram $T_c(\varkappa)$ becomes extremely complex, describing a phase transition to modulated phases. Here the wave vectors k_0 of the arising superstructures can change with decreasing T as a result of a finite (or even infinite) number of phase transitions.[52] Some of these properties of the ANNNI have been illustrated qualitatively for exactly solvable two-dimensional analogs of this model.[53] Although the simple ANNNI model can hardly correspond to any of the crystals with order-disorder structural phase transitions, it does show that the phase diagrams can assume a complicated shape and that modulated phases with $k_0 = k_0(T)$ can form in the presence of competing interactions.

2) Six-vertex models. Vertex models have been advanced for the description of crystals with double-well hydrogen bonds. These bonds are represented by arrows indicating the positions of the hydrogen ion in the bond, and for crystals with tetrahedral coordination (such as ice, KDP, etc.) there are 4 arrows connected with each site (vertex). If one considers only neutral configurations (the ice rule[12]), there are only 6 admissible configurations, which are shown in Fig. 6. As we have explained for the illustrative case of KDP, these configurations can have different energies e_i depending on the interactions within the lattice and on the
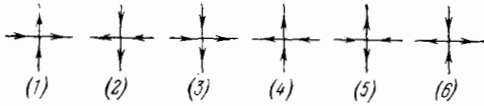
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[2] The upper bound of this inequality for J_2 was given inaccurately in Ref. 48.

FIG. 6. Admissible configurations in the 6-vertex model under the ice rule.

external fields, and the e_i are customarily written in the form[9]

$$e_{1,2} = \varepsilon_2 \mp (h + v), \quad e_{3,4} = \varepsilon_1 + \varepsilon_2 \mp (h - v), \quad e_{5,6} = \varepsilon_1.$$
(19)

Here h and v are called the horizontal and vertical fields, and it is taken into account that the reference level for e_i can be chosen arbitrarily. If one neglects the interaction of the non-nearest bonds, the energy of the lattice is equal to the sum of the energies $\mathscr{E}$ of all the vertices, and the calculation of the partition function reduces to the summation of $\exp(-\beta\mathscr{E})$ over all possible configurations. For the two-dimensional 6-vertex models this problem has been solved exactly[54,9] for arbitrary ε_1, ε_2, h, and v, and the phase transitions in these systems have turned out to be extremely peculiar. Let us summarize their features.

There are two types of phase transitions in the two-dimensional 6-vertex models: ferroelectric transitions, for which the arrows are directed identically at all the vertices in the ordered phase, and antiferroelectric transitions, for which two types of vertices alternate in a checkerboard arrangement in the ordered phase. In the absence of fields $h = v = 0$ the ferroelectric phase transitions occur at $\bar{\varepsilon} = \max(0,\varepsilon_1) - \varepsilon_2 > 0$, while the antiferroelectric phase transitions occur at $\bar{\varepsilon} < 0$. The simplest ferroelectric model, known as the KDP model, corresponds to the values $\varepsilon_2 = 0$, $\varepsilon_1 > 0$, and the ground-state configurations are (1) and (2) (with the ferroelectric axis directed at 45° to the axes in Fig. 6); for the simplest antiferroelectric model, the so-called F model, $\varepsilon_1 = 0$, $\varepsilon_2 > 0$, and the ground-state configurations (5) and (6) alternate in the ordered phase. If $\bar{\varepsilon} = 0$ (e.g., if $\varepsilon_2 = 0$ and $\varepsilon_1 < 0$, corresponding to the ADP crystal, which is discussed in Sec. 3), then in the absence of fields no phase transition occurs, and the system remains disordered all the way down to $T = 0$.

The ferroelectric and antiferroelectric phase transitions in all these models turn out to have the same character as in the KDP model and the F model, respectively, but there is a marked difference between these two types of phase transitions. The KDP model obviously reflects certain features of KDP-type crystals, but no real analogs are known for the F model. Therefore, as models for real order-disorder structural phase transitions the ferroelectric 6-vertex models evidently hold more interest than the antiferroelectric models.

At the ferroelectric phase transitions in these models the polarization σ in the absence of external fields $h = v = 0$ changes abruptly from zero to saturation, and below T_c the system remains "frozen"; the phase transition is of first order. The specific heat $C(T)$, however, grows as $(T - T_c)^{-1/2}$ as $T \to T_c + 0$, while the zero-field susceptibility obeys the Curie-Weiss law $\chi(T) \sim C/(T - T_c)$, even though the presence of singularities in $C(T)$ and $\chi(T)$ as $T \to T_c$ is usually

characteristic only of second-order phase transitions. When fields h and v are applied, the ferroelectric phase transition to the saturated state does not vanish but becomes second-order, with a transition point $T_c(h,v)$ determined by the relation (for $h + v > 0$, $h,v > -\varepsilon_1/2$)

$$(e^{2\beta h} - e^{-\beta\varepsilon_1})(e^{2\beta v} - e^{-\beta\varepsilon_1}) = e^{2\beta(\varepsilon_2 - \varepsilon_1)}.$$
(20)

The specific heat above $T_c(h,v)$ grows, as before, in proportion to $(T - T_c)^{-1/2}$, while the susceptibility at the phase transition in the field [e.g., for $v \to v_c$, where $v_c(h,T)$ is determined from (20)] goes as $\chi(v,T) = \partial\sigma/\partial v \sim (v_c - v)^{-1/2}$.

The antiferroelectric phase transition in zero field, on the other hand, turns out to be of infinite order[3]: All the temperature derivatives of the energy and specific heat are discontinuous, while the order parameter for $T \to T_c - 0$ falls off as[55] $\exp[-a(T_c - T)^{-1/4}]$. In spite of the extremely "soft" character of the phase transition, however, the antiferroelectrically ordered structure below T_c is extremely "rigid": upon application of an external field (say, $v \neq 0$) the polarization $\sigma(v)$ remains equal to zero for all v up to some critical value $v_c(T)$. At $v = v_c$ the antiferroelectric ordering vanishes, and $\sigma(v)$ begins to grow as $(v - v_c)^{1/2}$. Thus, in fields $h,v \neq 0$ the antiferroelectric phase transition occurs, as before, to an unpolarized state $\sigma = 0$, but it becomes second order. Here the specific heat above T_c grows as $(T - T_c)^{-1/2}$, while below T_c it remains regular. At rather high fields all these models (except for the F model with $h = 0$ or $v = 0$) undergo the aforementioned second-order ferroelectric phase transition to the saturated polarized state.

For the three-dimensional 6-vertex models we do not have exact solutions, but several results are known for the Slater model of KDP.[13] It has been shown[56] that the position and character of the ferroelectric phase transition in this three-dimensional model remains the same as in the two-dimensional model, i.e., at $T_c = \varepsilon_1/\ln2$ the polarization σ changes abruptly to saturation ($\sigma_s = 1$).

Let us now compare the exact and approximate results for the 6-vertex models. As we have mentioned, the MFA is inapplicable here, but the cluster approximation gives a good qualitative and, in a number of cases, also quantitative description. It can be shown that for the ferroelectric phase transition the cluster approximation accurately describes the character of the phase transition to the saturated state (first order in the absence of fields and second order for $h,v \neq 0$), the phase diagram $T_c(h,v)$ [Eq. (20)], and the Curie-Weiss law for $\chi(T)$ at $v \to 0$, with the exact value of the Curie-Weiss constant. True, for the specific heat $C(T)$ and susceptibility $\chi(v,T)$ near the phase transition one obtains finite values in the cluster approximation instead of singularities of the form $(T - T_c)^{-1/2}$, $(v_c - v)^{-1/2}$, but outside the immediate vicinity of T_c the divergences are small. For describing an antiferroelectric phase transition the accuracy of the cluster approximation turns out to be lower than for a ferroelectric transition, but it is still quite high. The curves of

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[3]We use the terminology of Ehrenfest, according to which an n-th order phase transition point is one at which the n-th derivatives of the thermodynamic potentials F, Φ, or Ω are discontinuous.

$T = T_c(h,v)$ in the cluster approximation coincide with the curves for the exact solution only at the end points $h = v = 0$ and $T_c \to 0$, but the curves remain close together at intermediate T as well. Instead of a phase transition of infinite order for $h = v = 0$ and of second order for $h,v \neq 0$, the cluster approximation gives an antiferroelectric phase transition which remains first order for all h and v, with saturation of the antiferroelectric order parameter at $T = T_c$ (i.e., it is analogous to the ferroelectric phase transition in the absence of fields). In the cluster approximation, the antiferroelectric phases retain the basic property of being "locked in," i.e., there is no polarization $\sigma(h,v)$ in these phases in fields less than the critical h_c, v_c. The cluster approximation also gives a fair description of the effect of a staggered field (i.e., one which induces an antiferroelectric ordering) of the form $s(-1)^{n_1 + n_2}$, where n_1 and n_2 are the row and column indices of the given bond, vertical or horizontal. In this case the exact solution[57] is known only for the F model at $T = 2\varepsilon_2/\ln 2 = 2T_c(h = 0, v = 0)$ but for any h and v. Comparison with Ref. 57 shows that the function $\sigma(h,v,s)$ in the cluster approximation is rather close to being exact, with the position of the ferroelectric phase transition in the field described exactly and that of the antiferroelectric phase transition given to good accuracy.

3) Models for SCD *and* CFT. The phase transition in the model[58] for SCD (tin chloride dihydrate, $SnCl_2 \cdot 2H_2O$) is extremely unusual, and the model apparently gives an accurate reflection of the character of the phase transition in this crystal.[59] The SCD structure is described in Refs. 58 and 59; the water molecules form a two-dimension network of O–H–O bonds. Figure 7 shows an element of this network. Each O_{II} ion is also connected by an interlayer bond O–H . . . Cl lying outside the plane of the figure, with the H ion of this bond always located near O_{II}. In the model of Ref. 58 it is assumed that the ice rule is obeyed at each of the vertices O_I and O_{II}. Then, of the three ions H^i in the bonds $i = 1, 2, 2$ in Fig. 7, two should always be located near O_I and one near O_{II}. In the approximation of only nearest-bond interactions the energies ε_i of these vertex configurations in the lattice add together, and the statistical problem reduces to evaluation of the partition function for the vertex model shown in Fig. 7.

The exact solution of this problem[58] shows that at a temperature T_c determined by the equation

$$e^{-2\beta\varepsilon_1} + e^{-2\beta\varepsilon_2} = e^{-2\beta\varepsilon_3}, \qquad (21)$$

the specific heat $C(T)$ has a singularity of the form $\ln|T - T_c|$, i.e., there is a second-order phase transition.
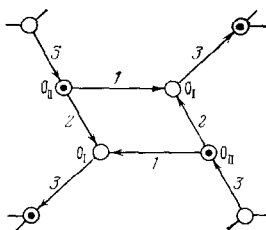
FIG. 7. Diagram of O–H . . . O bonds and the low-temperature ordering in the quasi-two-dimensional crystal SCD ($SnCl_2 \cdot 2H_2O$).

Here it is seen from (21) that the phase transition exists only if $\varepsilon_3 < \min(\varepsilon_1,\varepsilon_2)$. This second-order phase transition, however, has the extremely peculiar feature that one cannot define the order parameter η in the usual way as a quantity which is nonzero only in one of the phases, $T < T_c$ or $T > T_c$. Of course, Ehrenfest's general thermodynamic definition of a phase transition (see footnote 3) does not in general imply that the symmetry must change at the phase transition, and for isostructural first-order phase transitions (e.g., liquid-vapor or first-order ferroelectric phase transitions in an electric field) it does not change. For a second-order phase transition (moreover, in a simple disordered system) this is extremely unusual, and the model under discussion gives an apparently unique isostructural second-order phase transition.

As is discussed in Ref. 59, the microscopic quantity most intimately related to the phase transition in SCD is apparently the asymmetry parameter η for the proton on bond 3:

$$\eta = \rho_3(O_{II}) - \rho_3(O_I), \qquad (22)$$

where $\rho_3(O_j)$ is the probability of finding proton H^3 near ion O_j. At high temperatures one has $\eta < 0$, since as a consequence of the ice rule ion O_{II} on the average repels the H ion, while O_I attracts it. At $T = T_c$ one has $\eta(T) = 0$ (both in the model[58] and in real SCD[59]), and when $T \to 0$ one has $\eta \to 1$, since for the values considered, $\varepsilon_3 < \min(\varepsilon_1,\varepsilon_2)$, the ground state is the one indicated in Fig. 7. It has been proposed[59] to regard η as a kind of order parameter for SCD which, however, is nonzero on both sides of T_c and is an odd function of $(T - T_c)$ near T_c. However, the fact that the passage of η through zero is accompanied by a thermodynamic anomaly is a very unexpected consequence of the statistics of the system.

Another exactly solvable model[60] was proposed in connection with the ferroelectric order-disorder phase transition in the CFT crystal [copper formate tetrahydrate, $Cu(HCOO)_2 \cdot 4H_2O$]. As in SCD, there is a two-dimensional network of O–H . . . O bonds in this crystal containing two types of oxygen ions, O_I and O_{II}, each of which is connected to three hydogen bonds, and, in addition, there is always a hydrogen ion near O_{II} belonging to the interplanar bond.

The ordering of the protons at the phase transition in CFT within each plane is ferroelectric, while the ordering between adjacent planes is antiferroelectric; in Ref. 60 this weak interplanar coupling was neglected and a purely two-dimensional model was considered. When the ice rule is taken into account and only nearest-bond (belonging to the same vertex) interactions are considered, the resulting model (the "interacting-dimer" model)[60] is exactly solvable but does not give a phase transition: as T is lowered the system effectively decomposes into a set of uncorrelated one-dimensional chains. To obtain a phase transition it is necessary to take the interaction of non-nearest bonds into account, as was done in Ref. 60 for two different versions of exactly solvable models. Neither version, generally speaking, corresponds to the symmetry of the initial CFT lattice, but these two models are apparently adequate for taking these effects into account in a qualitative way. The phase transition in the

two models is the same as in the two-dimensional KDP model and corresponds qualitatively with the character of the phase transition observed in CFT (see Sec. 3).

The application of the cluster approximation to the SCD and CFT models as in the case of the 6-vertex models, gives a good description of the basic properties of the critical behavior, but not the details. For example, in the SCD model the cluster approximation gives a qualitatively correct description of the change in the "order parameter" (22) from the value $\eta_\infty \equiv \eta(T \to \infty) = -1$ (in the exact solution[56] $\eta_\infty = -0.88$) to zero at a temperature $T = T_c$ determined by (21). True, the phase transition at this temperature (a logarithmic singularity in the specific heat) does not appear in the cluster approximation, and as T is reduced further the value $\eta = 1$ is reached not at $T = 0$, as in the exact solution, but at a finite $T \sim T_c/2$, at which the cluster approximation gives a second-order transition to a "saturated" state; this transition is analogous to the ferroelectric phase transition in the KDP model in the presence of a field. However, the exact and approximate functions $\eta(T)$ are actually rather similar. In the CFT models the phase transitions are isomorphic to the ferroelectric phase transition in the KDP model and are therefore described by the cluster approximation to the same high accuracy as for KDP.

In summary, our examination of the exactly solvable vertex models has illustrated the peculiarity and diversity of the phase transitions in systems with the ice rule, the essential differences between these phase transitions and those in magnetic systems, and the inapplicability of the MFA and the good accuracy of the cluster approximation in the description of these phase transitions.

4) Other exactly solvable models and exact reults. Baxter[61] has solved the two-dimensional symmetric 8-vertex model, which corresponds to $h = v = 0$ and the addition of two "doubly-charged" configurations, for which all four arrows enter or leave the vertex, to configurations (1)–(6) in Fig. 6. This model is equivalent to two simple Ising lattices coupled by a 4-spin interaction.[62] The critical exponents turn out to depend on the interaction constants—an unusual circumstance in the theory of phase transitions, but one which is due to the special structure of the model of Ref. 62. Solutions have been obtained for certain other versions of the vertex models (see, e.g., Ref. 63) and for several systems with purely many-spin interactions: a three-spin interaction in a two-dimensional triangular lattice[64] and a four-spin interaction in several three-dimensional lattices.[65] It is not yet clear, however, what relationship all these models might have to any real order-disorder structural phase transitions.

For describing systems of type (1) in which the number q of states (orientations) at each site is greater than 2, the Potts model has been discussed in the literature (in particular, as the subject of a recent review of Ref. 66). The "standard" model which is usually considered takes into account only the interaction of nearest neighbors in the same state: $V_{ij}(\mathbf{R}) = \delta_{ij} V(\mathbf{R})$ (this is hardly applicable to real order-disorder structural phase transitions in alloys, many-well potentials, etc.). It has been shown for the two-dimensional Potts model that for $q \leqslant 4$ the phase transition is continuous, while for $q > 4$ there is a first-order phase transition. Values of T_c have

been found for a number of lattices, but no exact solutions have been obtained. Studies of the Potts model have dealt mainly with the critical behavior near the phase transition, with attempts to apply the results to several layered and surface systems.[66]

3. PHASE TRANSITIONS IN CRYSTALS WITH DOUBLE-WELL HYDROGEN BONDS

Let us begin our discussion of specific order-disorder structural phase transitions with phase transitions in crystals with double-well hydrogen bonds. For these systems the basic mechanism of the phase transitions and the adequacy of their description by models (2) and (3) usually seem clearer than for other types of phase transitions, and rather detailed microscopic theories have been developed for a number of these phase transitions. At the same time, these phase transitions clearly display many of the features mentioned earlier that distinguish order-disorder structural phase transitions from magnetic phase transitions.

1) Status of the theory of hydrogen bonds in solids. The hydrogen bond is a very common structural entity in the crystal chemistry of hydrogenous compounds. General information on the chemical, geometric, and spectroscopic characteristics of hydrogen bonds can be found in several reviews.[16,67–69] The most common and best-studied type of hydrogen bond is O–H . . . O, with an energy of formation $\varepsilon_f \approx 0.2$ eV. At lengths $R_{00} \gtrsim 2.5$ Å these bonds usually have a double-minimum structure,[16,67] and, depending on the crystalline environment, can be either symmetric (Fig. 1a) or asymmetric (Fig. 1b). The shape of the potential $U(\mathbf{x})$ for the proton in the hydrogen bond [which determines, in particular, the values of the parameters V_{ij}, Δ, and Ω in (2) and (3)] has been discussed in many papers (see, e.g., Refs. 16, 68, and 70). However, there are as yet no reliable quantum-chemical calculations for hydrogen bonds in solids, and $U(\mathbf{x})$ is usually estimated from spectroscopic data on the proton levels in the bond,[68,70] although these estimates are complicated by the pronounced anharmonicity and frequently also by the "collectivization" of these levels in the crystal. Therefore, in current practice the parameters V_{ij}, Δ, and Ω in Hamiltonians (2) and (3) are not calculated but are instead estimated by comparing the calculated phase-transition thermodynamics with experiment, although attempts at a microscopic approach to the calculation of these parameters have also been discussed.[70]

2) The residual entropy of ice and the ice rule. The idea that the hydrogen bonds have a double-well character and the so-called ice rule, which is important in the statistics of these bonds, were first proposed by Pauling[12] in connection with the problem of the residual entropy of ice. Measurements[71] of the specific heat of water over a wide temperature range, from high temperatures (where water vapor can be considered an ideal gas of H_2O molecules, and the entropy $S(T)$ can be calculated using ideal-gas statistics and the spectroscopic data on the vibrational and rotational levels) to extremely low temperatures $T \sim 10$ K (where ice has a hexagonal structure I_h with tetrahedral coordination of the hydrogen bonds around each oxygen atom and a large distance between non-nearest bonds), have shown that $S(T)$ does not

go to zero at $T \rightarrow 0$, but to a finite value $S_0 = 0.41 \pm 0.02$ per molecule.[71] Previously,[72] finite values $S_0 \approx 0.6$ had been observed in the molecular crystals CO and NO_2. The value $S_0 \neq 0$ for ice I_h was attributed by Pauling[12] to a disorder of the protons in double-well hydrogen bonds. Assuming that the ice rule is obeyed, i.e., that the population of "charged" configurations (with other than two protons near an oxygen atom) is negligibly small, and also that the energies of all the neutral configurations are equal, Pauling estimated S_0 in the following way. Two hydrogen atoms belong to each of the N oxygen vertex atoms in the crystal, and in a completely disordered situation there are $2^2 = 4$ states of these hydrogens in the bonds. But of the $2^4 = 16$ configurations at each vertex, only the 6 neutral configurations are allowed (and these have equal probability). Neglecting correlations of the configurations at different vertices, we obtain for the entropy per molecule

$$S_0 = \frac{1}{N} \ln \left[2^{2N} \left(\frac{6}{16} \right)^N \right] = \ln \frac{3}{2} = 0{,}405, \qquad (23)$$

in excellent agreement with the experimental value of S_0 given above. We note that Pauling's estimate (23) corresponds to applying the cluster approximation (14), (15) to the ice problem (if one sets $\varepsilon = \psi = u = 0$, $w \rightarrow \infty$). Exact calculations of the Pauling model yield $S_0 = (3/2)\ln(4/3) = 0.423$ for two-dimensional ice[9] and $S_0 = \ln(1.507) = 0.410$ for three-dimensional ice.[73] These results again illustrate the high accuracy of the cluster approximation for describing systems obeying the ice rule and confirm the applicability of the simple Pauling model for estimating S_0.

The basic assumptions of this model are also confirmed by structural studies[74] of ice I_h, although these studies do indicate that it is desirable that the model be improved. Applications of the Pauling model and the cluster approximation to the description of the dielectric properties[75] of ice I_h and the possible low-temperature ferroelectric phase transition (which has not yet been observed on account of the sluggishness of the kinetics at these temperatures) are discussed in Ref. 76 and the literature cited therein.

3) Ice-VII–VIII phase transition. Under application of pressure p ice undergoes a series of structural phase transitions, and its (p,T) phase diagram is rather complex. More than ten phases of ice are known, differing in the type of crystal lattice and in the character of the orderings of the hydrogens in the bonds.[77] At the present time, the only microscopic studies have dealt with the order-disorder phase transitions between the two densest and most symmetric modifications, ice VII and ice VIII (Fig. 8), which are stable at $p \gtrsim 15$–20 kbar. This phase transition has been described[78] in the MFA, which, as we have noted, has a low accuracy in systems which obey the ice rule (either strictly or approximately). The cluster approximation was applied to this phase transition in Ref. 41. The ordering in each of the sublattices in Fig. 8 is analogous to that which occurs in KDP (Fig. 3), so it is natural to use the methods[32–8] developed for that crystal. Several of the model parameters cannot be determined without more detailed data on the thermodynamics of the phase transition (which are as yet lacking), but for all realistic values of these parameters the phase transition turns out, in
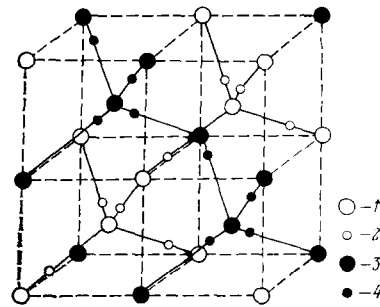

FIG. 8. Structure of ice VIII. In ice VII the protons in the H bonds are not ordered. 1, 2) Oxygen and hydrogen ions in one of the two diamond-type sublattices not connected by H bonds; 3), 4) the ions of the other sublattice. The solid lines denote H bonds, the dashed lines are the crystallographic axes.

agreement with experiment, to be of first order, with a jump in the order parameters σ_s nearly equal to the saturation value.

4) Phase transition in KDP-type crystals. The order-disorder structural phase transitions in crystals of the KDP type are among the best studied from both the experimental and theoretical standpoints. In addition to KDP, this family includes RbH_2PO_4, KH_2AsO_4, RbH_2AsO_4, CsH_2AsO_4 (RDP, KDA, RDA, CDA), and their deuterated analogs. Information on the phase-transition thermodynamics and the structure of these crystals can be found in Refs. 1–5, 15, 79, and 80. The relatively short lengths R_{00} of the H bonds and distances 2δ between maxima of the proton density in these crystals [at $T \approx T_c$ one has $R_{00} = 2.48$ Å and $2\delta = 0.32$ Å in KDP and $R_{00} = 2.52$ Å and $2\delta = 0.44$ Å in DKDP (KD_2PO_4)[79] compared, for example, to $R_{00} = 2.76$ Å and $2\delta = 0.76$ Å (Ref. 72) in ice I_h] has provoked a discussion of whether the H bond in KDP is of a double-well character. Evidence in favor of a double-well bond is provided both by structural studies[79,80] and by the good experimental agreement of the phase-transition thermodynamcis calculated[15,81] on the basis of such an assumption. For protons (in contrast to deuterons) in the bonds there is evidently an appreciable probability of tunneling between the potential minima, as is indicated by the characteristic changes upon deuteration (H→D) in the dynamical properties and dielectric relaxation[82,70,8] and in the phase-transition thermodynamics,[15] including the pressure dependence[80] (in particular, dT_c/dp decreased by a factor of more than 1.5). The displacements of the protons are strongly coupled with the displacements of the heavy ions[36,79]; in fact, the ferroelectric polarization in KDP is due mainly to the displacement of the ions K, P, and O, while the displacements of the H ions are almost perpendicular to the ferroelectric axis.[1–3] In the description of the phase-transition thermodynamics, however, the basic effect of this coupling evidently reduces to only a renormalization of the constants in Hamiltonians (2) and (3) (although in the presence of tunneling this assertion is not rigorous even in the approximation of small anharmonicity[8,70]).

A qualitative feature of the thermodynamics in these crystals is the narrowness of the phase transitions region:

$\sigma(\tau)$

KD$_2$PO$_4$

RbD$_2$PO$_4$

KH$_2$PO$_4$

RbH$_2$PO$_4$

0,6

0,2

o -1
• -2
$\triangle$ -3
▲ -4

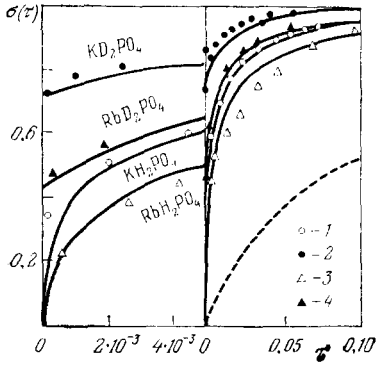0 $2 \cdot 10^{-3}$ $4 \cdot 10^{-3}$ 0   0,05 τ 0,10

FIG. 9. Curves of the order parameter $\sigma(T)$ for crystals of the KDP type. The solid curves are the theoretical results of Ref. 15, the dashed curve is the MFA result (6). The experimental points are: 1) KDP, 2) DKDP, 3) RDP, 4) DRDP.

almost the entire change in the order parameter $\sigma(\tau)$ occurs in the region $\tau = |T - T_c|/T_c \lesssim 10^{-2}$ (Fig. 9). This can be considered an indication of the proximity of this system to the Slater model[13] discussed in Sec. 2 and, hence, of the inapplicability of the MFA and the suitability of the cluster approximation for describing the phase transition. One can then use formula (18) for crystals of the type MeD_2XO_4, but for MeH_2XO_4 one must take the tunneling into account. In the latter case, in addition to "longitudinal field" terms, e.g., $\sigma^z(\varphi + Ep_e)$ in (9), one must include in the Hamiltonian "transverse field" terms of the type $\sigma^x(\hbar\Omega - \eta)$, where Ω is the same as in (3) and η is an effective field parameter analogous to φ (Refs. 33, 17,8).

In Ref. 15, detailed calculations of the phase-transition thermodynamics were done by this method, and the parameters ε, γ, w, and Ω were estimated for all the crystals in the KDP family.[4] For MeD_2XO_4 it was assumed that $\Omega \approx 0$, while the parameters ε_D, γ_D, and w_D were estimated from ε_H, γ_H, and w_H using relation (3b). Taking into account that the lattice parameters [and apparently also $w(\mathbf{R})$ in (3b)] change very little upon deuteration, while $x_{sa} \approx \delta$ changes significantly,[80,70] one expects on the basis of (3a), (3b), and (13) that[46,33,17]

$$\frac{\varepsilon_H}{\varepsilon_D} \approx \frac{\gamma_H}{\gamma_D} \approx \frac{w_H}{w_D} \approx \frac{(x_{sa}^H)^2}{(x_{sa}^D)^2} \approx \frac{(p_e^H)^2}{(p_e^D)^2} \; ; \qquad (24)$$

here $p_e^{H,D}$ is the effective dipole moment of the bond,[8] which is proportional to the saturation polarization P_s. Therefore, if P_s is known for every pair of crystals MeH_2XO_4 and MeD_2XO_4, there are only three unknown dimensionless parameters γ/ε, w/ε, and $\hbar\Omega/\varepsilon$ governing the thermodynamics of the phase transition, including the specific heat $C(\tau)$, the entropy $S(\tau)$, the polarization $P(\tau)$, the discontinuities in these functions at the first-order phase transition, the Curie-Weiss constants, etc. The successful description of these quantities in Ref. 15 for all ten crystals of the KDP family (see Fig. 9, in particular) evidently confirms the correctness

of the underlying ideas about these phase transitions and the methods used to describe them. These methods have also been applied[40] to the description of phase transitions in $K(H_x D_{1-x})_2PO_4$ solid solutions.

The methods of Refs. 33 and 15 were also used[5] to describe the effect of pressure p on the phase transitions in KDP and DKDP.[81] The values of ε, γ, w, and Ω were estimated by comparing the expansion of the free energy $F(\sigma,T)$ in powers of the order parameters σ (or the polarization P) with the phenomenological Landau expansions which are used for KDP.[6,7] In estimating the pressure dependence of the parameters ε, γ, and w it was assumed, by analogy with (24), that they all changed upon compression in proportion to the change in $x_{sa}^2 \sim \delta^2$. The conclusion was reached[81] that although the basic characteristics of the phase transition can be described by parameters close to those obtained in Refs. 33 and 17, the data on the T and p dependence of the coefficient of P^4 are described better by values $\gamma < 0$ rather than $\gamma > 0$ as in Refs. 17 and 33.[8]

We note in this regard that negativity of the term $\gamma\sigma^2$ in (18) would upset the basic property that F is minimum with respect to all the introduced parameters σ, φ, and η: the absolute minimum of F would correspond to $\sigma \to \infty$. This is not too important at small σ, when the "dangerous" region of large σ is not attained, but in DKP and, especially, in DKDP the values of $\sigma \gtrsim \sigma_c$ are not small.[9] Therefore, the accuracy of expanding F in powers of σ^2 and retaining only three terms is also in doubt,[7] particularly since in the "Slater" limit $w \to \infty$ all the terms of this expansion change sign at $T = T_c$, and the minimum of F is reached at $\sigma = \sigma_{max} = 1$. It also seems unsafe to assume that all the constants, ε, γ, and w are proportional to the single parameters δ^2, since experimentally the change in structure [and also, probably, of the quantities $\partial^2 w/\partial R_\alpha \partial R_\beta$ in (3b)] under applied pressure by no means reduces to a uniform compression.[80] It would seem desirable to have further studies of the effect of pressure on these phase transitions with allowance (in particular) for the data of Refs. 69 and 80 and the discussion of these data in Ref. 70.

Let us make one further remark on the application to KDP of the MFA and related approximations of the "decoupling" type[35,36] in dynamics. As we have mentioned, these approximations cannot give a quantitative description of the

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[4]Fig. 10 of Ref. 15 (a methodological figure) was drawn inaccurately; refined calculations have shown that with decreasing γ all the curves $\sigma_c(\gamma)$ go continuously to zero at a certain $\gamma = \gamma_t$, corresponding to a tricritical point.

[5]Translators's note: The method of Ref. 15, i.e., the analytical expansion of the free energy from Ref. 33 in "small" parameters, was in fact not used in Ref. 81.

[6]Translator's note: The values of ε, γ, w, and Ω for KDP were in fact estimated from the $P(T)$ curve for DKDP [using expression (24) and the value of T_0 in KDP], and not from a comparison with the Landau expansion.

[7]Translator's note: The coefficients of the Landau expansion were calculated in Ref. 81 solely to facilitate comparison with experimental values obtained at small P in the paraelectric phase under applied field E. The first three terms of the Landau expansion are of course manifestly insufficient for describing the ferroelectric phase.

[8]Translator's note: Taking $\gamma < 0$ also eliminates a significant discrepancy with the experimental values of the Curie-Weiss constants for KDP and DKDP.

[9]Translator's note: Realistic values $\gamma < 0$ in fact cause no difficulty anywhere in the physical region $\sigma < 1$. The free-energy minimum for $\sigma \to \infty$ can, of course, be avoided by the addition of an arbitrarily small positive σ^4 term.

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phase transitions in question, and the microscopic meaning of the "averaged" interactions (6b) introduced in them is not clear. However, they are often used[4,36,70] for KDP on account of their simplicity and also because of the lack of development of methods analogous to the cluster approximation for taking correlations into account in dynamics. For qualitative discussion (e.g., the presence of a "soft mode",[35–37] though a strongly damped one, in KDP-type crystals[82]) these methods may be adequate, but for the reasons indicated they can hardly be used to make quantitative estimates of the microsopic parameters, as is sometimes done.[69,70,37] It seems much more reliable to estimate these parameters from the phase-transition thermodynamics; such estimates are obtained and discussed in Ref. 15, for example.

5) Crystals of the ADP type, which include $NH_4H_2PO_4$ (ADP), $ND_4D_2PO_4$ (DADP), $NH_4D_2AsO_4$ (ADA), and $ND_4D_2AsO_4$ (DADA), correspond to the replacement of the Me atom in the analogous KDP-type crystals by ammonium. They have not been studied nearly as much as KDP, and, unlike KDP, are antiferroelectric. Information on their structure and thermodynamics can be found in Refs. 1, 5, 37, 83, and 84. The ordering of the protons below T_c corresponds to an alternation (at adjacent vertices) of the first two or last two configurations in the fourth row of Fig. 3a. The phase-transition thermodynamics has been examined[83,84] in the cluster approximation without allowance for tunneling or the contributions of charged configurations. The antiferroelectric phase is energetically favored over the ferroelectric phase for parameter values $\varepsilon < \lambda - \gamma$, where ε and γ are the same as in (15) and (18), and λ is a constant analogous to γ which characterizes the antiferroelectric interaction of non-nearest neighbors in the mean field approximation. The equation for T_c is[83,84] $\exp(\beta\lambda) = 1 + \frac{1}{2}\exp(\beta\varepsilon)$, and so for $\lambda > \varepsilon$ the antiferroelectric phase transition occurs at $\varepsilon > 0$. This first-order phase transition is analogous to the ferroelectric transition in the KDP model with $\Omega = 0$, $w = \infty$, $\gamma \geqslant 0$, i.e., it takes place to a "frozen" state with antiferroelectric order parameter $\sigma = \sigma_{max} = 1$, in qualitative agreement with the character of the phase transition observed in ADP.[1] The model parameters $\varepsilon, \lambda, \gamma, p_c^H, p_c^D$ for ADP, DADP, and ADA were estimated[84] by fitting the curves of the dielectric permittivities $\varepsilon_c(T)$ and $\varepsilon_a(T)$ for $T > T_c$ to the experimental curves. These curves are quite smooth, however, and no allowance was made in Ref. 84 for a relationship of the type in (24) between the constants for ADP and DADP, so the agreement with experiment that was found in this study cannot be regarded as proof of a high accuracy of the model or of the parameters found. These remarks are even more pertinent to the results of Ref. 37, since the "decoupling" of the equations for the Green's functions in that paper is thermodynamically equivalent to the MFA, and therefore can scarcely be applicable to the quantitative description of ADP-type crystals.

6) Phase transition in squaric acid ($H_2C_4O_4$). In recent years the phase transition in the quasi-two-dimensional antiferroelectric $H_2C_4O_4$ (H_2SQ) has attracted a great deal of interest. Information on the structure and phase-transition thermodynamics can be found in Refs. 85–88 and in the
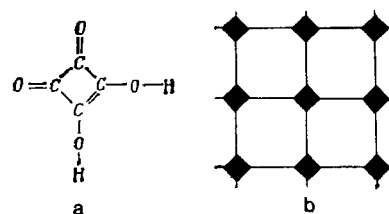

FIG. 10. a) Diagram of the valence bonds in the H_2SQ molecule ($H_2C_4O_4$); b) diagram of the H bonds of the H_2SQ crystal in the planes perpendicular to the tetragonal axis c of the high-temperature phase; the lines correspond to the H bonds, the squares to C_4O_4 groups.

theoretical papers of Refs. 89–94. Figure 10 shows a diagram of the molecule and the arrangement of the H bonds in the plane layers perpendicular to the tetragonal axis of the crystal for $T > T_c$; the layers are coupled by relatively weak van der Waals forces. At the phase transition the protons in each layer order ferroelectrically in one of the four positions of the type shown in Fig. 10a; the polarizations of adjacent layers are oppositely directed. The entropy of transitions $S_c = S(T_c + 0) = 0.114$ is very small,[86] amounting to less than 1/12 that of the "free" value 2 ln 2. In spite of a large isotope effect in $T_c(T_{cD}/T_{cH} \approx 1.4)$ the pressure derivatives dT_c/dp in H_2SQ and D_2SQ practically coincide.[87] This indicates that the tunneling is small,[87] in agreement with the rather large values $R_{00} = 2.55$ Å and $2\delta = 0.49$ Å in H_2SQ.[91] There are indications[85] that the positions of the hydrogens in the bonds are strongly correlated within the layers at $T > T_c$, with correlation lengths $l_c \gtrsim 25a$ (a is the lattice constant), and that these correlations have an anisotropic, possibly one-dimensional, character.[88,94]

The theoretical description of H_2SQ must take into account that configurations (5) and (6) in Fig. 6 (which will be called "antivalent") are forbidden by the conditions of saturation of the valence bonds (see Fig. 10a), i.e., the energy difference ε in Fig. 3a is negative and large: $-\varepsilon \gtrsim w' = w - \varepsilon$. . The ground-state configurations, according to Fig. 10a, are those numbered (1)–(4) in Fig. 6 or shown in the fourth row of Fig. 3a, which are degenerate on account of the tetragonal symmetry (for this reason the asymmetry parameter, which was also denoted ε in Refs. 89–91, evidently should be assumed equal to zero[92,93]). If only these 4 configurations are taken into account in the description of the crystal and all the contributions $\sim \exp(-\beta w')$ are neglected, then, as is seen from Fig. 6, the directions of the arrows remain unchanged at every vertex, and in a two-dimensional lattice (Fig. 10b) these directions are conserved along each of the N_v vertical and N_h horizontal rows. In the thermodynamic limit $N_v, N_h \to \infty$ this corresponds to a vanishing entropy $S = (N_v + N_h)\ln 2/N_v N_h \to 0$ (even though the orientations of different chains remain uncorrelated). Allowance for the charged configurations makes the correlation lengths l_c finite, but for $T < w'$ they are exponentially large: $l_c \sim a\exp(\beta w')$ (which is easily shown in the same way as for a one-dimensional Ising chain at low temperatures[29]). At the same time T_c is determined by the weak interaction of

non-nearest bonds[90,93] and $T_c \sim w'/\ln(w'/\gamma') \ll w'$ (as in an anisotropic Ising lattice[49] with $J_h \sim \gamma' \ll J_v \sim w'$). These considerations explain in a natural way both the smallness of S_c and the strong one-dimensional correlations.

For quantitative calculations it is natural to use the cluster approximation, which is highly accurate both for systems obeying the ice rule and for one-dimensional systems.[8] In accordance with the foregoing remarks, one should set $\varepsilon = 0$ and $\Omega = 0$ in the general cluster-approximation formulas for H_2SQ from Ref. 89 [where J should be corrected to $(-J)$ in formulas (5) and to $(-2J)$ in (4)] and assume that $\gamma' = \gamma - J \ll w$. One then obtains

$$T_c \approx \frac{w}{L}, \quad S_c \approx 2\frac{\gamma'}{w} L (1+L),$$

$$L = \ln\left(\frac{w}{\gamma'}\right) - \ln\ln\left(\frac{w}{\gamma'}\right). \tag{25}$$

Using the experimental values of T_c and S_c, one finds $\gamma'/w \approx 0.011$, $w \approx 1100$ K (this is close to the value of w for DKDP,[15] which has similar H-bond parameters) and $l_c \approx a\exp(\beta w') \approx aw/\gamma'L \sim 30a$, in agreement with the experimental estimate.[85] The calculated temperature dependence of the order parameter is quite close to the experimental one, although a second-order phase transition is obtained instead of the experimentally observed first-order transition. This circumstance may be due both to the influence of the nonlinear coupling with the lattice (elastic forces[95,96] in particular) and to the use of an insufficiently accurate description of the non-nearest-neighbor interactions.[91] Further verification and detailing of the theories of the phase transition in H_2SQ and D_2SQ would seem extremely interesting.

7) The phase transitions in SCD *and* CFT. Tin chloride dihydrate (SCD) and copper formate tetrahydrate (CFT) are the only known crystals having a two-dimensional H-bond network consisting solely of H_2O molecules. These crystals can be regarded[97] as a realization of "two-dimensional ice," and the peculiarity of the phase transitions in them apparently is intimately connected with the ice rule. Information on the phase transition and structure can be found in Refs. 97–101, 58, and 59 for SCD and in Refs. 97 and 102–105 for CFT, and a comparative study is made in Ref. 97.

As we mentioned in Sec. 2c, the SCD model of Ref. 58 gives a good description of the qualitative features of the phase transition in this crystal,[59] including the unusual symmetric change of the modulus of the "order parameter" η (22) and specific heat $C(\tau)$ at small $\tau = (T_c - T)/T_c$ on both sides of T_c. However, instead of the behavior $C(\tau) \approx a\ln|\tau|$ and the second-order phase transition implied by the theory, the experiment of Ref. 98 indicates a dependence of the form $C(\tau) \sim |\tau|^{-1/2}$ and a first-order phase transition (though one with an extremely small entropy jump $\Delta S \approx 0.03 S_c$), and instead of the theoretical linear dependence of $\eta(\tau)$ one actually finds a nearly square-root dependence[59]: $\eta \approx b\tau|\tau|^{-1/2}$. In Ref. 96 an attempt was made to attribute these discrepancies to a coupling with elastic forces—to a volume dependence of the model[58] parameters. Granted, the method of allowing for this coupling in Ref. 96 is not completely systematic (a

more rigorous discussion of these questions is found in Ref. 95 or in §23 of Ref. 8), but the observed behavior of $C(\tau)$ was successfully described at rather reasonable values of the compressibility and thermal expansion (which have not yet beem measured in SCD); the influence of these effects on $\eta(\tau)$ was not considered. A microscopic interpretation of the sharp anomalies in the dielectric properties[99] is also lacking; these anomalies have so far been discussed only in the language of the quasi-two-dimensional Ising model[100] or else phenomenologically,[101] with no direct relationship to the model of Ref. 58 for the phase transition in SCD.

At the phase transition in CFT the protons order ferroelectrically in the b direction in the plane of the bonds $[a, b]$ and antiferroelectrically between adjacent planes; the antiferroelectric coupling between planes is apparently very weak.[104,105] The phase transition is of first order, with the order parameter jumping discontinuously almost to saturation. This picture is consistent with the "Slater-like" character of the phase transition in the CFT model[60] discussed in Sec 2c, which also gives a value for S_c which is close to the observed value. Thus CFT can apparently be considered[97] one of the best realizations of the two-dimensional ferroelectric models with the ice rule.[9] Granted, the predicted growth in the specific heat $C(T) \sim (T - T_c)^{-1/2}$ as $T \to T_c$ is not observed in experiment,[97] but his may be due to the appreciable difference between T_c and the Curie-Weiss temperature T_0 (which is estimated from the dielectric measurements[102] to be $T_c - T_0 \approx 16$ K, with $T_c = 236$ K).

The features of the short-range order and of the correlations in CFT (and in other quasi-two-dimensional ferroelectrics and antiferroelectrics obeying the ice rule) were discussed in Ref. 102. Anomalies of the dielectric properties[103] have been discussed in the MFA for non-nearest neighbor interaction,[104,105] but this approximation is apparently unable to give a quantitative description of these properties and of the phase-transition thermodynamics.[105] Furthermore, since the exactly solvable models[60] for CFT display a breaking of certain symmetry properties of the CFT crystal, it would seem desirable to pursue further theoretical studies of this phase transition using (for example) the cluster approximation with clusters of a large enough size to include the non-nearest neighbor interaction responsible for the phase transition.[60]

8) Phase transitions in sodium and potassium trihydrogen selenites. Crystals of the type $MeH_3(SeO_3)_2$, where $Me = Li$, Na, K, Rb, or Cs (the corresponding crystals will be denoted LTS, STS, KTS, RTS, and CTS, respectively) have attracted considerable interest in regard to the diversity of their physical porperties. Although analogous in chemical composition, the different crystals of this family have marked differences in the structures of their high-temperature phases and in the types of phase transitions which they exhibit, and STS and RTS also display intermediate phases, i.e., have several phase transitions upon changes in temperature or pressure. Information on these crystals can be found in Refs. 69 and 106–112 and the literature cited in these papers. Microscopic theories of the phase transitions have so far been discussed only for STS (see Ref. 39 and the literature cited therein) and KTS.[109]

The STS crystal has a two-dimensional network of O–H . . . O bonds coupling the pyramidal SeO$_3$ groups.[39] As T is lowered, two ferroelectric phase transitions occur: first to the β phase, in which the polarization has two components (P_x and P_y) and the lattice period is doubled along the x and y axes, and then to the γ phase, which displays a polarization and a unit-cell doubling along the x axis only. Upon deuteration the existence region of the β phase shrinks, vanishing for concentrations $c_D > 35\%$. Both phase transitions are apparently due to ordering of the hydrogens in the bonds; the form of this ordering has been determined experimentally for the γ phase but has not yet been established for the β phase.

It was shown in Ref. 39 that these and other features of the phase transition can be explained by assuming that the nearest-neighbor interaction constants in STS [as in KDP (13)] are much greater than T_c, while the interactions in the second coordination spheres (interactions stemming from the strong coupling of the displacements of the protons and SeO$_3$ groups) are also extremely large. The high symmetry of the system of H bonds in STS results in a variety of phases with nearly equal energies, the degeneracy of which is lifted only by relatively weak interactions in the third and higher coordination spheres. A detailed analysis (using the cluster approximation for calculating the temperature dependences) has shown[39] that despite the presence of a number of unknown constants, these assumptions yield a natural explanation of the observed structure of the γ phase, the value of the entropy of transition S_c, and the peculiar dependence of P_x and P_y on the temperature T and on the fields E_x and E_y, and also enables one to predict the structures of the β phase and of several other phases which are close in energy to the γ and β phases [indications of whose appearance have been obtained in experiments under pressure[39] and near T_c (Ref. 108)]. Verification of these predictions would seem to be an interesting avenue for further development of the microscopic theories of the phase transitions in trihydrogen selenites.

The system of H bonds in KTS is of a one-dimensional character,[109] but the distances between different chains is small, so that it is not obvious that one can use "quasi-one-dimensional" approximations. The subject of Ref. 109 was a discussion of the symmetry relationship between the "antiferroelectric" ordering of the protons in the H bonds (which is realized here within a single unit cell, without period doubling) and the "ferroelastic" phonon modes which, according to Ref. 109, are the cause of an observed ferroelastic phase transition in which the order parameter is one of the components of the strain tensor and the corresponding elastic compliance displays a critical growth as T approaches T_c. The phase-transition thermodynamics was treated in Ref. 109 in the MFA, and the results were not subjected to a quantitative comparison with experiment.

9) Phase transitions in the quasi-one-dimensional ferroelectrics PHP and CDP. The crystals PHP (lead hydrogen phosphate, PbHPO$_4$)[113–115] and CDP (cesium dihydrogen phosphate, CsH$_2$PO$_4$)[116–118] contain one-dimensional chains of H bonds linking the PO$_4$ groups. These chains are rather far apart, so that the interaction between them can be considered weak. The large isotope effects in T_c (T_c is equal to 310

K and 452 K for PHP and PDP, respectively, and to 153 K and 267 K for the deuterated crystals CDP and DCDP) indicate the importance of these chains in the ferroelectric phase transition. In this connection quasi-one-dimensional theories of the phase transition in the PHP[113,114] and CDP[117,118] were proposed which used the exact solutions of the one-dimensional Ising model in a field E_{eff}, where E_{eff} included both the external field E and the non-nearest neighbor interactions (both within and between the chains) in the mean field approximation. The effect of tunneling (which is evidently extremely important in the undeuterated crystals[114,116]) was taken into account in Ref. 114 in the cluster approximation, which would seem entirely adequate inasmuch as the "zeroth order approximation"—the one-dimensional Ising chain without tunneling—is described exactly in this approximation.[8] The small entropy of transition $S_c \approx 0.11$ in PHP[115] [which apparently indiates a large intra-chain correlation length $l_c(T_c) > 10a$; see the analogous estimates (25)], the shape of the temperature curves $P(T)$ and $\varepsilon(T)$ in CDP and DCDP[117,118] and the conversion of the phase transition in CDP from ferroelectric to antiferroelectric at a rather low pressure[116,118] $p \gtrsim 3.3$ kbar evidently confirm the weakness of the interchain interactions. For a more quantitative check of these quasi-one-dimensional models for PHP an CDP, one would like to see measurements of the specific heat $C(T)$ in CDP and DCDP and a detailed comparison of all the thermal and dielectric data [$C(T)$, S_c, $\varepsilon(T)$, $P(T)$, etc.] with the theoretical formulas, with allowance for tunneling in the undeuterated crystals.[114]

10) Quasi-one-dimensional model of the phase transition in AHSe *and* RHSe (NH$_4$HSeO$_4$ *and* RbHSeO$_4$). The recently discovered ferroelectric phase transitions in AHSe and RHSe are evidently also due to ordering of the protons in the chains of hydrogen bonds which join the SeO$_4$ groups in these crystals.[119] There are three such chains and, in accordance with the symmetry of the crystal, the proton potential $U(\mathbf{x})$ in one of them should be symmetric, as in Fig. 1a, while in the other two the minima of $U(\mathbf{x})$ are apparently asymmetric and of opposite orientation, as in Fig. 1b. Calculations of
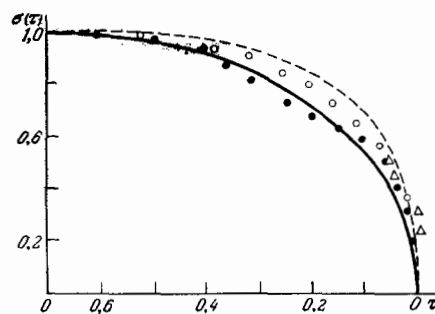

FIG. 11. Temperature dependence of the order parameters $\sigma(T) = P(T)/P(0)$ in triglycine sulfate. The solid curve is the MFA result (6); the dashed curve gives the results of numerical calculations of $\sigma(T)$ in a simple cubic Ising lattice with nearest-neighbor interactions; the points and triangles are the experimental data of Ref. 127.

the phase-transition thermodynamics of this model with the aid of the exact solutions of the one-dimensional Ising model and with the interchain interactions taken into account in the MFA[119] indicate the possibility of a number of features characteristic of phase transitions in asymmetric potentials (these are discussed in Sec. 4b). This circumstance can qualitatively explain certain anomalies in the phase-transition data—in particular, the presence of a lower Curie point in AHSe (the ferroelectric phase exists only in the range 100 K $\lesssim$ 250 K) and the nonmonotonic change in $\varepsilon(T)$ below T_c in RHSe, although this simple model cannot, for example, explain the second structural phase transition observed in RHSe.[119]

4. ORIENTATIONAL PHASE TRANSITIONS IN IONIC-COVALENT CRYSTALS

Orientational phase transitions are associated with an ordering of the molecules or molecular groups (H_2O, NO_2, NH_4, OH, SO_4, etc.) in the minima of the crystalline potentials $U(x)$. In ionic-covalent crystals (unlike molecular crystals) these potentials are, as a rule, rather strong, and transitions of the orienting groups between minima of $U(x)$ are strongly hindered. For example, in the ammonium halides NH_4X (where $X = Cl$, Br, or I), which will be discussed later, the barriers ΔU for the reorientation of the NH_4 groups are estimated[16] to be $\Delta U \sim 1500$–$2000K$, while $T_c = 200$–250 K. Therefore, for $T \lesssim T_c$ the librational oscillations about each of the minima are usually small in amplitude and can be taken into account in the harmonic approximation,[8,14] so that the phase-transition thermodynamics can be described by the discrete models (1)–(3). The number q of equivalent minima of $U(x)$ is governed by the symmetry of the disordered phase and can be rather large for crystals of high symmetry (e.g., $q = 12$, 8, or 6 in cubic lattices). In crystals of rhombic or lower symmetry in the disordered phase there are usually no more than two equivalent minima of $U(x)$, but cases are quite frequently encountered in which there are sublattices with inequivalent, oppositely oriented minima (see Fig. 1b).

In many cases these crystals characteristically display several (between 2 and 5 or 6) orientational phase transitions. The transition parameters also have a peculiar dependence on temperature, e.g., a ferroelectric phase exists only in a bounded interval $T_{c2} < T < T_{c1}$ and may sometimes reappear at $T < T_{c3} < T_{c2}$ (see Fig. 15 below). In a number of these crystals there are phase transitions to intermediate modulated (incommensurate or having large-period cells) phases which exist in temperature intervals with widths from a few degrees, as in $NaNO_2$,[120–122] to hundreds of degrees, as, for example, in crystals of the $(NH_4)_2ZnCl_4$ type.[123]

The structures and interactions in these crystals are usually too complex to permit a quantitative microscopic treatment of the phase transition. Therefore, the main thrust of the microscopic approach has been to consider the qualitative features of these phase transitions, including those mentioned above, with the aim of relating these features to the nature of the structure and interactions. The thermodynamics is usually treated in the MFA, and estimates of the

parameters of the Hamiltonians (1)–(3) have focused only on the electrostatic interactions (dipolar, quadrupolar, etc.), while the influence of the short-range forces has been described by phenomenological parameters. For sufficiently simple structures (NH_4X in particular), calculations of a more detailed nature have also been done using the cluster approximation,[42] and studies of the phase transitions in systems with asymmetric potentials have also made use of the exact solutions of the one-dimensional models[124,125] and the results of Monte Carlo calculations.[126]

a) Orientational phase transitions in potentials with two equivalent minima

1) Crystals with a single type of groups undergoing ordering. The best-studied of the orientational phase transitions in symmetric double-well potentials are apparently those in crystals of the types represented by TGS [triglycine sulfate, $(CH_2NH_2COOH)_3H_2SO_4$], KFCT [potassium ferrocyanide trihydrate, $K_4Fe(Cn)_6\cdot3H_2O$], sodium nitrate ($NaNO_2$), and the ammonium halides; the phase transitions in these cases are associated with the ordering of the glycine, H_2O, NO_2, and NH_4 groups, respectively.

1.1) Phase transitions in TGS and KFCT. The structure and interactions in crystals of the TGS type are extremely complex,[2,5] and there are as yet no calculations of the phase-transition mechanisms in these crystals. However, in spite of the structural complexity, these crystals are among the few for which the thermodynamics of the order-disorder structural phase transition turns out to be "simple" and fairly well described by the MFA (6), both in regard to the spontaneous polarizations $P(TR)$ (Fig. 11) and in regard to the thermal properties (in particular, the entropy of transition is only 20% less than the MFA value $S_c = \ln 2$). This may be because the ferroelectric phase transitions are governed mainly by long-range dipolar interactions, which suppress the critical fluctuations in such uniaxial ferroelectrics[8,128] and at the same time do not give rise to strong short-range correlations. Granted, for quantitative description of the details of the function $P(T,E)$ near T_c the values of V and p_c in (6) must be chosen differently[127,5] from those for the wide temperature range in Fig. 11. Furthermore, the value of the specific-heat discontinuity at the phase transition point as calculated from the experimental values of the coefficients of the Landau expansion for $F(P,T)$ turns out to be only about two thirds of the observed value.[157] To describe details of this sort and the possible renormalization of the interactions near T_c, one apparently must go beyond the simplest mean field approximation (6).

To a large extent, what we have said about the structure and character of the ferroelectric phase transitions applies to crystals of the KFCT type as well.[97] True, the growth of $P(T)$ below T_c is noticeably steeper here[129] than in the MFA (6), possibly indicating that short-range correlation effects are stronger in KFCT than in TGS.

An electrostatic calculation of the orientational potential $U(x)$ for the H_2O molecules in KFCT was made in Ref. 130. The charge distribution in the $Fe(CN)_6$ and H_2O groups was described (as usual in such calculations) by a set of equi-

valent point charges. The calculated function $U(\mathbf{x})$ turned out to have two symmetric minima for orientations of the H_2O molecules which are close to the observed positions. The value of the transition temperature T_c which was then calculated by the mean field method turned out to be very close to the experimental value (possibly as a result of some compensation of the inaccuracies of the model and of the MFA calculations). Various neglected effects and other approaches to the theory of the phase transitions in KFCT were also discussed.[130]

1.2) The phase transition in $NaNO_2$ turns out to be more complex than in TGS or KFCT, even though the crystal structure[5] is much simpler. For $T > T_N = 438\,K$, $NaNO_2$ has an orthorhombic structure with two equivalent equilibrium positions for the NO_2 group, corresponding to orientations of its dipole moment $\pm p_0$ along or against the b axis. The ferroelectric phase transition at $T_c = 436\,K$ is preceded in the interval $T_c < T < T_N$ by the formation of an incommensurate phase with a sinusoidal distribution of the dipole moments $\mathbf{p}(\mathbf{r})$:

$$\mathbf{p}(\mathbf{r}) = \mathbf{p}_0 \langle \sigma^z(\mathbf{r}) \rangle = \mathbf{p}_0 \sigma(T) \sin(\mathbf{k}_0 \mathbf{r} + \alpha)$$

where the superstructure vector $\mathbf{k}_0(T)$ varies from $\mathbf{a}^*/8.4$ at $T = T_N$ to $\mathbf{a}^*/10.3$ at $T = T_c$, with $\mathbf{a}^*$ being the parameter of the reciprocal lattice along the a axis.

The mechanism giving rise to the incommensurate phase in $NaNO_2$ was discussed in Refs. 120 and 121. In Ref. 120 the NO_2 groups were treated as rigid Ising dipoles and the constants $V(\mathbf{R})$ in Hamiltonian (2) were evaluated as the sums of the electrostatic dipole-dipole interaction $V_d(\mathbf{R})$ and the short-range interaction $V_s(\mathbf{R})$; the latter was described by three constants estimated from the neutron-scattering data. It was found that the Fourier component $V_d(\mathbf{k})$ has a maximum at $\mathbf{k} = \mathbf{k}_0^* \approx \mathbf{a}^*/5$, corresponding to the formation of an incommensurate phase with this $\mathbf{k}_0$ at $T = T_N$. Quantitative agreement with the observed value $\mathbf{k}_0 \approx \mathbf{a}^*/8$ can be obtained by suitable choice of the parameters of V_s. It was later noted[131] that such a "dipole-dipole" mechanism for the formation of incommensurate phases is possible in a wide class of orthorhombic lattices with not too similar values of the lattice parameters a, b, and c. Here the energy differences between the incommensurate and the ferroelectric or antiferroelectric phases are extremely small; this could correspond qualitatively with the narrowness of the stability intervals of the incommensurate phases.

When the coupling of the NO_2 reorientations to the displacements of the Na atoms is taken into account in the model of Ref. 120 (as usual, this leads to an additional interaction of the groups undergoing ordering through the exchange of phonons), the stability region of the incommensurate phase vanishes.[121] The view was expressed[121] that this is an indication that refinements are needed in the model; in particular, that the polarizability of the NO_2 groups must be taken into account. It should also be noted that all the discussion in these papers[120,121] is based on the random phase approximation, which, being equivalent to the MFA, is completely unsuitable for studying such small and approximation-sensitive quantities as the difference in the thermodynamic
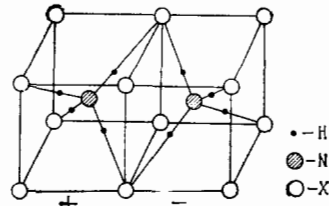

FIG. 12. Possible positions of the NH_4 tetrahedron in the lattices of NH_4X crystals.

potentials of the incommensurate and commensurate phases.

We should also mention the paper of Ehrhardt and Michel,[24] who constructed the crysalline potential $U(\mathbf{x})$ for reorientations of the NO_2 group in $NaNO_2$ on the basis of a rather realistic model of the repulsive forces (but without allowance for the long-range forces).

1.3) Orientational phase transitions in ammonium halides attract a great deal of interest by virtue of the combination of the structural simplicity of these crystals and the complexity and diversity of phase-transition phenomena in them (see Refs. 42 and 132–134 and the literature cited therein). In the disordered β phase NH_4X crystals have a structure of the CsCl type, and the NH_4 tetrahedra have the two equilibrium positions shown in Fig. 12. As the temperature is lowered the NH_4 groups become ordered in one of these positions: In the δ phase, which exists at low temperatures in NH_4CL and NH_4Br, the tetrahedra are oriented parallel ("ferromagnetically"), while in the γ phase, which is observed at low temperatures in NH_4I and at intermediate temperatures in NH_4Br, they are oriented "antiferromagnetically" in a checkerboard arrangement of alternating chains of a single orientation. The (p, T) phase diagram for NH_4Br is shown in Fig. 13a. The phase diagrams for NH_4I and NH_4Cl have a similar form, only the pressure scale is shifted upward by 4–5 kbar in NH_4I and downward by 5–6 kbar in NH_4Cl; this indicates that the effect of pressure on the phase transition is analogous to the isomorphic substitutions $I \rightarrow Br \rightarrow Cl$. Depending on p and X, the phase transitions in NH_4X are of first or second order, but in all cases the order parameters $\sigma_\delta(\tau)$ and $\sigma_\gamma(\tau)$ grow extremely rapidly with τ, so that the MFA gives a poor description of these functions (Fig. 13b).

The theories of the phase transitions in NH_4X were discussed in Refs. 132–134 and, in more detail, in Ref. 42. The features of these phase transitions are explained by the presence of competing orientational interactions: a direct octupole–octupole interaction of the NH_4 ions, favoring the formation of the δ phase, and an indirect interaction through the coupling with the lattice (in particular, with the halogen ions), which favors the γ phase. The parameters of the indirect interaction were estimated phenomenologically in Ref. 132, while in Ref. 42 they were calculated in an "electrostatic" model consisting of the octupole-dipole interaction of the NH_4 and X ions, with the polarizability of the halogen X (both the electronic component and the "ionic" component, which is due to the displacement of the ion as a whole) being charactrized by a single parameter ξ. The change in ξ with p and T was described by a "quasiharmonic" model in which ξ
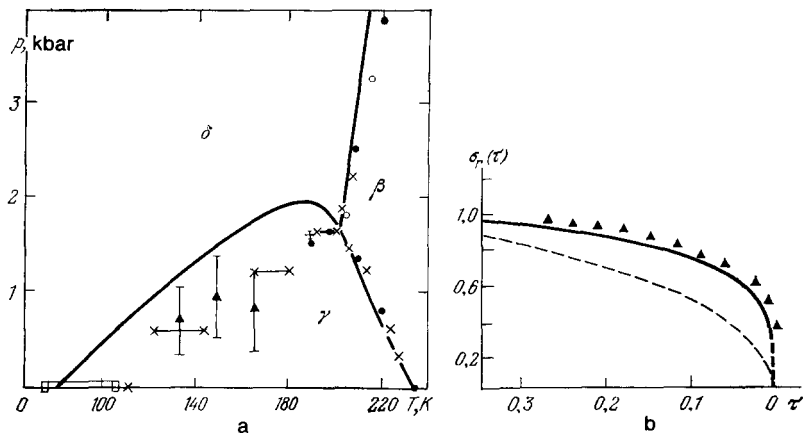
FIG. 13. a) The (p,T) phase diagram of the NH_4Br crystal (the curves are theoretical,[42] the points experimental); b) the temperature dependence of the order parameter $\sigma_\gamma(\tau)$ in NH_4Br at $p = 0$ (the solid curve was obtained in the cluster-approximation,[42] the dashed curve in the MFA, and the triangles in experiment).

for a given ξ depends only on the volume V: $\xi(V) = \xi_0 + a(V - V_0)/V_0$. The parameters ξ_0 and a were estimated from the experimental values of p, T, and $(dT_c/dp)_{\beta\gamma}$ at the triple point. The resulting values of the effective polarizability were smaller by a factor of 1.5–2 than that of the free ions X^-. As was discussed in the analogous estimates[135] of the quadrupole moments of the $(CN)^-$ ions in the KCN crystal (which turn out to be smaller by a factor of 2–3 than those of the free ions), a decrease of this kind is natural and should be taken into account in any estimates of the electrostatic interactions in crystals, since the electron density distributions in a crystal are generally "compressed" in comparison with the case of the free ions, and the addition of an "ionic" polarizability in NH_4X evidently does not completely compensate this decrease in ξ_0. Since ξ in the model of Ref. 42 is determined by all the orientational interactions, the aforementioned similarity of the (p,T) phase diagrams for NH_4X and the changes in these diagrams upon deuteration are naturally explained by a shift in ξ_0 upon the substitutions $Cl{\rightarrow}Br{\rightarrow}I$, $H{\rightarrow}D$.

The phase-transition thermodynamics was treated in the cluster approximation (with an 8-particle cubic cluster) in Ref. 42, since the strongly competing interactions mentioned earlier make the MFA unsuitable for quantitative estimates. The calculated (p,T) phase diagrams[10] and the calculated curve of $\sigma_\gamma(\tau)$ for NH_4Br are shown in Fig. 13. The agreement with experiment is surprisingly good for such a simple model, so that this model can apparently serve as a basis for more detailed calculations.

The method introduced in Ref. 42 for calculating the orientational interactions of the NH_4 ions was applied in Ref. 136 to the description of the recently discovered orientational phase transition in NH_4HgCl_3. It was noted that complex phase diagrams (such as those observed in NH_4X) are possible in crystals of this type, but the scarcity of experimental data makes quantitative estimates difficult.

2) Crystals with nonequivalent groups undergoing ordering. For many ferroelectric structural order-disorder phase

transitions there are indications of a "ferroelectric," many-sublattice character of the orderings. In this regard, phase-transition models with several order parameters (in particular, theories of improper ferroelectrics,[10,11] two-sublattice models,[137] etc.) are widely discussed. However, these discussions have generally been purely phenomenological and, in particular, do not differentiate between phase transitions of the order-disorder and displacive types.

Microscopic models for many-sublattice order-disorder phase transitions have so far been considered mainly for the case of mirror-image sublattices, which we shall discuss in Sec. 4b. On the other hand, the general case of nonequivalent sublattices undergoing ordering has been little studied for structural order-disorder phase transitions (in contrast to the case of magnetic phase transitions, where the thermodynamics of ferrimagnets has been studied in great detail). For example, in Ref. 138 the possible features of the phase-transition thermodynamics as they depend on the model parameters were discussed in the MFA for the case of two coupled Ising lattices, but the treatment was of a general, qualitative character, with no attempt to apply the model to a concrete order-disorder phase transition.

Model of the phase transition in AS [ammonium sulfate, $(NH_4)_2So_4$]. A detailed model calculation of the thermodynamics of the ferroelectric phase transition in AS was recently carried out.[139] The temperature dependence $P(T)$ in this crystal has an unusual shape (Fig. 14); in particular, it displays a "compensation point"—a point at which $P(T)$ changes sign—an extremely rare occurrence in ferroelectrics (in contrast to ferrimagnets). Proceeding from the structural data, Hasebe[139] assumed that the phase transition
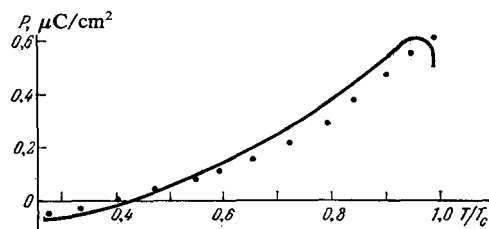
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[10]The curve of $(T_c)_{\gamma\delta}$ in Fig. 3 of Ref. 42 was drawn inaccurately. We remark in passing that the assertion made in Ref. 134 that the calculation of $(T_c)_{\beta\delta}$ in Ref. 42 contains an error is incorrect and is based on a misunderstanding.

FIG. 14. Spontaneous polarization $P(T)$ in ammonium sulfate. The points are experimental, the line theoretical.[139]

is due to the ordering, in symmetric double-well potentials, of ammonium ions of two structurally inequivalent types [NH_4 (1) and NH_4 (2), described by the "spin" variables σ_1^z and σ_2^z], and that the rotation angles θ of the SO_4 groups are coupled linearly with σ_1^z only. The thermodynamics of the corresponding two-sublattice "spin-phonon" model was calculated in the MFA, and the parameters of the model were estimated by fitting a number of calculated average quantities to experiment: $\langle\sigma_1^z\rangle = \sigma_1(T)$, $\sigma_2(T)$, $\theta(T)$, the spontaneous strains, etc. However, for describing these functions the free energy F had to be supplemented by three terms of fourth order in σ_i whose "microscopic origins are not clear."[139] Because of the large number of adjustable parameters the agreement with experiment (e.g., in Fig. 14) can hardly be regarded as confirmation of the accuracy of the model and the calculations, particularly since the calculated entropy of transition turns out to be too small by a factor of 1.5 compared to experiment and the Curie-Weiss constant in $\varepsilon(T)$ an order of magntiude too large. Nevertheless, Hasebe's paper[139] is unquestionably of interest as one of the first attempts to make a detailed estimate of the microscopic parameters for the complex phase transition in AS, while at the same time it illustrates the inadequacy of the simple model used in this paper and/or of the MFA (without the phenomenological addition of terms $\sim\sigma_i^2\sigma_j^2$ to F) for quantitative description of this phase transition.

b) Order-disorder phase transitions in asymmetric double-well potentials

As we have mentioned, the ordering in a number of order-disorder structural phase transitions occurs in nonequivalent mirror-image sublattices, so the crystalline potentials have the form shown in Fig. 1b. Phase transitions of this type (both orientational transitions and transitions in hydrogen-bonded crystals) have been discussed mainly for ferroelectrics, and we shall use ferroelectric terminology. The preferred occupation of the deeper minima gives rise to a polarization of each of the sublattices, but in the disordered antiferroelectric phase these polarizations compensate each other. The ferroelectric phase transitions are due to a disruption of this compensation by interactions of the groups undergoing ordering. As will be shown below, the presence of competing antiferroelectric and ferroelectric interactions can give rise to peculiar features in the phase diagrams and in the $P(T)$ curves, of the type shown in Fig. 15. A phase transition of this type apparently has no analogs among the magnetic phase transitions.

1) Thermodynamics of the phase transition in the Mitsui model for Rochelle salt ($NaKC_4H_4O_6\cdot4H_2O$). Information on the phase transition in Rochelle salts (Rs) and on the

structure of this crystal can be found in Refs. 2, 5, 8, 140–142 and the literature cited therein. Proceeding from this structure, Mitsui[28] proposed a "two-sublattice" model for describing the phase transition in Rs. The model Hamiltonian is of the form (2):

$$H = -\frac{1}{2}\sum_{rr'} J(R)\left[\sigma_1^z(r)\,\sigma_1^z(r') + \sigma_2^z(r)\,\sigma_2^z(r')\right]$$
$$-\sum_{rr'} K(R)\,\sigma_1^z(r)\,\sigma_2^z(r')$$
$$-\Delta\sum_r\left[\sigma_1^z(r) - \sigma_2^z(r)\right] - Ep_e\sum_r\left[\sigma_1^z(r) + \sigma_2^z(r)\right]; \quad (26)$$

here p_e is the effective dipole moment of the group undergoing ordering (apparently the proton of one of the OH groups), $J(R)$ and $K(R)$ describe the intrasublattice and intersublattice interactions, and Δ is the asymmetry of the minima of $U(x)$.

The thermodynamics of model (26) has been investigated[28,140,8] in the MFA for the case of homogeneous orderings $\langle\sigma_1^z(r)\rangle = \sigma_1$, $\langle\sigma_2^z(r)\rangle = \sigma_2$. Here the free energy per pair of spins σ_1 and σ_2 is

$$F = J\frac{\sigma_1^2 + \sigma_2^2}{2} + K\sigma_1\sigma_2 - T\ln(4\,\mathrm{ch}\,\beta H_1\,\mathrm{ch}\,\beta H_2), \quad (27a)$$

where $H_1 = J\sigma_1 + K\sigma_2 + \Delta$, $H_2 = J\sigma_2 + K\sigma_1 - \Delta$, J and K are related to $J(R)$ and $K(R)$ in (27) by the MFA equations (6b), and the σ_i are determined by the conditions $\partial F/\partial\sigma_i = 0$.

If the constants $J(R)$ and J in (26) and (27a) are negative, then the orderings $\langle\sigma_1^z(r)\rangle$ and $\langle\sigma_2^z(r)\rangle$ can be inhomogeneous. For example, in a discusssion of the phase transition in NH_4HSO_4 (see below), a model was considered[143] in which the constants $J(R) < 0$ and $K(R)$ correspond to nearest-neighbor interactions. Under the assumption of a four-sublattice ordering with spin values σ_{1a}, σ_{1b} and σ_{2a}, σ_{2b}, the following expression for F, a generalization of (27a), was obtained[143] in the MFA:

$$F = \frac{1}{4}J(\sigma_{1a}\sigma_{1b} + \sigma_{2a}\sigma_{2b}) + \frac{1}{2}K(\sigma_{1a}\sigma_{2a} + \sigma_{1b}\sigma_{2b})$$
$$-\frac{1}{2}T\ln(16\,\mathrm{ch}\,\beta H_{1a}\,\mathrm{ch}\,\beta H_{1b}\,\mathrm{ch}\,\beta\,H_{2a}\,\mathrm{ch}\,\beta H_{2b}), \quad (27b)$$

where $H_{1a} = J\sigma_{1b} + K\sigma_{2a} + \Delta$, $H_{1b} = J\sigma_{1a} + K\sigma_{2b} + \Delta$, $H_{2a} = J\sigma_{2b} + K\sigma_{1a} - \Delta$, and $H_{2b} = J\sigma_{2a} + K\sigma_{1b} - \Delta$.

A study of expressions (27a) and (27b) shows that the character of the phase transition and the shape of $\sigma_i(T)$ and $P(T) = (\sigma_1 + \sigma_2)/v_c$ are determined by two basic parameters $b = J/\Delta$ and $b' = K/\Delta$. The results of the analysis[28,140,8,143] are conveniently presented on the (b,b') phase diagram (Fig. 16). The equations of the boundary curves on this diagram are
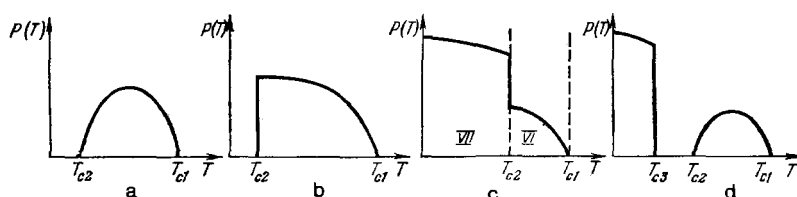

FIG. 15. Shape of the temperature dependence of the spontaneous polarization $P(T)$ in crystals with several ferroelectric phase transitions. a) Rochelle salt; b) $NH_4H(SO)_4$; $(NH_4)_3H(SO_4)_2$ under pressure $p > 5$ kbar; d) $(ND_4)_3D(SO_4)_2$ at $p > 0.2$ kbar.

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$$AF: \quad b' = 1, \quad DF: \quad b = 0; \quad FG: \quad b' = b + 1,$$

$$BCD: \quad b' = \frac{\sqrt{1 + 4bb'} + 1}{2} \, \text{th} \, \frac{\sqrt{1 + 4bb'} + 1}{2\,(b + b')}, \tag{28}$$

$$DE: \quad b' = b + b_0', \quad b_0' = \text{th} \, (1/b_0') \approx 0.833.$$

Let us first consider the case of homogeneous orderings (27a).[28,140,8] Minimizing expression (27a) with respect to σ_1 and σ_2, we find that for $T \to 0$ the ferroelectric phase $\sigma_1 = \sigma_2 = 1$ is energetically favored in regions I, II, and III in Fig. 16, while the antiferroelectric phase $\sigma_1 = -\sigma_2 = 1$ is favored in regions IV, V, and VI. In region VII expression (27a) as $T \to 0$ describes incompletely ordered phases[140] with $|\sigma_i| < 1$. These results for region VII, however, are apparently fictitious, due solely to the assumption of a homogeneous $\langle \sigma_i^z(\mathbf{r}) \rangle$, whereas in actuality inhomogeneous orderings arises in this region. Thus, in model (27b) the antiferroelectric phase considered in Ref. 143, with $\sigma_{1a} = \sigma_{2a} = -\sigma_{1b} = -\sigma_{2b} = \eta$ (which for the sake of brevity we shall call the η phase), exhibits the behavior $\eta \to 1$ as $T \to 0$, and throughout region VII the energy of the η phase is lower than the energies of the homogeneous phases[140] with $\sigma_{1a} = \sigma_{1b}$ and $\sigma_{2a} = \sigma_{2b}$.

Let us now discuss the ferroelectric phase transitions in model (27a,b). These phase transitions apparently exist only for $J > 0$, while for $J < 0$, according to the estimates of Ref. 143, the η phase in (27b) is thermodynamically favored over the ferroelectric phase at all T. By studying the expression obtained from (27a) for the dielectric permittivity $\varepsilon(T)$ at $E = P = 0$, we find[8] that in region I there is only one Curie point T_0 [a pole of $\varepsilon(T)$], while in regions II and IV there are two such points, T_{01} and T_{02}, and in regions III and V there is no T_0. Therefore, upon a change in T the ferroelectric phase also arises in region IV, but here it exists only between upper and lower Curie points in an interval $T_{c2} < T < T_{c1}$. For the case under consideration, $J > 0$, both these ferroelectric phase transitions turn out in the MFA (27a) to be of second order: $T_{c1} = T_{01}$, $T_{c2} = T_{02}$, as in Fig. 15a. At the same time, in Region III (and in a certain adjacent part of region II) the ferroelectric phase transition is of first order, since, as we have noted, in region III $\varepsilon(T)$ remains finite at all T. In addition, it was recently shown[158] that in a very narrow part of region II adjacent to region IV near point F in Fig. 16, model (27a) can exhibit two or three ferroelectric phase tran-
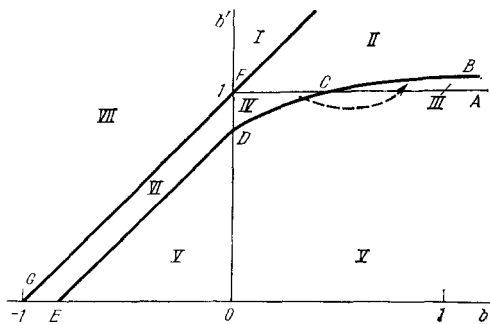

FIG. 16. Existence regions of ferroelectric and antiferroelectric phases in the Mitsui model (26), (27) in the plane of the variables $b = J/\Delta$, $b' = K/\Delta$ (see text).

sitions, and $P(T)$ has a temperature dependence of the type shown in Fig. 15c or 15d.

The transitions to the η phase in model (27b) were studied in Ref. 143. In region VII there is one such phase transition, while in region VI (analogous to region IV for the ferroelectric phase transition) the η phase exists beween two temperatures $T_{\eta 1}$ and $T_{\eta 2}$. On the whole, however, the phase transitions in approximation (27b) have been little studied, and the case of negative $J(\mathbf{R})$ in model (26) has not been studied at all. The presence of several competing interactions here can give rise to a large variety of phase transitions upon changes in T or in the model parameters; examples of such transitions include the phase transitions to modulated phases which are observed experimentally in a number of crystals of this type upon changes in the temperature, pressure, or concentration in solid solutions.

As is discussed in Ref. 8, the Mitsui model (26), (27a) gives a fair description of all the thermodynamic data on the ferroelectric transition in Rs if it is assumed that the parameters b and b' for this crystal lie in region IV of Fig. 16, near the point C. The values of J, K, Δ and p_c estimated in this way are given in Ref. 8. In addition, this model can explain the unusual concentration dependence of the ferroelectric properties in solid solutions between Rs and ammonium Rochelle salt ARs (obtained by substituting ammonium, NH_4, for the K ion in Rs). As the concentration x in $Rs_x ARs_{1-x}$ is increased from $x = 0$, the interval $T_{c1} - T_{c2}$ and the maximum polarization P_{max} in Fig. 15a decrease, and for $x > 0.03$ the ferroelectric phase transitions vanish, although for T close to the temperatures T_{ci} for pure Rs, $\varepsilon(T)$ displays a peak which becomes smeared out as x is increased further. For $x > 0.18$, however, the crystal again becomes ferroelectric. Here there is only one Curie point T_c, the polarization persists to $T = 0$, the phase transition is first order, and the growth of $\varepsilon(T)$ near $T_c(x)$ becomes progressively less pronounced as x increases.[2] According to what we have said, this extremely unusual change in properties can be understood in a natural way in terms of the model described if it is assumed that the change in x leads to an effective change in the constants, J, K, and Δ such that with increasing x the representative point is shifted along the dashed line in Fig. 16, passing successively through regions IV, V, and III.[28,2]

The effect of pressure p on the ferroelectric phase transition in $Rs_x ARs_{1-x}$ was studied in Ref. 141. It was found that at small $x < 0.03$ the existence region of the ferroelectric phase expands with increasing p, while at large $x > 0.18$ it contracts. It was believed[141] that this difference casts doubt upon the applicability of the simple model (26) for a unified description of the various ferroelectric phase transitions in $Rs_x ARs_{1-x}$. However, since the character of the p dependence of the parameters of model (26) can be different for large and small x, and since no estimates have yet been made for this dependence, the indicated difference in the p dependence of the existence region can hardly be considered a substantial discrepancy with the qualitative predictions of the simple model (26).

Upon deuteration the existence region $T_{c1} - T_{c2}$ of the ferroelectric phase of Rs expands[2] from 42 K to 57 K (although the T_{ci} themselves do not change much:

$(T_{c1})_{Rs} = 297$ K, $(T_{c1})_{DRs} = 308$ K). In this connection the possibility of appreciable tunneling effects in Rs, described by a Hamiltonian of type (3a), i.e., the addition of terms $\sim \hbar\Omega(\sigma_1^x + \sigma_2^x)$ to (26), has been discussed in several places.[4,142] However, no experimental indications of dynamical anomalies of the soft-mode type have been found in Rs (unlike the case of KDP).[8,142] Furthermore, the change in the pressure derivatives dT_{ci}/dp upon deuteration are insignificant in Rs (of the order of 10%, compared to 80% in KDP), and this is also an indication that the tunneling is small.[69] Therefore, the isotope effects in the values of T_{ci} and $P(T)$ for Rs can be mainly attributed not to tunneling but to changes in the interaction constants and effective dipole moments[8] upon deuteration, in accordance with relations of the type in (24), for example.

2) Phase transitions in AHS *and* RHS (ammonium and rubidium hydrogen sulfates, NH_4HSO_4 and $RbHSO_4$). The structures of AHS and RHS and the ferroelectric phase transitions in these crystals are described in Refs. 2, 69, and 143. In RHS the temperature dependence $P(T)$ has a "normal" shape of the type shown in Fig. 11, but in AHS, as in Rs, there is a lower Curie point T_{c2} (see Fig. 15b). The marked difference in the ferroelectric properties in the face of similar structures and values of T_{c1} in AHS and RHS might be an indication of the presence of competing, almost compensating, orientational interactions. As is discussed in Ref. 143, the phase transitions are apparently due to an ordering of the SO_4 groups in asymmetric double-well potentials, forming mirror-image sublattices.

These phase transitions were described[143] with the aid of model (26). The presence of the point T_{c2} in AHS leads one to think that the values of b and b' for this crystal, as for Rs, should lie in region IV of Fig. 16. However, in the MFA (27) (or in the two-particle cluster approximation[143]) the ferroelectric phase transition at $T = T_{c2}$ turns out to be always of second order rather than first order as in Fig. 15b. In order to obtain the observed functional dependence $P(T)$, it was assumed[143] that for AHS the quantity J in (27) depends on T and goes to zero near T_{c2}, but this assumption seems artificial. In addition, the calculated[143] value of the entropy of transition for RHS turns out to be 4–5 times larger than the observed values $S_c \approx 0.11$. One would clearly like to see further studies of these phase transitions.

3) Phase transition in SSN [sodium–silver nitrate, Ag-Na(NO$_2$)$_2$]. The SSN crystal has a relatively simple orthorhombic structure[144] analogous to that of NaNO$_2$, only here the Na ions alternate with Ag. Accordingly, in one of the two observed positions of the NO$_2$ group undergoing ordering its dipole moment (the vertex N) is directed toward the Na, while in the other it is directed toward the Ag. There are thus two inequivalent mirror-image sublattices of the NO$_2$ ions, and the ferroelectric phase transition in (SSN has also been described[144] in terms of model (26), (27).

The phase transition is of first order, close to second order, but the growth of $P(T)$ below T_c is extremely sharp—much sharper than in TGS (Fig. 11), for example. From the optical data one can also estimate the occupation parameters for each of the sublattices $\sigma_1(T)$ and $\sigma_2(T)$ above and below T_c. It has been shown[144] that all these data can be fairly well

described in terms of model (27) if one takes the values $b = b' \approx 1.12$, i.e., values close to the boundary curve BC between regions III and II in Fig. 16. The model also gives a satisfactory description of the temperature dependence of the dielectric permittivity and specific heat in the phase-transition region.[144]

4) Ferroelectric phase transitions in THDS *and* TDDS [triammonium hydrogen disulfate and its deuterated analog, $(NH_4)_3H(SO_4)_2$ and $(ND_4)_3D(SO_4)_2$]. The THDS crystal has a large number of structural phase transitions upon changes in T and p.[145-147] At $p = 0$ there are five known nonferroelectric phases I–V of different symmetries (one of these phases, III, is incommensurate), and at pressures $p \gtrsim 5$ kbar there are two more phases, ferroelectric phases VI and VII, having $P(T)$ curves of the type shown in Fig. 15c. In TDDS the ferroelectric phases are observed already at $p = 0$; for $p > 0.2$ kbar the $P(T)$ curve has a shape of the type shown in Fig. 15c, and for $p < 0.2$ kbar the curve is of the type shown in Fig. 15d.

The phase structures and the phase-transition mechanisms in THDS and TDDS remain little studied. However, the similarity of the (p,T) phase diagram in THDS to the (x,T) diagram in Rs$_x$Ars$_{1-x}$ and the aforementioned features of the ferroelectric phase transition permit the conjecture[145] that these phase transitions may also be due to ordering of certain groups—SO$_4$, NH$_4$, or H—in asymmetric potentials. So far only a qualitative theory of the two ferroelectric phase transitions in THDS under pressure (see Fig. 15c) has been discussed,[145] and for the sake of simplicity the presence of the nonferroelectric ordering in the high-temperature phase (which, depending on p, is phase II or III in THDS) has not been taken into account.

Gesi[145] conjectured that the ferroelectric phases VI and VII have the same symmetry and that the phase transition at $T = T_{c2}$ is a first-order isostructural transition due to the breaking of a fraction of the antiferroelectric bonds by a discontinuous reorientation of the dipoles in one of the sublattices of Fig. 1b. A phase transition of this type, generally speaking, could also occur in the framework of the model (26) and, as was later shown in Ref. 158, can be obtained even from expression (27a), though only for an extremely narrow region of parameters J, K, and Δ. In Ref. 145, on the other hand, a $P(T)$ curve of the shape shown in Fig. 15c was obtained by adding to (27a) terms with four-particle interactions of the form $\frac{1}{2}c(\sigma_1^4 + \sigma_2^4) + \frac{1}{4}d\sigma_1^2\sigma_2^2$ and studying the thermodynamics of the ferroelectric phase transition.

Assuming for the sake of definiteness that the coefficient $b' = K/\Delta$ varies linearly with p, while the quantities $b = J/\Delta$, $a_3 = c/\Delta$, and $a_4 = d/\Delta$ are independent of p, Gesi obtained a (p,T) phase diagram for the ferroelectric phase transition and a $P(T)$ curve which are qualitatively similar to those observed in THDS.

To be sure, the nature of the added four-particle interactions was not discussed in Ref. 145, and the values a_3, -0.5 and $a_4 = -0.2$ used in the calculations were not small (compared to $b = 0.045$ and $b' \sim 1$), so that these interactions can hardly be considered a small correction which might stem, for example, from an anharmonic coupling with the lattice.[14,95] Also omitted from discussion in Ref. 145 was

the behavior of $P(T,p)$ for TDDS, i.e., the "splitting" of the phase transition at the point T_{c2} (see Fig. 15c) into two ferroelectric phase transitions at the points T_{c2} and T_{c3} (see Fig. 15d); as we have mentioned, such a splitting is observed[147] in TDDS at $p \lesssim 0.2$ kbar. However, the model of Ref. 145, like the result of Ref. 158 mentioned earlier, and serve to illustrate the diversity and uniqueness of the order-disorder phase transitions in systems with asymmetric potentials and to point up the sensitivity of the thermodynamics of these phase transitions to details of the models and approximations used.

5) Quasi-one-dimensional models and Monte Carlo calculations for order-disorder phase transitions in asymmetric potentials. It is seen from what we have said that in the presence of competing, almost compensating, interactions (conditions typical of the phase transitions under study), the accuracy of the calculations for a chosen model becomes an important question. This is particularly relevant to results showing the presence of intermediate phases and results on the character (first or second order) of the phase transitions to the given phases, since the accuracy of the MFA can be insufficient for elucidating these questions. For examle, $P(T)$ curves such as those shown in Fig. 15b–15d usually do not arise in the MFA (27), but this can be attributed not to the inadequacy of model (26) for describing the given phase transitions but only to the insufficient accuracy of the MFA.

Attempts at refining the MFA results for model (26) were discussed in Refs. 124–126. In Ref. 124 a study was made of the exact solution of a one-dimensional version of model (26) in an external field E. It was shown that in spite of the familiar result[29] that formally no phase transition occurs in one-dimensional systems, at sufficiently small values of the effective fields acting on the spins (i.e., under conditions of compensating interactions) the $\sigma_i(T)$ curves can have sharp anomalies of the sort which occur at smeared phase transitions. Here the smearing can be made extremely small by varying the field E, for example. It was found that in "lability" regions of the phase diagrams (in particular, near line AF in Fig. 16) unusual $P(T)$ curves can arise, not only of the type shown in Fig. 15a, but also of the type shown in Fig. 15b, which are absent in the MFA.

In Ref. 125 a study was made of a quasi-one-dimensional version of model (26): The interactions of nearest neighbors within the two nonequivalent chains and between the nearest of these chains were taken into account exactly, while the interactions with other chains and with more remote neighbors were taken into account in the MFA. It was shown that such a "partial" refinement of the calculations leads to a certain upward shift of the curve BCD in Fig. 16 and to a certain broadening of the region of parameter values (in comparison with the region obtained[158] in the MFA) in which $P(T)$ is of the form shown in Fig. 15d. Also, in regions IV and VI the phase transition from the intermediate ferroelectric phase to a nonferroelectric phase at $T = T_{c2}$ is not necessarily a second-order transition, as in Fig. 15a, d, but can also be a first-order transition, as in Fig. 15b. These results again illustrate the thermodynamic lability and diversity of the phase transitions in models of type (26) and the possible inaccuracies of the MFA in describing them.

For several types of two-dimensional and three-dimensional lattices the phase transition in model (26) has been studied by the Monte Carlo method.[126] The number of particles ("spins") in the calculations was $N \lesssim 2 \cdot 10^3$. The finite value of N leads to a smearing of all the phase transitions, complicating the study of intermediate ferroelectric phases characterized by small values of $T_{c1} - T_{c2}$ and P_{max}. However, the results of Ref. 126 again indicate the high sensitivity of the thermodynamics of model (26) to the details of the structure and interactions. It was found, in particular, that in contrast to the MFA results the possibility of intermediate phases depends substantially on the type of lattice and that the transitions to these phases are always of second order. We note, however, that only nearest-neighbor interactions were considered in Ref. 126. In real systems there are also both long-range Coulomb interactions and other non-nearest-neighbor interactions, so that the MFA can have higher accuracy here than for the short-range-interaction model discussed in Ref. 126.

Further studies of the Mitsui model (26) and its generalization and specification for real crystals would appear to be extremely interesting, particuarly since the presence of mirror image sublattices with asymmetric potentials seems to be characteristic of very many crystals with order-disorder structural phase transitions.

c) Polyorientational order-disorder phase transitions

Studies in recent years have revealed the widespread occurrence of sequential structural phase transitions in which a series of intermediate phases, commensurate or incommensurate, is observed between the high- and low-temperature phases. For example, the THDS crystal discussed earlier undergoes four structural phase transitions at $p = 0$, many crystals of the type $Me^I Me^{II} BX_4$, e.g., $LiRbSO_4$ or $[(N(CH_3)_4]_2ZnCl_4$, have up to 4 or 5 phase transitions,[148,149] and so on; additional phases are often observed under pressure. The mechanisms of most of these phase transitions have been little studied. In particular, it is not always clear whether the transitions are of the order-disorder or displacive type (although the rather large values of the entropy of transition $S_c \gtrsim 1$ observed in a number of cases permit the hypothesis of order-disorder mechanisms[2,8]). These phase transitions have therefore been described mainly with the aid of phenomenological expansions of the thermodynamic potentials (of the usual Landau type) in powers of several order parameters η_i; these expansions contain a large number of unknown coefficients which in general depend on both temperature and pressure (see, e.g., Refs. 11 and 148).

The existing attempts at a microscopic approach to sequential order-disorder phase transitions have been made in connection with the study of polyorientational phase transitions, in which the orienting group in the (real or virtual) disordered phase has $q > 2$ equivalent potential minima. As we shall see, the presence of a series of phase transitions with decreasing T is both typical and characteristic of polyorientational systems. This situation is due either to the formation of intermediate, partially ordered phases in which only certain of the $q > 2$ admissible orientations are preferentially

occupied, or to a first-order phase transition between almost ordered phases of different symmetry. So far only the relatively simple polyorientational phase transitions to commensurate phases have been discussed, although it is natural to expect that the presence of additional degrees of freedom due to the polyorientational character may also be conducive to the formation of complex orderings and incommensurate phases.

1) General MFA *formulas for polyorientational phase transitions.* It has been noted[150] that the problem of polyorientational phase transitions with Hamiltonian (1) is formally analogous to the problem of order-disorder phase transitions in many-component substitutional alloys. Therefore, in describing the thermodynamics of polyorientational phase transitions in the MFA (which has been used in all the existing studies on the theory of polyorientational phase transitions[149-154]) it is convenient to use a version of the MFA developed specifically for alloys—the method of "concentration waves."[7] This method makes for simpler and more standarized calculations than the other possible formulations (e.g., that of Ref. 153) on account of its maximal use of the symmetry relations of the crystal.

Let us for simplicity limit our discussion of (1) to the symmetric case $\Delta_i = 0$. Then the MFA expressions for the free energy F and for the average occupation $n_i(\mathbf{r}) = \langle c_i(\mathbf{r}) \rangle$ of the i-th orientation can be written[150-152]

$$F = \frac{1}{2} \sum_{ri} V_i(\mathbf{r}) n_i(\mathbf{r}) - T \sum_r \ln \sum_i \exp[\beta V_i(\mathbf{r})], \quad (29a)$$

$$n_i(\mathbf{r}) = \frac{\exp[\beta V_i(\mathbf{r})]}{\sum_j \exp[\beta V_j(\mathbf{r})]}, \quad V_i(\mathbf{r}) = \sum_{r'j} V_{ij}(\mathbf{r} - \mathbf{r}') n_j(\mathbf{r}'), \quad (29b)$$

$$n_i(\mathbf{r}) = \sum_{\alpha s} \eta_{\alpha s} \sum_l \gamma_\alpha(\mathbf{k}_{ls}) u_\alpha^i(\mathbf{k}_{ls}) \exp(i\mathbf{k}_{ls}\mathbf{r}). \quad (29c)$$

Here the vectors $\mathbf{k}_{ls}$ of the start $\mathbf{k}_s$ define the periods of the superstructures, $\eta_{\alpha s}$ are the order parameters, and $u_\alpha^i(\mathbf{k}_{ls})$ is the eigenvector of the equation

$$\sum_j V_{ij}(\mathbf{k}_{ls}) u_\alpha^j(\mathbf{k}_{ls}) = \lambda_\alpha(\mathbf{k}_s) u_\alpha^i(\mathbf{k}_{ls}), \quad (30a)$$

$$V_{ij}(\mathbf{k}_{ls}) = \sum_r V_{ij}(\mathbf{r}) \exp(-i\mathbf{k}_{ls}\mathbf{r}), \quad (30b)$$

corresponding to the eigenvalue $\lambda_\alpha(\mathbf{k}_s)$. The normalization factors $\gamma_\alpha(\mathbf{k}_{ls})$ in (29c) are determined from the condition that in the ordered phase, when $\eta_{\alpha s} = 1$, the variable $n_i(\mathbf{r})$ takes on only two values, 0 or 1. The consistency equations (29b), as usual, are equivalent to the conditions that F be minimum with respect to the $\eta_{\alpha s}$: $\partial F / \partial \eta_{\alpha s} = 0$, which also find use in real calculations. The expressions for F (29a) in terms of $\eta_{\alpha s}$ and the interaction parameters $\lambda_\alpha(\mathbf{k}_s)$ turn out to be rather simple even in cases when there are several sublattices undergoing ordering.[149,151] Details of this method and its application to the description of a number of phase transitions in alloys are discussed in Ref. 7, and applications to polyorientational phase transitions are discussed in Refs. 149-152.

2) Model for phase transitions in $\mathrm{Me^I Me^{II} BX_4}$ *crystals.* In crystals of the family $\mathrm{Me^I Me^{II} BX_4}$, where Me is a univalent ion (alkali metal, $\mathrm{NH_4}$, $\mathrm{N(CH_3)_4}$, etc.) and $\mathrm{BX_4} = \mathrm{SO_4}$, $\mathrm{SeO_4}$, $\mathrm{ZnCl_4}$, $\mathrm{CuBr_4}$, etc., a variety of structural phase transi-

tions (including sequential transitions) are observed; these transitions are apparently due mainly to orientational ordering of the $\mathrm{BX_4}$ groups. The structure of these crystals is described in Ref. 149. In the high-temperature β phase they usually have symmetry D_{2h}^{16} and contain 4 molecules in the unit cell, with the $\mathrm{BX_4}$ groups distributed in a disordered fashion between two orientations. There are, however, experimental indications that the β phase is a distorted form of the high-temperature hexagonal α phase (the paraphase), which has symmetry D_{6h}^4 with two molecules in the unit cell.[11,149] In Ref. 149 it was assumed that the $\mathrm{BX_4}$ group in the α phase has 4 equivalent orientations, the Hamiltonian (1) for this model was written out with allowance for the symmetry of the lattice, and various polyorientational phase transitions were studied in the MFA (29), (30). For the sake of simplicity this study was limited to the four different completely ordered phases γ_i which are most frequently encountered in crystals of this family.

The results of Ref. 149 illustrate well the general properties of polyorientational phase transitions mentioned above. In all the cases considered the transitions from the α phase to the ordered phases γ_i occur through one or several partially ordered phases. In addition, for certain relations among the model parameters, first-order phase transitions between almost completely ordered phases are possible. As an illustration calculations were done[149] for the phase transitions in $(\mathrm{NH_4})_2\mathrm{SO_4}$ (AS), $(\mathrm{NH_4})_2\mathrm{BeF_4}$, and $\mathrm{LiRbSO_4}$. It was shown that the sequences of phases observed in these crystals and the character of the transitions (first or second order) between these phases can be described by the simple model used in that paper, although for discussion of the phase-transition thermodynamics the model needs to be extended and refined. For example. to describe the ferroelectric phase transition in AS one must also apparently take into account the two-sublattice ordering of the $\mathrm{NH_4}$ ions, as was discussed in Sec. 4a, and for quantitative estimates of the specific heat, entropy of transition, etc., the MFA (29) is apparently insufficient.

3) The phase transitions in $(\mathrm{CH_3NH_3})_2\mathrm{MeCl_4}$ *crystals,* where Me = Cd or Mn, are at present the only polyorientational phase transitions for which sufficiently detailed model theories have been proposed and quantitative estimates attempted.[151,153] These phase transitions are due to ordering of the methyl ammonium (MA) groups $\mathrm{CH_3NH_3}$, which have 4 equiprobable orientations in the high-temperature tetragonal phase. As T is decreased there is a sequence of 3 phase transitions: to a rhombic phase, to a low-temperature tetragonal phase, and to a monoclinic phase. As was shown in Refs. 153 and 151, when model (1) is used in the MFA (29), (30), only a single phase transition, from the high-temperature tetragonal phase to the rhombic phase, is possible in these crystals. In order to describe the transition from the rhombic to the low-temperature tetragonal phase, terms with three- and four-particle interactions of the MA groups were added[151,153] to Hamiltonian (1); the presence of these additional terms was attributed to covalent effects of the N–H . . . Cl bonds. These efforts succeeded in yielding an intermediate low-temperature tetragonal phase, but the low-temperature phase in this case was again the rhombic phase and
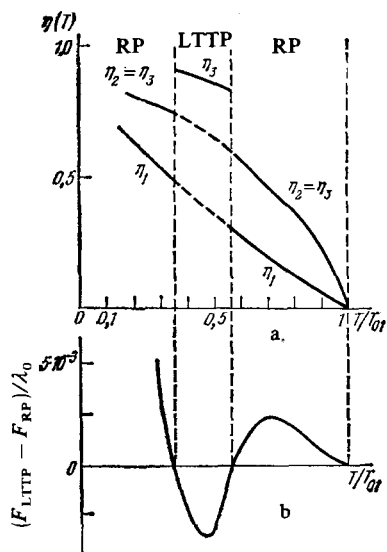
FIG. 17. Temperature dependence of the order parameters (a) and of the difference between the free energies (b) of the rhombic and low-temperature tetragonal phases (RP and LTTP) for the crystal $(CH_3NH_3)_2CdCl_4$ in the model of Ref. 151 with three- and four-particle interactions (see text).

not the monoclinic phase observed in experiment (Fig. 17).

As is discussed in Ref. 153, the observed monoclinic phase evidently cannot be described at all in a "rigid lattice" approximation [model (1)], and to obtain this phase a nonlinear coupling between the lattice strains and the orientational variables was introduced phenomenologically in that paper. The origin of the nonlinearity of this coupling was attributed to the influence of the aforementioned N–H . . . Cl bonds on the structural stability of the crystal. It should also be noted that to obtain the intermediate low-temperature tetragonal phase in the models of Refs. 151 and 153, extremely large many-particle interaction constants were used, exceeding by factors of 20 [153] or 1.5–2 [151] the binary interaction constants, in rather poor agreement with the model expressions for these constants in those papers.[153,151] This again illustrates the need for refinements of the simple model (1) and/ or the MFA for attempts at quantitative description of real polyorientational phase transitions.

4) Models for the phase transitions in alkali metal cyanides and in $RbNO_3$-type crystals. Model (1) in the MFA (29), (30) has also been applied to the description of the phase transitions due to ordering of the CN groups[152] in crystals of the MeCN type (Me = Na, K, Rb, Cs). The crystals NaCN, KCN, and RbCN, which have the NaCl structure, were described by a 12-orientation model, and CsCN, which has the CsCl structure, by an 8-orientation model. Just as in the case of $Me^I Me^{II} BX_4$ crystals, these models and this method are sufficient, with a certain choice of constants, to give the observed sequences and characters (first or second order) of the phase transitions in NaCN, KCN, and CsCN and to describe qualitatively the thermodynamics of these phase transitions. For RbCN, however, the description of the observed phase transition, which is accompanied by a quadrupling of the unit cell, is complicated. In addition, the more complex orderings that have been observed,[154] for example in KCN at

$p \gtrsim 2$–5 kbar were not considered in Ref. 152. Finally, we note that the MeCN crystals belong more to the ionic-molecular type than to the ionic-covalent type, and the amplitudes of the librational oscillations of the CN groups in these crystals are not small.[135] Therefore, for quantitative description the "continuous" models (4) and (5) are apparently more suitable than the "discrete" model (1).

The RN and AN crystals ($RbNO_3$ and NH_4NO_3) have 3 and 4 structural phase transitions, respectively,[55] which are due to both the orientational ordering of the NO_3 groups and the rearrangement of the lattice (e.g., from the NaCl to the CsCl lattice in RN). In Ref. 155 a 12-orientation model was discussed for the phase transitions between phases III and IV in RN and between phases I and II in AN; these phase transitions are due to the ordering of the NO_3 groups in a structure of the CsCl type. The discussion centered on the correlations in the NO_3 orientations and did not go into details on the phase-transition thermodynamics. It was noted,[155] however, that the entropy of transition for RN as calculated in the MFA comes out twice as high as in experiment. This may be an indication of substantial correlation effects and of the inapplicability of the MFA for quantitative calculations of the thermodynamics of these phase transitions.

In summing up what we have said in this section, we might note that model (1) and the MFA (29), (30) can evidently be used for qualitative discussions of the possible sequences of the polyorientational phase transitions and for estimation of the interaction parameters, a necessary first step in an investigation of these transitions. More-detailed discussions require extension and refinement of the model and of the calculational methods.

5. CONCLUDING REMARKS

On the basis of the foregoing discussion, we can draw the following conclusions regarding the status of the microscopic theories of order-disorder structural phase transitions.

1. The large majority of real order-disorder structural phase transitions are characterized by the presence of rather strong short-range correlations, which must be taken into account in attempts at quantitative description of these phase transitions. In many systems (e.g., hydrogen-bonded crystals which either strictly or approximately obey the ice rule) these correlations give rise to qualitative differences in the thermodynamics of these phase transitions in comparison to phase transitions of other types.

2. With due allowance for these correlations (for which purpose the cluster approximation is sufficient in a number of cases) the use of simple Hamiltonians of the type (1)-(3) yields a quantitative description of the phase-transition thermodynamics (see, e.g., Figs. 9 and 13).

3. Attempts at microscopic calculations of the parameters in Hamiltonians (1)–(3) are still few in number and mainly involve taking the electrostatic interactions into account and describing the short-range effects phenomenologically. For ionic-molecular and molecular crystals these calculations seem more reliable, but even here the values of

the multipole moments of the molecules are usually treated as adjustable parameters of the theory (see, e.g., Refs. 135 and 30). Nevertheless, in a number of cases calculations of this kind have made it possible to understand the essential features of certain order-disorder phase transitions, e.g., in the models for KFCT,[130] $NaNO_2$,[120,24] NH_4X,[42] KCN,[135] etc. In cases where the parameters of Hamiltonians (1)–(3) can be sufficiently reliably estimated from the phase-transition thermodynamics for a number of analogous crystals (as for the KDP family[15] or for crystals of the NH_4X type[42]), it seems to be extremely useful for refining ideas about the phase transitions to compare these estimates with semi-microscopic calculations of the same parameters and with experimental data on the change in structure with composition and pressure (e.g., with Refs. 70, 79, and 80 for KDP).

4. The presence of nonequivalent groups undergoing ordering, asymmetry of the potential minima, and many-well potentials an explain the unique features of the thermodynamics and phase diagrams observed in a large number of order-disorder structural phase transitions (see Figs. 14–17). These features can also be adequately described by simple models (1)-(3). However, in attempts at quantitative comparisons with experiment the use of the mean field approximation often leads to difficulties which have usually been overcome by adding rather sizable many-particle interaction terms to Hamiltonians (1)–(3), as was done by Hasebe[139] for $(NH_4)_2SO_4$, Gesi[145] for $(NH_4)_3H(SO_4)_2$, Blinc, Žekš, and Kind[153] for $(CH_3NH_3))_2CdCl_4$, etc. As was discussed above (in Sec. 4b in particular), it is possible that when approximations of higher accuracy than the MFA are used it will not be necessary to add terms of this sort.

5. Even the qualitative consequences of the simple models (1), (2) for order-disorder phase transitions have not been adequately studied. For example, the thermodynamic behavior of the Mitsui model (26) is not completely understood in cases where all or several of the constants J (R) are negative (in particular, in regions VI and VII of Fig. 16). As we have already noted, the possibility has not been ruled out that incommensurate phases arise here. No investigations have been made of the effects of correlations and the presence of anisotropic interactions in models (1) for polyorientational phase transitions, where there is also reason to expect the appearance of incommensurate phases (which are often observed in experiment), etc.

6. Finally, an obvious general problem in the microscopic description of order-disorder structural phase transitions is to refine the data on the structure and mechanisms of real phase transitions for the purpose of specifying the details of the microscopic Hamiltonians. This might include, for example, elucidating the nature of the groups undergoing ordering and the structures of the intermediate phases in complex crystals such as $(NH_4)_3H(SO_4)_2$, $Me^I Me^{II} BX_4$, etc., describing the possible nonlinear interactions with lattice distortions in crystals such as $(CH_3NH_3)_2CdCl_4$,[153] etc. As we have noted, however, for discussing the thermodynamic consequences of such refinements the simple mean field approximation can be insufficient for answering quantitative questions (e.g., questions regarding sequential phase transitions). In considering such questions one should apparently

try to refine our calculations along with the models.

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Translated by Steve Torstveit