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# Mean-field theory of structural phase transitions in the $A'A''BX_4$-type compounds

M. Kurzyński and M. Halawa*

*Institute of Physics, A. Mickiewicz University, 60-769 Poznań, Poland*

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The class of compounds with crystallographic structures incorporating slight distortions from the prototype $\alpha$-$K_2SO_4$ structure is studied. Various experimentally reported ferroelectric and ferroelastic phase transitions are considered as resulting from the ordering of the orientations of the $BX_4$ groups accompanied by ionic displacements. The four-state Hamiltonian, with no dynamics, of the orientational interactions is formulated and the possible modes of displacement are identified. The thermodynamics of a four-sublattice model is examined in the molecular-field approximation. In this model 25 different phases are possible. The three-dimensional phase diagram obtained allows a variety of sequences of successive temperature transitions. A classification of experimentally studied compounds is proposed.

## I. INTRODUCTION

We study a class of $A'A''BX_4$-type compounds with crystallographic structures that can be considered as slight distortions of the prototype $\alpha$-$K_2SO_4$ structure of $P6_3/mmc$ symmetry[1] (Fig. 1). Examples are ionic compounds with cations $A',A''=Li^+,Na^+,K^+,Rb^+,Cs^+$, $NH_4^+,N_2H_5^+,N(CH_3)_4^+$ and doubly charged anions $BX_4=SO_4^{2-},SeO_4^{2-}$, $M^{VI}O_4^{2-},M^{II}F_4^{2-},M^{II}Cl_4^{2-}$, $M^{II}Br_4^{2-}$ ($M^{VI}$ and $M^{II}$ represent hexavalent and bivalent metals, respectively) with the exception of several crystals with extremely small cations. In the nondistorted and nonpolar $\alpha$-$K_2SO_4$ structure the orientation of the $BX_4$ tetrahedra is random. The variety of ferroelectric and ferroelastic phase transitions reported in a multitude of experimental papers is due to partial or total ordering of orientations of the $BX_4$ groups, accompanied by ionic displacements.[1,2]

To our knowledge, there have been only two papers[3,4] published so far dealing with the statistical theory of the class of compounds considered here. Both papers treat rather special compounds, however, and neither discusses the physics of the phenomena in depth. It is the aim of this paper to propose a simple but sufficiently general theory of structural phase transitions for the entire class. Because of the complexity of the system, we begin with the molecular-field approximation using a model with no dynamics. It follows that the picture obtained should be treated as a qualitative rather than a quantitative one. The paper is addressed to experimentalists. We hope it will facilitate classification of a large number of known experimental facts as well as help in planning for further research.

In the present paper we define a nondynamical model of the orientational subsystem and examine the effects of the interaction between orientations of neighboring $BX_4$ tetrahedra that lie in the same $c$ plane. Effects of short- and long-range orientational interactions between tetrahedra along the $c$ direction will be the subject of a succeeding paper.

## II. ORIENTATIONAL STATES OF $BX_4$ TETRAHEDRA

Like all molecular crystals, the system under study has translational, rotational, and intramolecular degrees of freedom. We treat the translational motions in the ionic lattice in the harmonic approximation and neglect the intramolecular degrees of freedom because they are not excited in the experimental range of temperatures. We consider only the rotational degrees of freedom of $BX_4$ groups, the problem of ordering of cationic molecular groups like $NH_4^+$ or $N(CH_3)_4^+$ requires a separate treatment.

In the prototype structure, $BX_4$ anions form a hexagonal close-packed (hcp) lattice, expanded ($c/a > 1.63$) or contracted ($c/a < 1.63$) along the $c$ axis. Each $BX_4$ anion is surrounded by five $A'$ and six $A''$ cations. The local

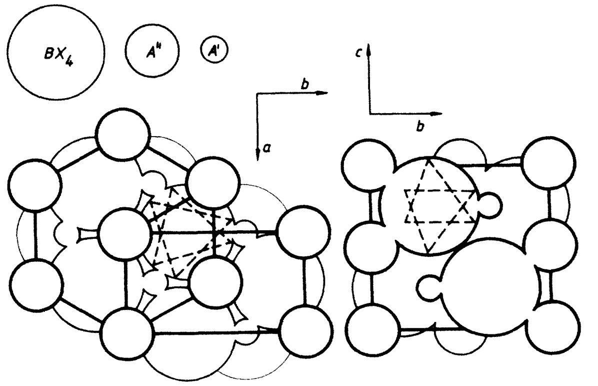


FIG. 1. High-temperature nonpolar and nondistorted $\alpha$-$K_2SO_4$ structure of $P6_3/mmc$ symmetry. Hexagonal ($Z=2$) and orthorhombic ($Z=4$) unit cells are shown. Notation of axes is used throughout the paper. It is assumed that smaller cations occupy $A'$ positions, although this is not a general rule. Relative magnitudes of ions apply approximately to $A'=Li^+$, $A''=K^+$, and $BX_4=SO_4^{2-}$. Note impossibility of free rotation of $BX_4$ tetrahedra. The projection of four different sterically allowed orientations of the tetrahedra is shown.

rotational potential is dominated by steric repulsion—no free rotation of tetrahedra is possible in the nondistorted static lattice (Fig. 1). The only sterically allowed configuration of the $BX_4$ tetrahedron has one of the apices above and the remainder below the plane of $A'$ cations, or the reverse. The three basal apices of the tetrahedron have to be contained somewhere between the $A'$ and the $A''$ cations so that each of the two sterically allowed configurations splits further into two subconfigurations. Assuming the distinguished apex to be approximately directed along the hexagonal $c$ axis, one can imagine these subconfigurations as a result of small turns of the tetrahedron to the right or to the left from an average but sterically prohibited position when the basal apices point to the $A'$ or the $A''$ cation (Fig. 1). The average position is determined by electrostatic interactions, mainly attraction of opposite charges located on the atoms $X$ and $A$. The attraction of $A'$ cations dominates if the ratio $c/a$ is large enough, whereas in the case of $c/a$ small the attraction of $A''$ cations is stronger.

Thus, there are four different subsets of sterically allowed orientations of the $BX_4$ tetrahedron and no transitions between these subsets are sterically possible in the nondistorted static lattice (the corresponding energy barriers are of infinite height). We will label these four discrete orientational states with the help of two Ising variables: $\sigma=\pm 1$ (position with the apex up and down, respectively) and $\tau=\pm 1$ (turn to the right and to the left, respectively). However, the local symmetry of cationic environment is described by the group $\bar{6}m2$ ($D_{3h}$) of 12 elements so that there are, in general, 12 different equivalent orientations of the $BX_4$ tetrahedron of minimum potential energy. It follows that there are three orientations of minimum energy within each of the four sterically allowed subsets labeled by the pair $(\sigma,\tau)$. One can imagine these three orientations as corresponding to slight tiltings of the trigonal axis of the tetrahedron in three distinct vertical planes rotated mutually by 120° around the $c$ axis.

The energy barrier that has to be overcome while changing the direction of tilting is not of steric nature and presumably low. For this reason we propose to describe the orientational states in the orientational isomerism approximation in terms of the four discrete states $(\sigma,\tau)$ and anharmonic librations, rather than in terms of 12 positions of minimum energy and the harmonic librations. This point of view seems to be justified by experiment. Indeed, the assumption of statistical disorder, both with respect to the up-and-down orientations and the right-and-left orientations, enabled earlier investigators to refine perfectly the $\alpha$-$K_2SO_4$ structure from the scattering data.[1] On the other hand, an attempt to refine the structure incorporating statistical disorder in the tiltings failed.[5] Also strong anharmonicity of librations has been confirmed experimentally.[6]

Until now we have considered rotational states of $BX_4$ tetrahedra for the nondistorted static lattice. It is obvious that a translation of cations relative to the centers of the anions may provide additional decreases of the rotational energy. Moreover, only such a translation allows transitions between different discrete orientational states $(\sigma,\tau)$. For an adequate description of the system under discussion it is thus necessary to consider the rotation-translation coupling. Further on, we take into account only the coupling of translations to the discrete states $(\sigma,\tau)$ and not to the librations. This allows us to neglect the librational subsystem as independent of the remaining degrees of freedom. Because we are not studying the dynamics of structural phase transitions here, we consider the rotational-translational Hamiltonian to be expressed only in terms of operators diagonal in the orientational states $(\sigma,\tau)$.

In the four-dimensional space spanned by the states $(\sigma,\tau)$ there are four diagonal operators $I$, $\sigma$, $\tau$, and $\sigma\tau$ that transform according to one-dimensional representations $\Gamma_1(A_1')$, $\Gamma_4(A_2'')$, $\Gamma_2(A_2')$, and $\Gamma_3(A_1'')$ of the local symmetry group $\bar{6}m2$ ($D_{3h}$), respectively. Consistent with a harmonic approximation of the lattice vibrations, we consider only their linear coupling to local modes of translation of the cationic environment. As the coupling Hamiltonian has to be invariant under local symmetry operations, we are interested only in normal modes of $\Gamma_2$, $\Gamma_3$, and $\Gamma_4$ symmetry (fully symmetrical $\Gamma_1$ normal modes couple identically to all the four orientational states). Using standard group-theoretical methods we found that there are one $\Gamma_2$, one $\Gamma_3$, and four $\Gamma_4$ normal modes of translation of the hexagonal environment under consideration composed of five $A'$ and six $A''$ cations. We denote these normal modes as $q_2$, $q_3$, and $q_4^{(1)},\ldots,q_4^{(4)}$, respectively. All of them are shown in Fig. 2. Thus, the most general rotational-translational Hamiltonian under the assumed restrictions is of the form

$$\mathcal{H}^{r\text{-}t}=\sum_{j=1}^{4} V_4^{(j)}\sigma q_4^{(j)}+V_2\tau q_2+V_3\sigma\tau q_3 \; . \tag{1}$$

Expressing the local normal modes in terms of collective normal modes (phonons) and performing canonical displacement transformation,[7] the Hamiltonian (1), together with the harmonic lattice Hamiltonian, gives an effective indirect orientation-orientation interaction of the form

$$\mathcal{H}^{\text{eff}}=\tfrac{1}{2}\sum_{\alpha,\alpha'}\sum_{l,l'} I_{l-l'}^{\alpha\alpha'}\alpha_l\alpha'_{l'} \; , \tag{2}$$

where $\alpha,\alpha'=\sigma,\tau,\sigma\tau$, and indices $l,l'$ label all anion sites in the prototype lattice. Due to the commutation of operators $\sigma$, $\tau$, and $\sigma\tau$, i.e., the neglect of dynamical aspects, the displacement transformation is exact.

The indirect interaction parameters $I_{l-l'}^{\alpha\alpha'}$ include also a modification of a single-site reference energy ($l=l'$, $\alpha=\alpha'$) and are determined by both the coupling parameters $V_\alpha^{(j)}$, Eq. (1), as well as the parameters describing the lattice dynamics. Because of the complexity of the latter (18 phonon branches) we do not quote the detailed expression. More important for further discussion is the relation between a lattice distortion described in the terms of averaged displacements of local modes of translation and an orientational ordering:

$$\langle q_{\alpha l}^{(j)}\rangle=(V_\alpha^{(j)})^{-1}\sum_{\alpha',l'} I_{l-l'}^{\alpha\alpha'}\langle\alpha'_{l'}\rangle \; . \tag{3}$$

Obviously, besides indirect orientational coupling, there is

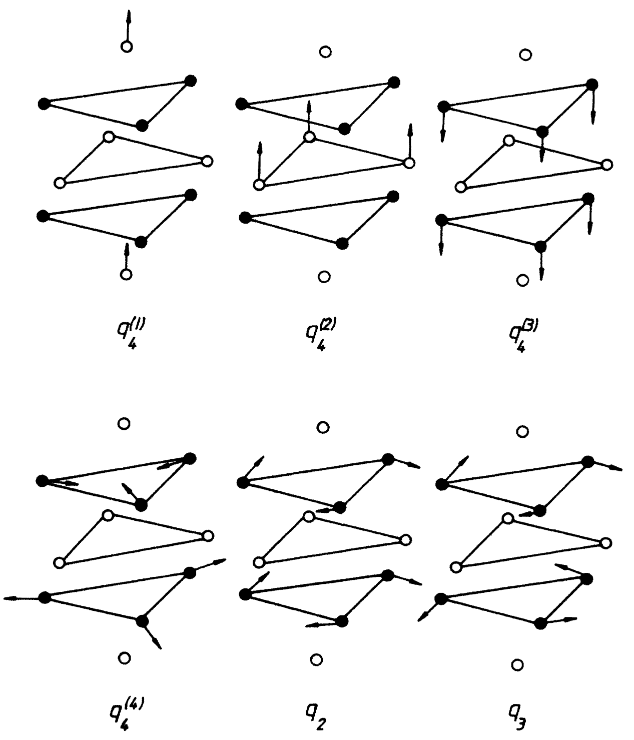


FIG. 2. Six translational normal modes of the cationic environment of $\bar{6}m2$ ($D_{3h}$) symmetry that couple linearly with the four orientational states of the $BX_4$ anion. Open and solid circles denote $A'$ and $A''$ cations, respectively.

also a direct orientational coupling resulting mainly from octupole-octupole electrostatic interaction. This is of a form identical to Eq. (2), only with the terms $l=l'$ omitted. Both interactions are of comparable strength.[8,9] In contrast to the former, however, the latter is extremely short ranged.

## III. THERMODYNAMICS OF A FOUR-SUBLATTICE MODEL

In proposing a general theory for a wide class of compounds we wish to avoid introducing too many parameters. For this reason we have decided to consider at the beginning only the nearest-neighbor (NN) orientational interactions. There are two inequivalent NN pairs in an hcp lattice: those that lie in and those that lie out of the plane perpendicular to the hexagonal $c$ axis. In-plane pairs have $mm2$ ($C_{2v}$) symmetry, while out-of-plane pairs have $2/m$ ($C_{2h}$) symmetry. These symmetries reduce the most general Hamiltonian of NN interactions to the form

$$\begin{aligned}\mathcal{H}=&J\sum_{\substack{\text{NN}\\ \text{in}}}\sigma_l\sigma_{l'}+K\sum_{\substack{\text{NN}\\ \text{in}}}\tau_l\tau_{l'}+L\sum_{\substack{\text{NN}\\ \text{in}}}\sigma_l\tau_l\sigma_{l'}\tau_{l'}\\ &+J'\sum_{\substack{\text{NN}\\ \text{out}}}\sigma_l\sigma_{l'}+K'\sum_{\substack{\text{NN}\\ \text{out}}}\tau_l\tau_{l'}+L'\sum_{\substack{\text{NN}\\ \text{out}}}\sigma_l\tau_l\sigma_{l'}\tau_{l'}\\ &+M{\sum_{\substack{\text{NN}\\ \text{in}}}}'\sigma_l\sigma_{l'}(\tau_l-\tau_{l'})+M'{\sum_{\substack{\text{NN}\\ \text{out}}}}'\tau_l\tau_{l'}(\sigma_l-\sigma_{l'})\ ,\end{aligned}\tag{4}$$

where NN in and NN out denote summation over nearest neighbors lying in and out of the $c$ plane, respectively. Primes in the sums for the two antisymmetrical terms indicate summation only over distinct pairs of sites.

Of course the Hamiltonian (4) without antisymmetrical terms is capable of describing structural phase transitions that involve, at most, a doubling of the crystallographic unit cell. As the unit cell of the prototype lattice contains two anionic sites we will consider, accordingly, the four-sublattice structure of the hcp lattice that is shown in Fig. 3.

To examine the thermodynamics of the Hamiltonian (4) in the mean-field approximation, we apply a variational procedure using the Bogolyubov upper bound of the free energy

$$\begin{aligned}F(A_1,\dots,A_4;B_1,\dots,B_4)=&-kT\ln\operatorname{tr}\exp(-\mathcal{H}_0/kT)\\ &+\langle\mathcal{H}-\mathcal{H}_0\rangle\ ,\end{aligned}\tag{5}$$

with the trial Hamiltonian

$$\mathcal{H}_0=\sum_s A_s\sum_{l\in s}\sigma_l+\sum_s B_s\sum_{l\in s}\tau_l\ ,\tag{6}$$

and the index $s$ running over all four sublattices 1, 2, 3, and 4. The average in Eq. (5) means the thermodynamic average with the Hamiltonian $\mathcal{H}_0$. It should be noted that Eq. (6) is not the complete molecular-field Hamiltonian for the original Hamiltonian (4) because it does not include the term

$$\sum_s C_s\sum_{l\in s}\sigma_l\tau_l\ .$$

Neglecting this term is equivalent to the approximation

$$\langle\sigma_l\tau_l\rangle=\langle\sigma_l\rangle\langle\tau_l\rangle\ ,\tag{7}$$

which presumably has no qualitative consequences but simplifies the calculations considerably.

The variational free energy (5) depends on variational parameters $A_s$ and $B_s$ (molecular fields) either explicitly or through conjugate thermodynamical variables (order parameters)

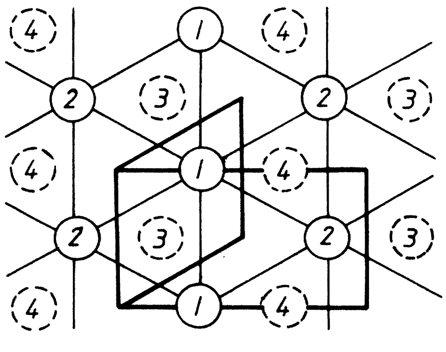


FIG. 3. Four-sublattice structure of the hcp lattice. Sites in and above (below) the $c$ plane are marked with solid and dashed line circles, respectively. Hexagonal ($Z=2$) and orthorhombic ($Z=4$) unit cells are shown.

$$\begin{aligned} m_s &\equiv \langle \sigma \rangle_s = -\tanh(A_s/kT)\ , \\ n_s &\equiv \langle \tau \rangle_s = -\tanh(B_s/kT)\ . \end{aligned} \tag{8}$$

The minimization condition

$$\frac{\partial F}{\partial A_s} = \frac{\partial F}{\partial B_s} = 0 \tag{9}$$

leads, following one-to-one functional dependence (8), to the relations

$$A_s = N^{-1} \frac{\partial \langle \mathscr{H} \rangle}{\partial m_s}, \quad B_s = N^{-1} \frac{\partial \langle \mathscr{H} \rangle}{\partial n_s}\ , \tag{10}$$

where $N$ is the number of sites on each sublattice. Equations (10), together with Eqs. (8), compose a set of eight self-consistent equations for eight variational parameters $A_s$ and $B_s$ or, equivalently, for eight order parameters $m_s$ and $n_s$. The proper solution is the one that gives the minimum free energy (5) at the point (10).

The solution of eight nonlinear coupled equations is time-consuming, even with a computer. For that reason we have assumed that there are no ferri-ordering-type solutions of Eqs. (8) and (10) and set

$$m_s = a_s m, \quad n_s = b_s n\ , \tag{11}$$

with $a_s = \pm 1$ and $b_s = \pm 1$. We verified this assumption to be true for the ground state. Under assumption (11), there are five possible orderings for each thermodynamical variable $m \equiv \langle \sigma \rangle$ or $n \equiv \langle \tau \rangle$ in the hcp lattice with four sublattices:

$$\begin{aligned}
&\langle\ \rangle_1 = \langle\ \rangle_2 = \langle\ \rangle_3 = \langle\ \rangle_4 = 0, \quad \text{para (P)}\ , \\
&\langle\ \rangle_1 = \langle\ \rangle_2 = \langle\ \rangle_3 = \langle\ \rangle_4 \neq 0, \quad \text{ferro (F)}\ , \\
&\langle\ \rangle_1 = \langle\ \rangle_2 = -\langle\ \rangle_3 = -\langle\ \rangle_4 \neq 0, \quad \text{antiferro (A)}\ , \\
&\langle\ \rangle_1 = -\langle\ \rangle_2 = -\langle\ \rangle_3 = \langle\ \rangle_4 \neq 0, \quad \text{antiferro (B)}\ , \\
&\langle\ \rangle_1 = -\langle\ \rangle_2 = \langle\ \rangle_3 = -\langle\ \rangle_4 \neq 0, \quad \text{antiferro (C)}\ .
\end{aligned} \tag{12}$$

With these assumptions the problem of solving eight equations for eight order parameters $m_s$ and $n_s$ is reduced to the problem of solving two equations for two order parameters $m$ and $n$ in 25 versions (5 for $m$ times 5 for $n$), and a comparison of the corresponding free energies. In fact, we have to consider only $3 \times 3 = 9$ versions, because of the invariance of both the self-consistent equations (8) and (10) and the free energy (5) with respect to "gauge" symmetry operations

$$\begin{aligned} & m_3, m_4, J', L' \rightarrow -m_3, -m_4, -J', -L'\ , \\ & n_3, n_4, K', L' \rightarrow -n_3, -n_4, -K', -L'\ . \end{aligned} \tag{13}$$

It should be pointed out that for the assumed structure of sublattices both antisymmetrical terms in the Hamiltonian (4) do not contribute to the free energy (5).

For $L = L' = 0$ our model is reduced to two independent anisotropic Ising systems with NN interactions. The phase diagram of a single anisotropic Ising system on the hcp lattice in the molecular-field approximation is given in Fig. 4. It is seen that all the five phases P, F, A, B, and C, as specified by Eqs. (12) are realized. The complete phase diagram is simply a Cartesian product of two phase diagrams for $\langle \sigma \rangle$ and $\langle \tau \rangle$, respectively. In general, there are 25 phases possible PP,PF, . . . , BC,CC, where the first and the second letter correspond to the variable $\langle \sigma \rangle$ and $\langle \tau \rangle$, respectively.

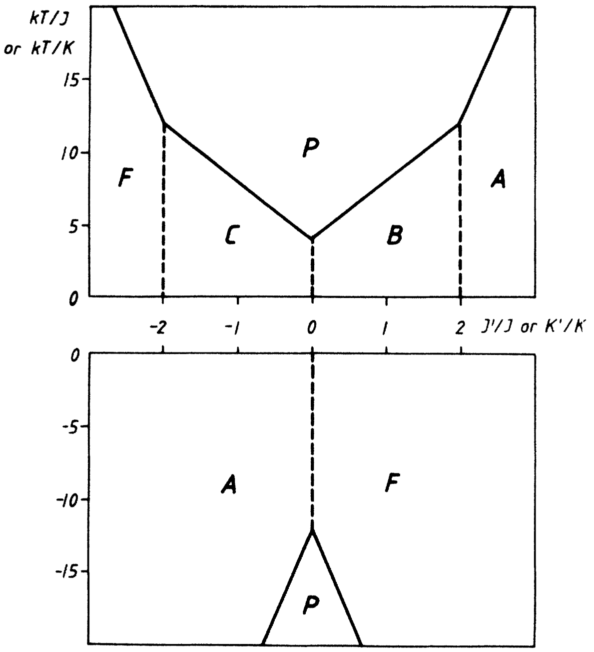


FIG. 4. Phase diagram in the molecular-field approximation of the anisotropic Ising model on an hcp lattice. Dashed and solid lines correspond to phase transitions of the first and the second kind, respectively. Note the mirror symmetry with respect to the plane $J'/J = 0$ $(K'/K = 0)$: the phase F interchanges with the phase A, and the phase B interchanges with the phase C.

Simple geometrical considerations suggest that the interaction in plane described by $J$ should be of the antiferro type $(J > 0)$ whereas that described by $K$ should be the ferro one $(K < 0)$. The sign of the interactions out of plane, $J'$ and $K'$, depends on the ratio $c/a$. To examine the effects of coupling between the $\sigma$ and the $\tau$ subsystem, we have assumed

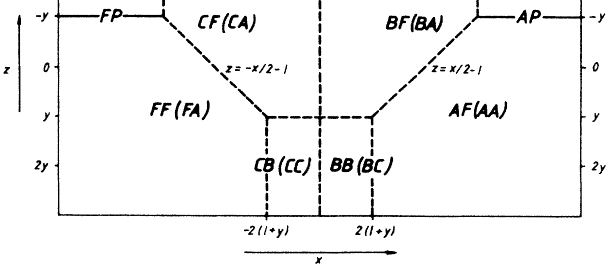


FIG. 5. Ground-state $(x,z)$ phase diagram for $K' = L' = 0$ and arbitrary $y < 0$. Dashed and solid lines correspond to phase transitions of the first and the second kind, respectively.

$$K'=0,\quad L'=0 \tag{14}$$

(the neglected interactions for out-of-plane pairs are planned to be studied in a future paper together with next-neighbor interactions).

In the following we use dimensionless quantities

$$x \equiv J'/J,\quad y \equiv K/J,\quad z \equiv L/J,\quad t \equiv kT/J\ . \tag{15}$$

The ground-state phase diagram for $y<0$ ($J$ antiferro and $K$ ferro) is given in Fig. 5. In Fig. 6 we give finite-temperature phase diagrams found numerically for the physically reasonable value $y=-\frac{1}{2}$ and various strengths of coupling described by the parameter $z$. The ambiguity in phase determinations (e.g., either BF or BA) results because we have neglected the $K'$ interaction. This ambiguity can be removed by assuming an infinitesimally small value for $K'$.

Comparing the diagram for $z=0$ in Fig. 6 with the remaining diagrams, we find that the effects of the four-spin coupling term are considerable indeed. They are

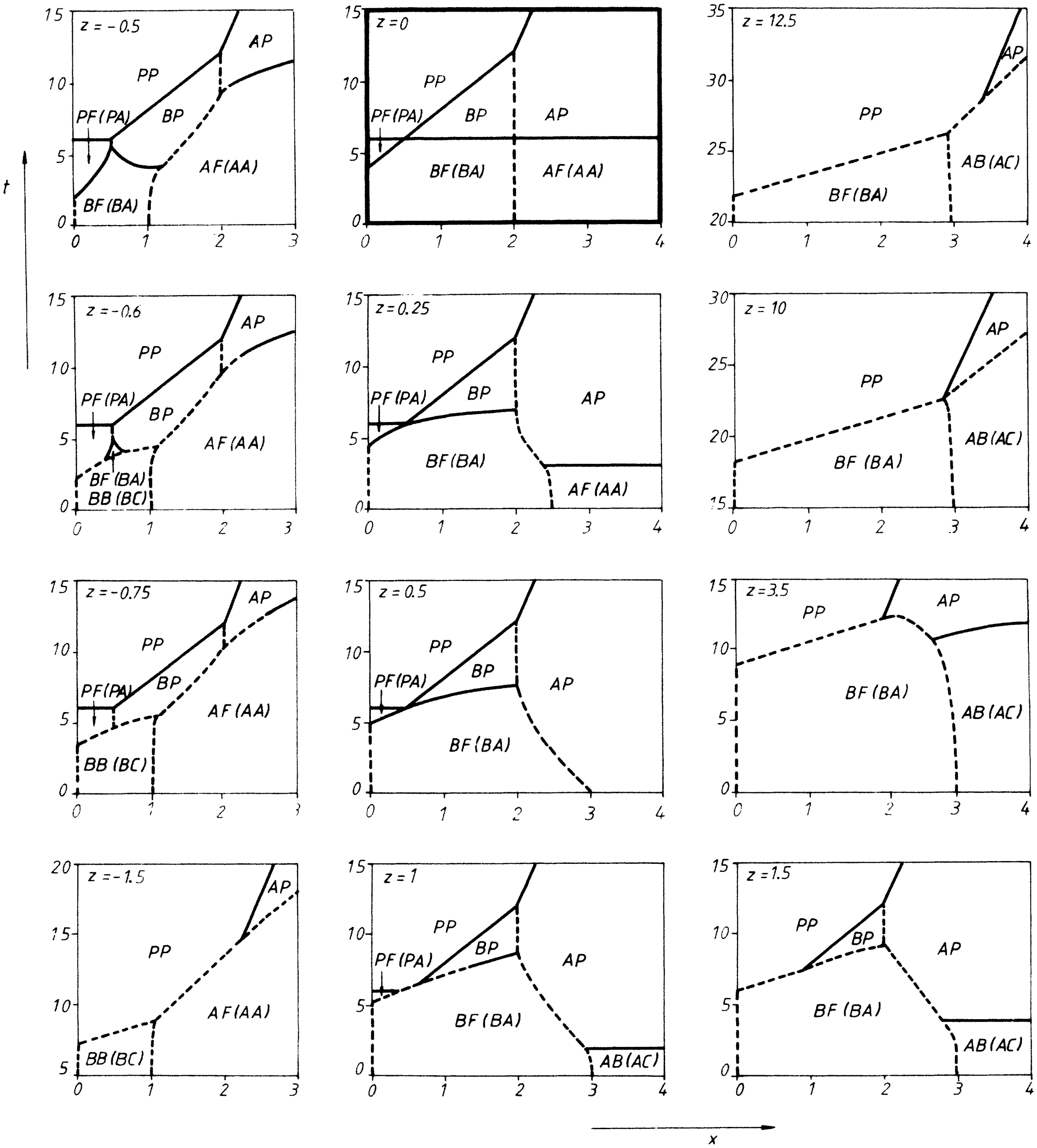


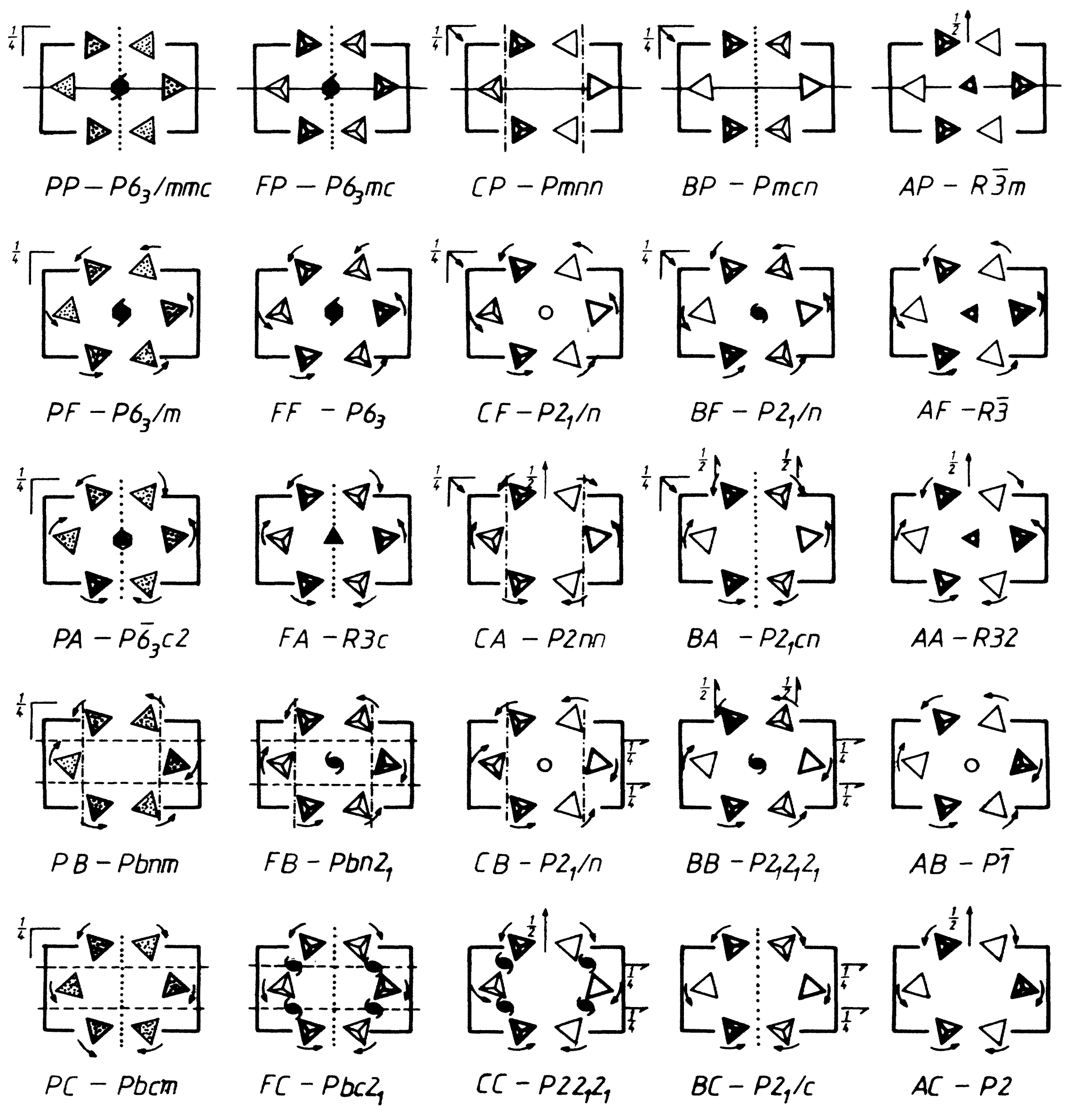
FIG. 6. Cross sections of $(t,x,z)$ phase diagram found numerically for $K'=L'=0$ and $y=-\frac{1}{2}$. Dashed and solid lines correspond to phase transitions of the first and the second kind, respectively. Only half-planes $x \geq 0$ are shown; the results for $x \leq 0$ are mirror images with respect to reflection in the plane $x=0$. For $x \leq 0$ phases A$X$ and B$X$ ($X$—any of $\tau$ orderings) should be interchanged with phases F$X$ and C$X$, respectively (see Fig. 4). The case of the uncoupled Ising subsystems ($z=0$) is shown in the graph with a heavy border.

manifested as changes in the transition order, appearance of triple as well as critical end points, and the possibility of new sequences of successive temperature transitions. Let us note that the tetracritical point characteristic for $z=0$ exists in the range $-\frac{1}{2}\leq z\leq\frac{1}{2}$. In general, we have verified that the form of phase diagrams given in Fig. 6 remains qualitatively unaltered for a wide range of the parameter $y<0$.

Identification of all 25 theoretically predicted phases is given in Fig. 7, where average orientation of tetrahedra in each sublattice enables one to determine the space symmetry. In making Fig. 7, we have assumed the tetrahedra as turned to the right or to the left from the position when the basal apices point to the $A'$ cation (Fig. 1), though turning from the position with the basal apices pointing to the $A''$ cation is rather typical for most compounds occurring in B$X$ or A$X$ phases ($X=$P,F,A,B,C).

The space symmetry thus found determines whether a given phase is ferroelectric or ferroelastic. In the listing given below we use the $F$-operation notation of Aizu.[10]

(i) *Ferroelectric along the c axis* (more correctly, *pyroelectric* as it is quite impossible to change simultaneously the orientation of most tetrahedra from up to down position):



$PP-P6_3/mmc$ $FP-P6_3mc$ $CP-Pmnn$ $BP-Pmcn$ $AP-R\bar{3}m$

$PF-P6_3/m$ $FF-P6_3$ $CF-P2_1/n$ $BF-P2_1/n$ $AF-R\bar{3}$

$PA-P\bar{6}_3c2$ $FA-R3c$ $CA-P2nn$ $BA-P2_1cn$ $AA-R32$

$PB-Pbnm$ $FB-Pbn2_1$ $CB-P2_1/n$ $BB-P2_12_12_1$ $AB-P\bar{1}$

$PC-Pbcm$ $FC-Pbc2_1$ $CC-P222_1$ $BC-P2_1/c$ $AC-P2$

FIG. 7. Patterns of orientational order for all 25 phases of the four-sublattice model. Main elements of symmetry are indicated.

FP ($6/mmm\,F\,6mm$) ,

FF ($6/m\,F\,6$) ,

FA ($\bar{6}m2\,F\,3m$) ,

FB and FC ($mmm\,F\,mm2_z$) .

(ii) *Ferroelectric along a axis:*

BA and CA ($mmm\,F\,mm2_x$) ,

AC ($\bar{3}m\,F\,2_x$) .

(iii) *Ferroelastic orthorhombic:*

PB, PC, PB, and CP ($6/mmm\,F\,mmm$) ,

BA and CA ($\bar{6}m2F\,mm2_x$) ,

FB and FC ($6mm\,F\,mm2_z$) .

(iv) *Ferroelastic monoclinic:*

BF and CF ($6/m\,F\,2_z/m$ or $mmm\,F\,2_z/m$) ,

BC and CB ($mmm\,F\,2_x/m$) .

(v) *Ferroelastic triclinic:*

AB ($\bar{3}m\,F\,\bar{1}$ or $mmm\,F\,\bar{1}$) .

Five phases are hexagonal (PP,PF,PA,FP,FF), four are trigonal (FA,AP,AF,AA), two phases are nonferroelastic orthorhombic (BB and CC), and one nonferroelastic monoclinic (AC). Let us note that in real compounds the region of stability of the prototype phase may occur above the melting or decomposition temperature, so all the ferroelectric and ferroelastic phases listed above should be understood in theoretical rather than in practical terms.

The orientation itself is not directly related to the ferroelectric or the ferroelastic order parameter. Physically, a quantity having more direct meaning is the lattice distortion. To determine displacements of ions corresponding to the orientational ordering, we applied Eq. (3) with an interaction form identical to that occurring in the Hamiltonian (4). All possible modes of ionic displacements accompanying particular orientational orderings found in this manner are given in Fig. 8.

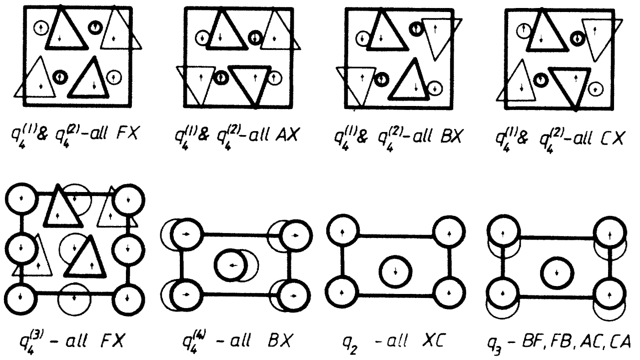


FIG. 8. Possible modes of ionic displacements accompanying particular orientational orderings. Letter $X$ denotes any of orderings P, F, A, B, or C.

## IV. CONCLUDING REMARKS

With a knowledge of the extensive experimental literature, although certainly not complete, we find that it is possible to classify all compounds studied to date as belonging to three main groups. The first group, comprising almost all compounds, is distinguished by a sequence of transitions

PP→BP→BF (BA)

as the temperature is reduced (diagrams for $-0.5 \le z < 3.5$ in Fig. 6). The second group, to which $NaKSO_4$ belongs,[11] probably has the sequence

PP→AP→AF (AA)

(diagrams for $z<0.5$ in Fig. 6). The third group, comprising $LiKSO_4$, is distinguished by the following sequence:[5,6,12,13]

PP→CP→FF (FA)

(diagrams for $-1.5<z<0$ and negative $x$ in Fig. 6).

On referring to phase diagrams in Fig. 6 we find that all these sequences are realized for $y$ and $z$ close to

$$y=-\tfrac{1}{2},\quad z=-\tfrac{1}{2}\ , \tag{16}$$

and the crucial parameter that distinguishes between the sequences is $x \equiv J'/J$. From a geometrical point of view it is quite reasonable to assume that both the sign and magnitude for $J'$ depend mainly on the ratio $c/a$. Indeed, $c/a=1.28$ for $NaKSO_4$ (Ref. 1) and 1.68 for $LiKSO_4$ (Ref. 6); these values are rather extreme cases compared with the remaining compounds. It is puzzling to note that there appear to be no compounds with other sequences of transitions:

PP→CP→CF (CA) ,

PP→PF (PA)→CF (CA) ,

PP→PF (PA)→BF (BA) ,

PP→BP→AF (AA) ,

for parameters satisfying Eq. (16) and intermediate values of $x$. Experimental investigations are in progress, however, and one can expect the discovery of additional compounds. We hope this simple introductory theory will be helpful to encourage further research.

In view of the theory developed in the preceding section we are forced to treat the joined symbol $X$F($X$A) ($X$=P,B,A,F, or C) in each of the schemes above as a notation of a single superphase rather than two alternatives. This follows, however, not only from the omission of a detailed discussion of $K'$ and $L'$ interactions. The mirror symmetry described by Eqs. (13) does not allow transitions $X$F↔$X$A with only a temperature variation (also temperature transitions $X$B↔$X$C, F$X$↔A$X$, and B$X$↔C$X$ are not allowed). This disagrees with the observation of a

FF→FA transition in $LiKSO_4$ (Ref. 12) and, in a sense, of BA→BA-BF and BA-BF→BF transitions in $LiNH_4SO_4$ (Ref. 14) and $LiRbSO_4$ (Ref. 15), respectively (BA-BF denotes a superstructure of the symmetry $P2_1/c$ made up of BF structures pointing in opposite directions and alternating along the $c$ axis[14]). These transitions, as well as the numerous commensurate-incommensurate transitions observed, must originate in longer-range interactions for pairs lying out of the $c$ plane. These are planned to be examined in a succeeding paper, together with $K'$ and $L'$ interactions omitted in the present work. Most important is that all transitions originating from interactions of pairs out of the $c$ plane may be considered as transitions within a single $X$F($X$A) or $X$B($X$C) superphase in terms of the present theory. This justifies our decision to divide our studies into two separate stages.

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[*] Permanent address: Department of Mathematics, Faculty of Science, Ain Shams University, Cairo, Egypt.

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