Basal-plane incommensurate phases in hcp structures

I. Luk’yanchuk¹,², *, A. Jorio¹, M. A. Pimenta¹,**

¹Departamento de Física, Universidade Federal de Minas Gerais, Caixa Postal 702, 30161-970, Belo Horizonte, Minas Gerais, Brazil
²L.D. Landau Institute for Theoretical Physics, 117940, Moscow, Russia. (October 11, 2013)

An Ising model with competing interaction is used to study the appearance of incommensurate phases in the basal plane of an hexagonal closed-packed structure. The calculated mean-field phase diagram reveals various 1q-incommensurate and lock-in phases. The results are applied to explain the basal-plane incommensurate phase in some compounds of the $A’A''BX_4$ family, like $K_2MoO_4$, $K_2WO_4$, $Rb_2WO_4$, and to describe the sequence of high-temperature phase transitions in other compounds of this family.

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I. INTRODUCTION

The microscopic origin of incommensurate phases in ferroelectrics, magnetic materials, binary alloys and other related systems is subject of interest since the early 60th (for a review see Ref. [1]). It is now well established that incommensurate modulation in the majority of those systems is caused by the frustrating competition between different interatomic or interspin forces responsible for structural or magnetic ordering.

The first approach proposed for studying frustration-induced incommensurate phases was based on the axial next-nearest-neighbor Ising (ANNNI) model with competing uniaxial nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions in which the structural units have been described by binary Ising pseudo-spin variables $\sigma^\alpha$. Depending on the coupling parameters and temperature, this model was shown to exhibit a rich diagram of commensurate and incommensurate modulated phases when the wave vector jumps between rational and irrational values of the reciprocal lattice period, a phenomenon known as a devil’s staircase.

A large variety of incommensurate systems is adequately described by the ANNNI model and its analogous $\sigma^\alpha$. The common feature of these models is that the modulation occurs in the uniaxial high-symmetry direction. There are, however, examples of incommensurate phases where wave vector is perpendicular to the high-symmetry axis and can occur in more than one equivalent direction. The appearance of this kind of incommensurate modulation was studied for the simple cubic lattice with competing NN and NNN interactions along the cubic axes and their diagonals $\sigma^\alpha$, for the simple hexagonal lattice with NN and NNN interactions $\sigma^\alpha$ and for distorted triangular lattice with only NN interaction $\sigma^\alpha$.

In this paper we employ the mean-field approximation to study the Ising model on the hexagonal closed-packed (hcp) lattice, where frustration is uniquely related to the topology of the lattice and is provided by the in-plane NN antiferromagnetic interaction. We show, for the first time, that this frustration being stabilized by the out-plane NN interaction gives rise to incommensurate phases with the modulation vector lying in the basal plane. We also study the phase diagram of the system when small out-plane NNN interaction is included and show that it leads to a rich sequence of phase transitions. The used mean-field consideration is complementary to the previous cluster-approximation studies of the hcp Ising model $\sigma^\alpha$ and of the related hexagonal honeycomb-lattice Ising model $\sigma^\alpha$.

Our interest to the hcp Ising model is provided by the transition sequence in several ionic $A’A''BX_4$ compounds where the orientational ordering of $BX_4$ tetrahedra drives a series of structural phases including incommensurate states $\sigma^\alpha$. The variety of transitions can be explained on the basis of the hcp-Ising model where the orientational states of $BX_4$ tetrahedra are described by two discrete Ising variables as proposed by Kurzyński and Halawa $\sigma^\alpha$. The review of the recent studies of the two-spin Kurzyński and Halawa model is given in $\sigma^\alpha$. We demonstrate that the rigorous treatment of the model explains the experimentally observed basal-plane incommensurate phases in some $A’A''BX_4$ compounds and several other features not explored in the previous studies.

The paper is organized as follows. In Sect. 2 the structural properties of $A’A''BX_4$ family and the motivation of the hcp Ising model are considered. In Sect. 3 we treat the frustrated hcp Ising model within the mean-field approximation in order to demonstrate the appearance of basal-plane incommensurate phases. We derive the phase diagram of the system and discuss their relation with the low-temperature cluster-approximation diagram of $\sigma^\alpha$. In Sect. 4 we discuss the application of the obtained results to the experimental properties of $A’A''BX_4$ compounds at high temperatures.

Exploring the Ising model, we use the formal terminology of magnetic systems. The properties of $A’A''BX_4$ compounds are characterized by the electrostatic interaction of $BX_4$ tetrahedra. Consequently, the para-, ferro-
and antiferromagnetic terms of the Ising model correspond to the para-ferro- and antiferroelectric terms for $A''BX_4$ compounds.

**II. COMMENSURATE AND INCOMMENSURATE PHASES IN $A''BX_4$ COMPOUNDS**

The structures and transition sequences in the $A''BX_4$ family were described in detail in the review articles [13]. Shorty, the $A''BX_4$ compounds can be presented as a set of $BX_3^2$ tetrahedral anions and $A''^+$ cations that are regularly placed in the sites of a hcp structure. The $A''^+$ cations form a simple hexagonal lattice.

The order-disorder transitions in these compounds are related to the ordering of degenerate orientations of $BX_4$ tetrahedra in the $A''A''$ matrix. A possible degree of freedom is given by the vertical up/down orientation of the tetrahedron apices and another one by the planar orientation of the tetrahedra. Orientational ordering of the tetrahedra breaks the initial hexagonal symmetry $P6_3/mmc$ and leads to a sequence of structural transitions when temperature decreases. In the Kurzyński and Halawa model [13] the vertical and planar orientations are described by two coupled binary spin variables, the orientational ordering being provided by the interaction between neighboring tetrahedra. The ground states of the related two-spins Ising Hamiltonian were shown [13] to correspond to the experimentally observed variety of phases in the $A''BX_4$ compounds. There is a common hierarchy in the transition sequence of $A''BX_4$ compounds. The vertical orientational ordering occurs at higher temperatures (typically of 600 – 900K) than the planar one (below 600K).

Characteristic feature of $A''BX_4$ family is the existence of the incommensurate modulations associated with tetrahedra orientation that often appear as intermediate phases at structural transformations. They can be related either to the planar or to the vertical orientational degrees of freedom of the tetrahedra and occur in the low- and in the high-temperature regions, respectively.

The incommensurate phases of the first type have been observed in a great number of $A''BX_4$ compounds [13]. They have the modulation vector directed along the pseudo-hexagonal axis. The appearance of this kind of incommensurate phase was proposed to be related either to specific

... antisymmetric interaction of the planar orientations of tetrahedra in the unit cell [13] or to ANNNI like interaction of the tetrahedra in neighboring basal planes [13].

The incommensurate phases of the second type are the subject of the present study. The modulation wave vector associated with the vertical tetrahedra orientation has the incommensurate component directed in the basal plane of the hcp structure. This phase occurs in alkali molybdates and tungstates $K_2MoO_4$, $K_2WO_4$, $Rb_2WO_4$ in the temperature interval of 590 – 750K [21, 22]. There is no consistent explanation of this kind of incommensurate phase although several ideas were proposed in [14]. In this work we explain the appearance of the basal-plane incommensurate structure as a result of competitive interactions between the vertical orientations of neighboring tetrahedra localized in the same basal plane and in the NN basal planes, as shown in Fig. 1.

In the high-temperature region the planar orientation of the $BX_4$ tetrahedra is disordered and the corresponding planar spin variable is equal to zero. Thus, in this region, Kurzyński and Halawa model is effectively reduced to the one-spin Ising model where the vertical up/down tetrahedra orientations are described by the spin variable $S_i = \pm 1$. The following analysis will be restricted to this region.

The interaction between tetrahedra has an electrostatic nature. The uniaxial anisotropy of the hcp lattice induces dipolar moments of $BX_4$ tetrahedra parallel to the c-axis. Therefore, the interaction between the NN tetrahedra is dominated either by their induced dipolar moments or by intrinsic octupolar moments. In both cases the interaction $J_{in}$ between two NN $BX_4$ tetrahedra localized in the same basal plane favors opposite vertical orientations and therefore has antiferromagnetic nature. In contrast, the sign of the NN out-plane interaction $J_{out}$ depends on structural details of the system, like e.g. ratio $c/a$, effective charges etc.. Thus we consider both the cases of the ferro- and antiferromagnetic interaction for $J_{out}$.

The mean-field minimization of the free energy given in the next section shows that the incommensurate structure does exist in a certain region of interaction parameters $J_{in}$ and $J_{out}$. It appears, however, that the account of only NN interaction leads to a degeneracy between different phases. To remove this degeneracy, we introduce the weak out-plane interaction $J'_{out}$ between NNN tetrahedra. We show that this interaction results in structures that are found experimentally.

**III. MODEL AND RESULTS**

We use the Ising spin variable $S_i = \pm 1$ to explore the idea about frustration induced basal-plane incommensurate phases. The Hamiltonian is written as:

$$ H = \frac{1}{2} \sum_{ij} J_{ij} S_i S_j. $$

where
as shown on Fig. 1. The negative and positive sign of interaction constants correspond to ferro- and antiferromagnetic interactions. As discussed in the previous Section, we assume that $J_{in} > 0$, and that $J_{out}$ and $J_{out}'$ can take both positive and negative values. It is convenient to introduce the driving dimensionless parameters: \( \kappa = J_{out}/J_{in} \); \( \lambda = J_{out}'/J_{in} \); the last one being assumed to be smaller than one.

Note the following properties of the Hamiltonian \( \mathbb{H} \) that will be used later:

(i) When the ground state for some interaction parameters \( \kappa, \lambda \) is known, the ground state for \( -\kappa, -\lambda \) is easily obtained by inversion of signs of the spins in alternated planes.

(ii) The three-dimensional hcp Ising model can be mapped onto a two-dimensional honeycomb hexagonal lattice Ising model with NN, NNN, and NNNN interactions \[23\].

The ground state of the system is found by the minimization of the free energy:

\[
F = -kT \ln \text{Tr} \exp(-H/kT). \quad (3)
\]

At \( T = 0 \) the problem reduces to minimization of the Ising energy \( \langle 1/2 \rangle \sum J_{ij}S_iS_j \) over all the possible spin configurations. The effective procedure for solve this problem was developed in \[10\]. Using the mapping honeycomb \( \rightarrow \) hcp lattice and adopting the results of \[10\] to our variables, we find that six phases: I, II, III, V, XII and XIII (in notations of \[10\] ) whose structures are shown in Fig. 3, occur at \( T = 0 \). Their energies per one spin are:

\[
\begin{align*}
E_I &= J_{in}(3+3\kappa+3\lambda) \\
E_{II} &= J_{in}(3-3\kappa-3\lambda) \\
E_{III} &= J_{in}(-1+\kappa-3\lambda) \\
E_{V} &= J_{in}(-1+\kappa-3\lambda) \\
E_{XII} &= J_{in}(-1+\kappa+\lambda) \\
E_{XIII} &= J_{in}(-1-\kappa+\lambda).
\end{align*}
\quad (4)
\]

The coexistence lines of these phases (shown in the Fig. 2 by the dots) are defined by the equilibrium of their energies. An important observation given in \[14\] is that the infinite number of other degenerate ground states exists along these lines. These states become stable at finite temperature due to the entropy factor. The finite-temperature cluster-approximation study shows that the phase sequence can be quite complex (see \[14\] and Refs. therein).

The low-temperature approach is useful when the values of the spins are assumed to take a fixed value of either +1 or -1. Close to \( T_c \), the fluctuations of spins are important and the absolute value of the average \( \sigma_i = <S_i> \) can be substantially smaller than 1. To consider this regime, we minimize the free energy \[3\] within the mean-field approximation, the variables \( \sigma_i \) being considered as variational parameters of the model. The standard mean-field treatment \[24\] gives the following expression for the free energy:

\[
F = \frac{1}{2} \sum_{ij} J_{ij}\sigma_i\sigma_j + kT \sum_i \int_0^{\sigma_i} \tanh^{-1} s \, ds. \quad (5)
\]

In the vicinity of the transition, the absolute values of \( \sigma_i \) are much smaller than 1. Expanding \[5\] in Taylor series we obtain the Ising-like expression with additional nonlinear terms \( \sigma_i^4 \):

\[
F = \frac{kT}{2} \sum_i \sigma_i^2 + \frac{1}{2} \sum_{ij} J_{ij}\sigma_i\sigma_j + \frac{kT}{12} \sum_i \sigma_i^4. \quad (6)
\]

Note that, unlike to the discrete Ising spins \( S_i = \pm 1 \), the variables \( \sigma_i \) sweep the continuous spectrum between +1 and -1. Expression \[6\] with arbitrary coefficients is frequently used as a starting phenomenological functional for considering of incommensurate phases in systems with competing interactions \[13\]. We use this expression as a basic functional that provides the phase diagram of the system. The critical temperature of the transition is given by the highest value of \( T \) where the functional \[6\] firstly becomes unstable with respect to formation of the pattern of non-zero \( \sigma_i \).

Let us calculate the critical temperature and the phase diagram below the transition as a function of the interaction parameters \( \kappa, \lambda \). It is convenient to work with the Fourier transformed variables \( \sigma_q = \sum_i \sigma_i \exp(\text{i}q r_i) \). Fourier decomposition of \( \mathbb{H} \) gives the following energy per one spin:

\[
f = \frac{1}{2} \sum_q [kT + 2J(q)\sigma_q\sigma_{-q} + \frac{kT}{4} \sum\sigma_q\sigma_{-q}]^2 + \frac{kT}{4} \sum_{q \neq q'} \sigma_q\sigma_{-q}\sigma_{q'}\sigma_{-q'}.
\quad (7)
\]

where

\[
J(q) = J_{in} \cdot [\varepsilon'(n_i - n_j) + \kappa \varepsilon(n_i) \cos q_z + \lambda \varepsilon(2n_i) \cos q_z],
\]

and

\[
\varepsilon(n_i) = \cos qn_1 + \cos qn_2 + \cos qn_3,
\]

\[
\varepsilon'(n_i - n_j) = \cos q(n_1 - n_2) + \cos q(n_2 - n_3) + \cos q(n_3 - n_1).
\]

We take \( n_1 = (0, b/3, 0), n_2 = (a/2, -b/6, 0), n_3 = (-a/2, -b/6, 0) \) as shown in Fig. 1.

An important assumption was made that expression \[7\] contains no umklapp terms provided by commensurate modulation of the lock-in phases. Actually, the only phases that give this contribution are these with modulation vector \( q = (0, 0, 0), (0, 0, 2\pi/c), (0, 2\pi/b, 0), (0, 2\pi/b, 2\pi/c) \). Their spin configuration \( \sigma_j \) corresponds to the states I, II, III and V of Fig. 3 with equal in-site
amplitudes $σ|σ_j|$. Free energy of these states will be calculated in a more direct way later.

The finite-$q$ incommensurate structure becomes stable when the coefficient $kT + 2J(q)$ is negative. Softening of $kT + 2J(q)$ occurs simultaneously in several symmetry equivalent points of the $q$-space. The resulting state is provided by the superposition of the corresponding degenerate plane waves that can give either a $1q$ stripe phase, or a multi-$q$, double-periodic phase. Later we will show that the $1q$-phase is more preferable. The modulation amplitude $σ_q$ is a complex value satisfying $σ_q = σ^* q$. Since the functional (11) does not lock its phase we consider $σ_q$ to be real.

The transition temperature and the modulation vector are defined by $kT_{inc} = -\min(\sigma) 2J(q)$. We found that the $q_c$ component of the modulation vector $q$ is always commensurate with the reciprocal lattice vector $c^* = 2\pi/c$ and takes the values of either 0 or $2\pi/c$. The incommensurate modulation appears in the basal plane along of either the $a$ or $b$ symmetry directions. Four incommensurate phases $(q_a, 0, 0)$, $(q_a, 0, 2\pi/c)$, $(0, q_b, 0)$ and $(0, q_b, 2\pi/c)$ are possible.

The critical temperatures for the phases $(q_a, 0, 0)$ and $(q_a, 0, 2\pi/c)$ are given by

$$kT_{a}^{\pm}/J_{inc} = \frac{(κ - 2\lambda)^2}{1 \pm 2\lambda} + 3,$$

where the upper sign corresponds to $q_c = 0$ and the lower one to $q_c = 2\pi/c$. The modulation vector

$$q_a = \frac{2}{a} \arccos\left(\frac{1 \pm κ}{2 \pm 4λ}\right)$$

changes from $q_a = 0$ (lock-in phases I or II) to $q_a = 2\pi/a$ (lock-in phases V or III).

The critical temperatures for the phases $(0, q_b, 0)$ and $(0, q_b, 2\pi/c)$ are given by

$$kT_{b}^{\pm}/J_{inc} = -4(4λx^4 + 4x^3 + (κ - 2\lambda)x^2 + 4(κ - 3)x \mp (κ + λ) + 1)$$

$$+ 8(κ - 3)^2 - 8λ(κ + 3)^{1/2})/8λ,$$

where $x = ±((−3 ± 2λ) + [(−3 ± 2λ)^2 - 8λ(κ + 3)]^{1/2})/8λ$.

The modulation vector

$$q_b = \frac{2}{b} \arccos x$$

changes from $q_b = 0$ (lock-in phases I or II) to $q_b = 2\pi/b$ (lock-in phases V or III).

The incommensurate phases can exist only in that region of parameters $κ$ and $λ$ when the arguments of $\arccos$ in (12) and in (10) are between $+1$ and $−1$.

Depending on the interaction parameters $κ$ and $λ$, all four incommensurate phases can be stable. To find the regions of their stability one should compare $T_{inc} = T_{a,b}^{\pm}$ with the critical temperatures of the lock-in phases I, II, III, V, XII and XIII. The later is found directly from (8) since the necessary summation $\sum J_{ij}σ_iσ_j$ was already performed when calculating (8). For the free energy of the lock-in phases we obtain

$$f_{com} = \frac{1}{2}(kT + 2E_{com})σ^2 + \frac{kT}{12}σ^4,$$

where $E_{com}$ is the energy (8) of corresponding commensurate phase at $T = 0$. The critical temperatures of transitions are given by

$$kT_{com} = −2E_{com}.$$

After calculation of the maximal critical temperature from $T_{a,b}^{\pm}$ and $T_{com}$, we obtain the resulting phase diagram as shown in Fig. 2 by solid lines. The symmetry of the diagram with respect to change of sign of the both interaction parameters $κ$ and $λ$ follows from the property (i) of the Hamiltonian (8).

To follow the evolution of this diagram when temperature decreases one should solve the infinite system of the coupled nonlinear variational equations obtained from the mean-field functional (8). The rigorous solution of this problem is beyond the scope of our study. However, qualitative aspects obtained in a more simple way are discussed below.

Note, first, that the stripe region of incommensurate phases in Fig. 2 appears at the same place where the infinite degenerate lines of phase transitions are predicted by the cluster calculations at $T = 0$ (doted lines). This indicates, similarly to the ANNNI model (14), the devil’s staircase behavior of the transition sequence below $T_{inc}$. An infinite number of lock-in phases, where the wave vector jumps between different rational multiples of the reciprocal lattice periods, appear at low temperatures. Their phase boundaries converge to the doted lines at $T = 0$. Phases XII and XIII that are stable at low temperatures can appear from paramagnetic state only via intermediate incommensurate phases. The evolution of the incommensurate phases when temperature decreases is shown qualitatively in Fig. 4 for $J_{out} = 0$. The analogous phase diagram obtained in (13), when the possibility of incommensurate phase was not considered, is shown in the same Figure by the dashed lines.

The phase diagram of Fig. 4 is obtained within the approximation when the nonlinearity of the functional is modeled by the quartic terms of the Taylor expansion (8) and when the harmonic plane-wave approximation for the modulation is used. The incommensurate phase is described by a superposition of $n$ harmonic plane waves with temperature independent modulation wave vector, corresponding to the symmetry equivalent points in the $q$-space and with equal real amplitudes $σ_q$. Either stripe phase with $n = 1$ or double-modulated phases with $n = 2$ or $3$ are possible; in the $3q$-case, $q_1, q_2$ and $q_3$ form an equilateral $120^\circ$ star. The harmonic approximation
is as exact as $T$ is closer to $T_{inc}$. Variation of $q$ and contribution of higher harmonics at $T < T_{inc}$ is expected to be small and leads to shift of the phase boundaries of the commensurate low temperature phases towards the lower temperature like it happens in the ANNNI model.

Under these approximations the energy of the incommensurate state (13) is written as:

$$f_{inc} = nk(T - T_{inc})\sigma_q^2 + \frac{n}{2}kT\sigma_q^4 + n(n-1)kT\sigma_q^4. \quad (15)$$

or, after minimization over $\sigma_q$ as:

$$f_{inc} = -\frac{1}{2\pi} \left[ \frac{3}{4}\frac{k}{T}T_{inc}^2 \right] (T - T_{com})^2, \quad (16)$$

Note that (14) is minimal when $n = 1$, i.e., $q$ is the most stable incommensurate phase. Comparison of (14) at $n = 1$ with the energy of corresponding commensurate phase obtained from (13), by minimization over $\sigma$

$$f_{com} = -\frac{3}{4}\frac{k}{T}(T - T_{com})^2, \quad (17)$$

gives the phase sequence below $T_{inc}$. When temperature decreases, the incommensurate phase is stable up to the temperature

$$T_c = T_{inc} - (3 + \sqrt{6})(T_{inc} - T_{com}), \quad (18)$$

defined by the condition $f_{inc} = f_{com}$. Below $T_c$ a first order transition occurs to one of the commensurate phases I, II, III, V, XII, or XIII. The region of $|\sigma| \ll 1$ where the above approximations are valid is placed above the dotted line on Fig. 4. Below this line one can get only qualitative ideas about the behavior of the transition boundaries.

### IV. APPLICATION TO $A'\, A''\, BX_4$ COMPOUNDS

We use now the results of the hcp Ising model with competing interaction to study the high-temperature phase transitions in the $A'\, A''\, BX_4$ compounds provided by the vertical orientation of the apexes of the $BX_4$ tetrahedra. The calculated mean-field phase diagram (Fig. 2) reveals various incommensurate and lock-in phases that appear just below the transition and at lower temperatures. Some of the commensurate phases (I, II, III and V) were discovered by Kurzyński and Halawa [13]. The occurring commensurate phases, their correspondence with notation of [13], their lock-in wave vectors and corresponding symmetry groups are enumerated in Table I.

Our calculations reveal the following new features of the phase diagram. The $aq$ basal-plane incommensurate phases directed either in the $a$ or $b$ crystallographic direction appear in the model. The direct first order transition between phases I and V and between phases II and III is possible when NNN interaction is included. The new phases XII and XIII can occur at low temperatures.

Table II presents the high-temperature transition sequences for several typical $A'A''\, BX_4$ compounds and their correlation with the ratio $c/a$. (The data were collected on the basis of [14,25,26].) Only few compounds reveal the high-symmetry parent phase $P6_3/mmc$ associated with dynamically disordered $BX_4$ tetrahedra. One can imagine that in the other compounds the phase $P6_3/mmc$ is virtually present above the melting point.

According to their high-temperature transition sequence and to their ratio $c/a$ the $A'A''\, BX_4$ compounds can be classified in a following way (see also [14]):

(i) Located in the middle part of the Table II the non underline compounds with the direct transition (real or virtual) from the phase $P6_3/mmc$ to $Pmcn$ (phase V). Only a few compounds of this numerous group are given; for other examples see: [14,25,26]. Notably, for all the compounds of this group the ratio $c/a$ varies from 1.27 to 1.64.

(ii) Located in the middle part of the Table II the underline compounds where the phase $P3\_m1$ (phase II) occurs. Two of them, $Cs_2SO_4$ and $Rb_2SO_4$ demonstrate the reconstructive transition $Pmcn - P3\_m1$. Compounds of this group have the similar ratio $c/a$ as compounds of (i).

(iii) Located in the upper part of Table II the alkali molybdates and tungstates $K_2MoO_4$, $K_2WO_4$, $Rb_2WO_4$ [20–22] that have the intermediate incommensurate phase modulated along crystallographical direction $b$. The actual transition sequence there is: $Pmcn \rightarrow (0, q_b, 2\pi/c) - P6_3/mmc$. To our knowledge, there are no compounds with $a$-directed incommensurate phase, although this phase already appears in the NN approximation. This group has the smallest ratios $c/a \simeq 1.23 - 1.25$. The other compounds of this group, $K_2ZnCl_4$, $K_2CoCl_4$, $K_2CoBr_4$, have similar ratio $c/a$ but the high-temperature phase $P6_3/mmc$ was not reported. They can be candidates for the basal-plane incommensurate phase if the melting does not precede the $Pmcn - Inc - P6_3/mmc$ transition.

(iv) Located in the lower part of Table II compounds that demonstrate the phase $P6_3$ that is a subgroup of $P6_3/mmc$ (phase I). Several $A'\, A''\, Be\, F_4$ compounds and $KLi\, MoO_4$, with virtual $P6_3 - P6_3/mmc$ transition belong to this group. Two other compounds, $KLi\, SO_4$ and $RbLi\, CrO_4$, have the sequence $P6_3 - Pmcn - P6_3/mmc$ [22–24]. These are particular systems since the complete vertical ordering of the tetrahedra occurs only in the room-temperature hexagonal phase $P6_3$. The orthorhombic phase $Pmcn$ is characterized by a partial vertical disorder of tetrahedra. These compounds reveal the reconstructive transition I-V. They can probably be considered as an intermediate case between classes (i) and (iii). Compounds of the group (iii) have the largest ratios $c/a \simeq 1.64 - 1.70.$
Following Kurzyński and Halawa \[13\], we assume that sign and magnitude of $J_{\text{out}}$ (and therefore of $\kappa$) depend critically on the ratio $c/a$. The interactions $J_{\text{in}}$ and $J_{\text{out}}$ are less sensible to variation of $c/a$. Compounds of the groups (i), (iii), (iii) reproduce the phase diagram of Fig. 2 if one supposes that $\lambda < -0.5$ and that $J_{\text{out}}$ changes its sign from negative (ferromagnetic) to positive (antiferromagnetic) when hcp lattice goes from its expanded along $c$-axis form with $c/a > 1.63$ to the contracted form with $c/a < 1.63$. It is interesting to observe that the dipolar-dipolar interaction between two NN out-plane $BX_4$ tetrahedra changes its sign exactly at $c/a = 1.63$. The value of the modulation vector $q_6$ in molybdates and tungstates is correlated with the ratio $c/a$ in the following way: the smaller the ratio $c/a$ the more $q_6$ deviates from the lock-in value $2\pi/b$ of the phase $Pmcn$ \[12\]. Compounds of the group (ii) seem to have a positive $\lambda$ and are placed in the upper right corner of the diagram.

It would be interesting to study the evolution of the phase sequences in $A' A'' BX_4$ compounds with a continuous variation of the interaction parameters. One can achieve this, e.g., by the application of uniaxial pressure along the hexagonal axes that slightly changes the ratio $c/a$. In particular, one can expect to obtain the commensurate - incommensurate transition, $\omega$-directed incommensurate phases and the phase XII with symmetry $Pbca$ (or their subgroups). The classical compound $K_2SeO_4$ from the group (i), having the smallest ratio $c/a = 1.27$ could be a good candidate to achieve a tricritical Lifshitz point and a basal-plane incommensurate phase when submitted to an uniaxial pressure.

Another interesting result could be obtained by the application of an electrical field $E$ along the hexagonal axis that breaks the mirror-basal-plane symmetry $S_i \rightarrow -S_i$ in the Hamiltonian $\[1\]$. This results in the additional invariants $E \sum_i \sigma_i$ and $E \sum_i \sigma_i^3$ in the functional $\[3\]$. The first one slightly favors the ferroelectric phase I. The second one gives the additional third order term $E \sum_i \sigma_i \sigma_j \sigma_k$ in $\[3\]$ where the vectors $q_1, q_2, q_3$ form the equilateral triangle (calculations are analogous to those in $\[3\]$). This would lead to the splitting of the transition $(0, q_6, 2\pi/c) \rightarrow P6_3/mmc$ onto two transitions, with intervention of the 3$q$ modulated incommensurate phase.

In our consideration an interaction with elastic degrees of freedom that is known to be important in ferroelectrics has been neglected. We expect that this coupling breaks the discontinuity of the transition from $P6_3/mmc$ to the low temperature phase as it was observed in several $A' A'' BX_4$ compounds. The corresponding analysis is currently in progress.

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* E-mail: lukyanc@itp.ac.ru.
** Present address: Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. E-mail: mpimenta@fisica.ufmg.br.
TABLE I. The lock-in wave vectors \((q_a, q_b, q_c)\) and space symmetry groups of the commensurate phases appearing in the hcp-Ising model (see also Fig. 3). The correspondence between the notation of Ref.\(^a\) used also in this paper and the notations used in Ref.\(^b\) is given.

| Notations of \(^a\) | Notations of \(^b\) | Lock-in vector \((q_a, q_b, q_c)\) | Symmetry group |
|---------------------|---------------------|-------------------------------|---------------|
| \(I\)               | \(PP\)             | \((0, 0, 0)\)                 | \(P6_{3}mc\)  |
| \(II\)              | \(AP\)             | \((0, 2\pi/c)\)               | \(P3m1\)      |
| \(III\)             | \(CP\)             | \((0, 2\pi/b, 0)\)            | \(Pmmm\)      |
| \(V\)               | \(BP\)             | \((0, 2\pi/b, 2\pi/c)\)       | \(Pcma\)      |
| \(XII\)             | -                   | \((\pi/a, 0, 0)\)             | \(Pbca\)      |
| \(XIII\)            | -                   | \((\pi/a, 0, 2\pi/c)\)        | \(Pbna\)      |

\(^a\) T. Kudo and S. Katsura, Prog. Theor. Phys., 56, 435 (1976).
\(^b\) M. Kurzyński and M. Halawa, Phys. Rev., B34, 4846 (1986).
TABLE II. The ratio \(c/a\) and the high-temperature sequences of transitions for several \(A^\prime A^\prime B X_4\) compounds. Question mark signifies that either the information about the transitions at higher-temperature is not available or the melting occurs. The basal-plane incommensurate phase \(Inc\) has the modulation vector \((0, q_b, 2\pi/c)\).

| \(c/a^a\) | Transition sequence |
|------------|---------------------|
| \(K_2ZnCl_4\) | 1.23 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(K_2WO_4\) | 1.24 | \(\ldots \rightarrow Pmcn \rightarrow Inc \rightarrow P6_3/mmc\) |
| \(K_2CoCl_4\) | 1.24 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(K_2CoBr_4\) | 1.24 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(K_2MoO_4\) | 1.24 | \(\ldots \rightarrow Pmcn \rightarrow Inc \rightarrow P6_3/mmc\) |
| \(Rb_2WO_4\) | 1.25 | \(\ldots \rightarrow Pmcn \rightarrow Inc \rightarrow P6_3/mmc\) |
| \(K_2SeO_4\) | 1.27 | \(\ldots \rightarrow Pmcn \rightarrow P6_3/mmc\) |
| \(Rb_2MoO_4\) | 1.27 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(KNaSO_4\) | 1.29 | \(\ldots \rightarrow P\overline{3}m1 \ldots\) |
| \(Cs_2WO_4\) | 1.29 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(Rb_2SeO_4\) | 1.29 | \(\ldots \rightarrow Pmcn \rightarrow P6_3/mmc\) |
| \(K_2SO_4\) | 1.30 | \(\ldots \rightarrow Pmcn \rightarrow P6_3/mmc\) |
| \(Cs_2MoO_4\) | 1.30 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(K_2CrO_4\) | 1.30 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(K_2MnO_4\) | 1.30 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(NaLiBeF_4\) | 1.34 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(Cs_2SO_4\) | 1.37 | \(\ldots \rightarrow Pmcn \rightarrow P\overline{3}m1 \ldots\) |
| \(Rb_2SO_4\) | 1.39 | \(\ldots \rightarrow Pmcn \rightarrow P\overline{3}m1 \ldots\) |
| \(CsLiBeF_4\) | 1.62 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(CsLiSO_4\) | 1.62 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(RbLiSO_4\) | 1.64 | \(\ldots \rightarrow Pmcn \ldots\) |
| \(KIbeF_4\) | 1.64 | \(\ldots \rightarrow P6_3 \ldots\) |
| \(KLiWO_4\) | 1.65 | \(\ldots \rightarrow P6_3 \rightarrow \text{Cubic}\) |
| \(KLiMoO_4\) | 1.67 | \(\ldots \rightarrow P6_3 \rightarrow \text{Cubic}\) |
| \(TLiBeF_3\) | 1.68 | \(\ldots \rightarrow P6_3 \ldots\) |
| \(KLiSO_4\) | 1.69 | \(\ldots \rightarrow P6_3 \rightarrow Pmcn \rightarrow P6_3/mmc\) |
| \(RbLiBeF_3\) | 1.69 | \(\ldots \rightarrow P6_3 \ldots\) |
| \(RbLiCrO_4\) | 1.70 | \(\ldots \rightarrow P6_3 \rightarrow Pmcn \rightarrow P6_3/mmc\) |

\(^a\) Since the ratio \(c/a\) for different compounds is given at different temperatures the error bars are estimated as \(\pm 0.02\) as the typical variation of thermal expansion. For compounds having an orthorhombic \(Pmcn\) symmetry this ratio was estimated as \(c/(ab/\sqrt{3})^{1/2}\).
FIG. 3. Spin patterns of the commensurate phases that appear in the hcp Ising model. Large and small circles correspond to the spin sites in alternating planes of hcp structure. The corresponding lock-in vectors are given in Table I.

FIG. 4. Phase diagram of hcp Ising model as function of the NN interaction parameter $\kappa = J_{\text{out}} / J_{\text{in}}$ and the reduced temperature $kT / J_{\text{in}}$, when the NNN interaction $J_{\text{out}}^{\prime} = 0$. The transition from the paramagnetic (P) state to the commensurate phase (roman numbers) occurs either directly or via intermediate incommensurate phases ($q_a, q_b, 0$), ($q_a, 0, c^*$). Dashed lines correspond to the Kurzyński and Halawa (Phys. Rev. B34, 4346 (1986)) phase diagram. $\sigma^4$ expansion of the free energy used for the construction of this diagram is applicable above the dotted line.