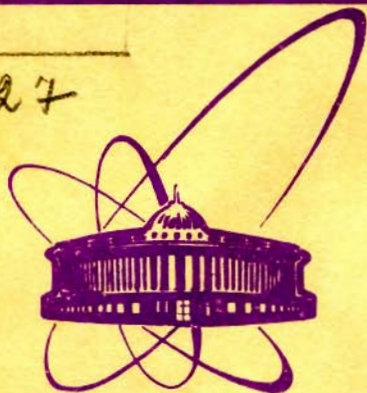


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Фазовые переходы в соединениях $[M(NH_3)_6](XY_4)_2$

Проведен теоретико-групповой анализ фазовых переходов в ионных кристаллах $[Ni(NH_3)_6](ClO_4)_2$, $[Mg(NH_3)_6](ClO_4)_2$ и $[Ni(NH_3)_6](BF_4)_2$ сопровождаемых изменением пространственной группы $Fm\bar{3}m$ на $P2_1/b$. Показано, что снижение симметрии связано с двухмерным неприводимым представлением τ^{10} звезды $\{k_{10}\}$, которая соответствует точке X зоны Бриллюэна на решетке г.ц.к. Анализ решеточных нормальных мод в фазе $Fm\bar{3}m$ позволил определить структурные изменения, происходящие в точке фазового перехода. Моноклинная кристаллическая структура с пространственной группой $P2_1/b$ возникает вследствие трансляционных перемещений всех ионов в плоскости, параллельной единой плоскости симметрии. Относительная ориентация анионов становится также определенной.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Parlinski K.

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Phase Transitions in $[M(NH_3)_6](XY_4)_2$ Compounds

The group-theoretical analysis of the phase transitions in the ionic crystals $[Ni(NH_3)_6](ClO_4)_2$, $[Mg(NH_3)_6](ClO_4)_2$ and $[Ni(NH_3)_6](BF_4)_2$ accompanied by the lowering of the space groups from $Fm\bar{3}m$ to $P2_1/b$ has been carried out. It has been shown that the symmetry reduction is associated with the two-dimensional irreducible representation τ^{10} of the star $\{k_{10}\}$, which corresponds to the point X of the fcc Brillouin zone. The analysis of the lattice normal modes in $Fm\bar{3}m$ phase allowed one to specify the structural changes created at the phase transition point. The monoclinic crystal structure with the space group $P2_1/b$ may arise as a result of translational displacements of all ions in the plane parallel to the unique symmetry plane. The relative orientations of anions become also fixed.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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1. INTRODUCTION

There has been considerable interest recently in the phase transitions which occur in the hexammine complexes. Particular attention has been paid to the nickel hexammine perchloride $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2(\text{NHP})$, magnesium hexammine perchloride $[\text{Mg}(\text{NH}_3)_6](\text{ClO}_4)_2(\text{MHP})$ and nickel hexammine tetrafluoroborate $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2(\text{NHT})$. In the high temperature phase these compounds have the space group $\text{Fm}\bar{3}\text{m}$ and crystallize in fcc lattice with hexammine octahedrals ions at the corners (000) of the primitive unit cell and perchloride or tetrafluoroborate ions at $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$ positions.

Each hexammine group consists of a central nickel or magnesium ion surrounded by six octahedrally arranged ammonia groups. The anions ClO_4^- and BF_4^- have a structure of regular tetrahedrons.

The adiabatic calorimetry measurements made in the region of temperature from 100 to 300K revealed in these compounds two anomalies of heat capacity^{1,3/}. The X-ray diffraction studies confirmed the existence of the two anomalies and suggested that the space groups of the intermediate phases are monoclinic with the space group $\text{P}2_1/\text{b}(\text{C}_{2\text{h}}^5)$ and with four molecular units in the unit cell^{3,5/} (Table 1). The phase transitions from the cubic phase I to the intermediate monoclinic phase II are of the first order. The lower anomalies of the heat capacity related to the transition from phase II to phase III are much less pronounced and the diffraction patterns are essentially the same as those of the intermediate phase except one additional diffraction peak which might be indexed in the frame of the same $\text{P}2_1/\text{b}$ space group^{3,5/}.

Extensive studies of the Raman and infrared spectra^{6-8/}, and quasielastic neutron scattering^{8,9/} have been carried out also. The infrared absorption spectra of NHP and NHT below 400 cm^{-1} are not sensitive to both phase

Table 1
Phases and structures of $[M(NH_3)_6](XY_4)_2$ Compounds

	NHP	MHP	NHB
Phase I, cubic $Fm\bar{3}m$, $Z=1$			
a [Å]	11.41	11.55	11.22
T_{I-II} [K]	173	154.35	140.1
Phase II, monoclinic $P2_1/b$, $Z=4$			
$a_0 = b_0$ [Å]	11.23	11.38	11.02
c_0 [Å]	11.72	11.89	11.45
γ	94.07°	93.6°	94.9°
T_{II-III} [K]	143	139.5	115

transitions^{7/}. This concerns also the infrared active lattice mode T_{1u} which involves a combined translational motion of cations and anions. The Raman spectra of NHP and MHP give evidence for broadening of the internal modes E (463 cm^{-1}) and T_2 (625 cm^{-1}) of ClO_4^- ions in the cubic phase I^{6,8/}. In phase II the mode E narrows, and the mode T_2 splits into two asymmetric peaks. No splitting of internal modes of the hexammine octahedrals has been observed.

Large amount of work has been done to relate the observed stochastic motion of ammonia groups with the phase transitions from phase I to phase II. The quasielastic neutron measurements and Raman^{6/} and infrared experiments^{7/} show undoubtedly no influence of these phase transitions on the stochastic motion of the ammonia groups.

In this paper we carry out a group-theoretical analysis for NHP, MHP and NHT in order to elucidate the mechanism of the phase transitions from phase I to phase II. Thus, in the next section we discuss the possible space groups of the low symmetry phase II. Then, the analysis of the normal modes of the high symmetry phase is made. Special attention is paid to the mode which becomes active in the phase transition. The group-theoretical predictions then allow one to give the general structure of the monoclinic phase II. Final remarks close the paper.

2. MONOCLINIC SPACE SUBGROUPS OF $Fm\bar{3}m$

According to the diffraction pattern the unit cell of the monoclinic phase of the considered hexammine complexes is four times as large as that of the cubic one. Following^{10/} such an enlargement is permitted for the order parameter characterized by the wave vector at the point

$X(0, 0, 2\pi/a)$, $L(\pi/a, \pi/a, \pi/a)$ and $W(\pi/a, 2\pi/a, 0)$ of the fcc Brillouin zone. The points L and W lead to the one-face- and body-centered Bravais unit cell, respectively, and since the expected Bravais unit cell of the hexamine complexes is simple monoclinic, they can be excluded from further considerations. Hence the phase transition should occur at the point X of the fcc Brillouin zone.

The star of the wave vector designed by $\{k_{10}\}$ in Kovalev's^{11/} classification and corresponding to the point X^{12/} consists of three arms $(0,0,2\pi/a)$, $(0,2\pi/a,0)$, $(2\pi/a,0,0)$. The little group $G(k_{10})$ of the wave vector k_{10} is the D_{4h} point group. There exist ten irreducible multiplier representations of $G(k_{10})$, eight of which, τ^1 - τ^8 , are one-dimensional and two, τ^9 and τ^{10} , are two-dimensional^{11/}.

The techniques for the derivation of the lower-symmetry space group are well-known^{13,14/} and involve finding a space subgroup for which the density function

$\rho(r) = \rho_0(r) + \sum_{i=1}^{\ell} c_i \phi_i$ is invariant. $\rho_0(r)$ is the density function of the higher symmetry phase $Fm\bar{3}m$ and ϕ_i ($i=1,2,\dots,\ell$) are the bases for the irreducible representation, and ℓ is the dimension of the irreducible representation of the space group to the star $\{k_{10}\}$ and the multiplier irreducible representation τ^j . Three arms of the star $\{k_{10}\}$ make the number of the bases $\ell=3$, or $\ell=6$ for one- and two-dimensional representations, respectively. If all coefficients c_i vanish, the density function $\rho(r)$ describes the higher-symmetry phase. Any appearance of non-zero value of c_i lowers the symmetry of the phase group manifesting the phase transition. To characterize the phase transition caused by τ^9 or τ^{10} at $\{k_{10}\}$, one should specify six coefficients c_1, c_2, \dots, c_6 . Then c_1, c_2 describe the contribution of the doubly degenerate mode propagating along $k_{10}^{(z)} = (0,0,2\pi/a)$. Likewise, c_3, c_4 and c_5, c_6 correspond to modes propagating along $k_{10}^{(y)}$ and $k_{10}^{(x)}$, respectively.

Table 2 gives a list of all monoclinic space groups which result from the reduction of symmetry of the space group $Fm\bar{3}m$ and are connected with the multiplier irreducible representations τ^9 and τ^{10} of the star $\{k_{10}\}$. The relations which have to be obeyed by the components of the order parameter and the elements of the factor group of the resulting lower-symmetry space group are also quoted. The fractional translations present in the symmetry elements are written in terms of the basic vectors a of the cubic conventional unit cell to which the basic vectors of the monoclinic pseudocubic unit cell are related as follows

Table 2

List of all symmetry reductions from the space group $Fm\bar{3}m$ to the triclinic and monoclinic systems associated with the star $\{k_{10}\}$

Low sym. sp. group	Elements of low symmetry space group /Except identity/	Ir. rep. at X	Specification of c_1, c_2, \dots, c_6
P1	-	τ^{10}	-
$P\bar{1}$	$\{i 0,0,0\}$	τ^9	-
$P2_1$	$\{2_z a/2,0,a/2\}$	τ^9	$c_3=c_4, c_5=c_6$
	$\{2_z 0,a/2,a/2\}$	τ^9	$c_3=-c_4, c_5=-c_6$
	$\{2_z a/2,0,a/2\}$	τ^{10}	$c_3=c_4, c_5=c_6$
	$\{2_z 0,a/2,a/2\}$	τ^{10}	$c_3=-c_4, c_5=-c_6$
Fm	$\{\sigma_z 0,0,0\}$	τ^{10}	$c_3=-c_4, c_5=c_6$
Pb	$\{\sigma_z a/2,a/2,0\}$	τ^{10}	$c_3=c_4, c_5=-c_6$
$P2_1/m$	$\{2_z a/2,0,a/2\}, \{i a/2,0,a/2\},$ $\{\sigma_z 0,0,0\}$	τ^{10}	$c_3=c_4=0, c_5=c_6$
	$\{2_z 0,a/2,a/2\}, \{i 0,a/2,a/2\},$ $\{\sigma_z 0,0,0\}$	τ^{10}	$c_3=-c_4, c_5=c_6=0$
	$\{2_z a/2,0,a/2\}, \{i 0,a/2,a/2\},$ $\{\sigma_z a/2,a/2,0\}$	τ^{10}	$c_3=c_4, c_5=c_6=0$
$P2_1/b$	$\{2_z 0,a/2,a/2\}, \{i a/2,0,a/2\},$ $\{\sigma_z a/2,a/2,0\}$	τ^{10}	$c_3=c_4=0, c_5=-c_6$

$a_0 = (a_1, b_1, d_1, 0)$, $b_0 = (0, d_1, 0)$, $c_0 = (0, 0, c_1)$ and for cubic unit cell $a_1=b_1=c_1=d_1=a$ and, consequently, $a_0=b_0=c_0=a$. We remind that the conventional monoclinic unit cell is defined by vectors $a' = (a_1, b_1, 0)$, $b' = (0, d_1, 0)$, $c' = (0, 0, c_1)$.

The reduction of the $Fm\bar{3}m$ space symmetry group by all one-dimensional irreducible representations $\tau^1 - \tau^8$ of $\{k_{10}\}$ provides the space groups which belong to the orthorhombic, tetragonal, and cubic systems, but not to monoclinic one.

To obtain the list of possible phase transitions we proceeded as follows. First, we induced the representation of full space group $Fm\bar{3}m$ for τ^9 and τ^{10} at $\{k_{10}\}$. Next, the location of all point symmetry elements, screw axes and glide plane of the $Fm\bar{3}m$ symmorphic space group were found. Then a set of symmetry elements appropriate for a given monoclinic space group were selected. The transformation properties of the bases ϕ_i under the selected symmetry elements, defined by the six-dimensional irreducible representation of the space group $Fm\bar{3}m$, supplied the restric-

tions on c_1, c_2, \dots, c_6 . All cases listed in Table 2 are accompanied by four times enlargement of the fcc primitive unit cell. The symmetry of the $Fm\bar{3}m$ space group can be also reduced to the remaining monoclinic space groups, namely, $P2 (C_2^1)$, $B2 (C_2^3)$, $Bm (C_s^3)$, $Bb (C_s^4)$, $P2/m (C_{2h}^1)$, $B2/m (C_{2h}^3)$, $P2/b (C_{2h}^4)$ and $B2/b (C_{2h}^6)$ can be obtained by τ^9 and τ^{10} and $Pm (C_s^1)$, $Pb (C_s^2)$, $P2_1/m (C_{2h}^2)$ and $P2_1/b (C_{2h}^5)$ can be obtained by τ^9 of $\{k_{10}\}$. These groups, however, are not maximal subgroups with respect to given restrictions obeyed by c_1, c_2, \dots, c_6 . For example, the irreducible representation τ^{10} together with $c_1 = c_2 = 0, c_3 = c_4, c_5 = c_6$ leads to $P2/b$, but the same conditions give the $Pmmn (D_{2h}^{13})$ space group of the orthorhombic system containing as a subgroup $P2/b$.

Concluding, the symmetry reduction of $Fm\bar{3}m$ to a monoclinic space group with a simple Bravais lattice, having the volume four times as large as the original fcc one, is possible only with the star $\{k_{10}\}$ and two-dimensional representations, namely τ^9 , which leads to $P2_1$ and τ^{10} , which leads to $P2_1, Pm, Pb, P2_1/m$ and $P2_1/b$.

3. NORMAL MODES IN CUBIC PHASE

The structure and binding energies present in the hexammine complexes allow us to apply the rigid ion model^{15/}. Each cation $[Ni(NH_3)_6]^{++}$ or $[Mg(NH_3)_6]^{++}$ and anion group $(ClO_4)^-$ or $(BF_4)^-$ can be treated as a rigid body with three rotational and three translational degrees of freedom. The separation of the internal modes of ions from the lattice modes is an advantage of such an approach.

In the cubic phase I, with one molecular unit in the elementary cell the normal lattice modes of the hexammine are represented by eighteen phonon branches. The reducible representation Γ of lattice modes at the wave vector consists of the following irreducible representations of $m\bar{3}m$ point group $\Gamma_k = 0-2T_{1g} + T_{2g} + 2T_{1u} + T_{2u}$. The T_{2g} involves a pure translational and T_{2u} pure rotational motion of only (ClO_4) or (BF_4) ions. Two T_{1g} represent pure rotational and two T_{1u} pure translational modes involving all ions. One T_{1u} is an acoustic mode. Since the hexammine complexes are ionic the electric field splits the second T_{1u} optic infrared-active translational mode into a longitudinal singlet and a transfer doublet. The T_{2g} mode which involves solely the translational motion of anions is Raman active. None of the rotational modes, either T_{1g} or T_{2u} is Raman or infrared active.

The point X at the boundary of the fcc Brillouin zone is of special interest for hexamines. A mode which freezes at the X point is expected to be responsible for the structural changes caused by the phase transition. The reducible representation of the modes at the point X can be expanded into the irreducible representations of the little group $G(k_{10})^{11/}$, then $\Gamma_X = \tau^1 + \tau^2 + \tau^3 + \tau^4 + \tau^5 + \tau^6 + 3\tau^9 + 3\tau^{10}$. Three one-dimensional modes correspond to a pure translational motion in [001] direction of either cations (τ^4) or anions (τ^1 and τ^6). Three others specify a pure longitudinal rotational motion in [001] direction (the axis of rotation lies along [001]) of either cations (τ^3) or anions (τ^2 and τ^5). By means of the projection operator^{14/} the eigenvector of phonons can be easily established. Figure 1 shows a cubic unit cells together with the displacement vectors which form longitudinal phonons specified by the wave vector $k_{10}^{(z)}$ and propagating along [001] direction.

The two-dimensional irreducible representations τ^9 and τ^{10} describe the transverse phonons. Let us denote the general eigenvector for the wave vector $k_{10}^{(z)}$ and irreducible representation τ^j by

$$e_i^{(j)} = (u_x^{(1)}, u_y^{(1)}, u_z^{(1)}; u_x^{(2)}, u_y^{(2)}, u_z^{(2)}; u_x^{(3)}, u_y^{(3)}, u_z^{(3)}; \\ \omega_x^{(1)}, \omega_y^{(1)}, \omega_z^{(1)}; \omega_x^{(2)}, \omega_y^{(2)}, \omega_z^{(2)}; \\ \omega_x^{(3)}, \omega_y^{(3)}, \omega_z^{(3)}),$$

where $i = 1, 2, \dots, 6$ for $j = 9$ and 10 , and $u_x^{(\kappa)}, u_y^{(\kappa)}, u_z^{(\kappa)}$ are the Cartesian components of translational displacements of ion and $\omega_x^{(\kappa)}, \omega_y^{(\kappa)}, \omega_z^{(\kappa)}$ are the Cartesian components of the axial vector which describes the rotation of ion κ . We label the cation at $(0,0,0)$ by $\kappa=1$ and the anions by $\kappa=2$ $(1/4, 1/4, 1/4)$ and $\kappa=3$ $(3/4, 3/4, 3/4)$. Applying the projection-operator technique, we found for τ^9

$$e_1^{(9)} = (0, 0, 0; p, -p, 0; -p, p, 0; q, q, 0; s, s, 0; s, s, 0),$$

$$e_2^{(9)} = (0, 0, 0; -p, -p, 0; p, p, 0; q, -q, 0; q, -q, 0; -s, s, 0; -s, s, 0)$$

and for τ^{10}

$$e_1^{(10)} = (a, a, 0; b, b, 0; b, b, 0; 0, 0, 0; d, -d, 0; -d, d, 0),$$

$$e_2^{(10)} = (a, -a, 0; -b, b, 0; -b, b, 0; 0, 0, 0; -d, -d, 0; d, d, 0).$$

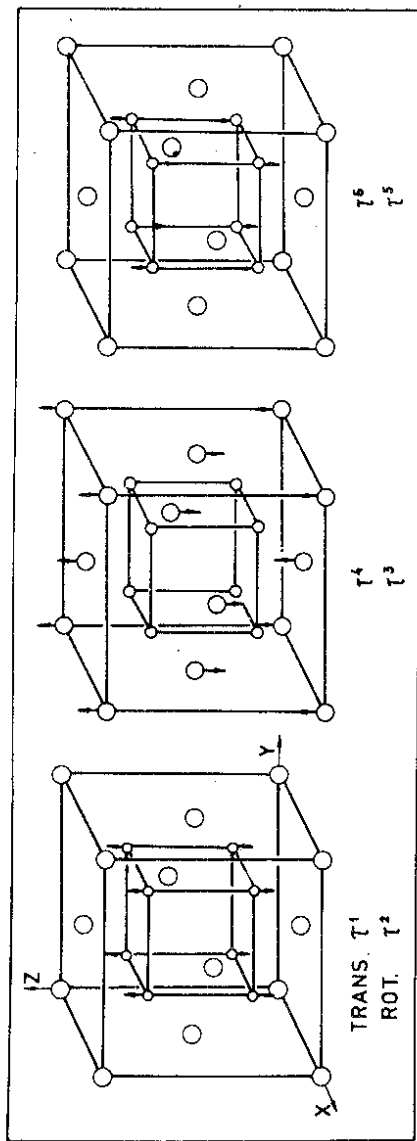


Fig. 1. The displacement vectors of the normal modes at the point X $(0, 0, 2\pi/a)$ of the fcc Brillouin zone. For the irreducible representations τ^1, τ^4 and τ^6 the vectors represent translational ion displacements, for τ^2, τ^3 and τ^5 the same vectors denote axial rotation of ions.

Two eigenvectors $e_1^{(j)}$ and $e_2^{(j)}$ correspond to a doubly degenerate transverse mode propagating along $[001]$ direction. They are orthogonal to each other. The normalization condition requires $4p^2 + 2q^2 + 4s^2 = 1$ and $2a^2 + 4b^2 + 4d^2 = 1$. On the basis of symmetry alone, it is not possible to find out the value of two remaining parameters for each pair of eigenvectors. Therefore, the translational and rotational displacement vectors involved in three modes of the same symmetry τ^9 or τ^{10} have the same directions but generally different magnitudes. To describe their magnitudes, it is necessary to take into account the interatomic potential incorporated in the dynamical matrix. Figure 2 illustrates the translational and rotational displacements of ions described by $e_1^{(10)}$ eigenvector. The ions marked by 1, 2 and 3 belong to the fcc primitive unit cell. The displacements

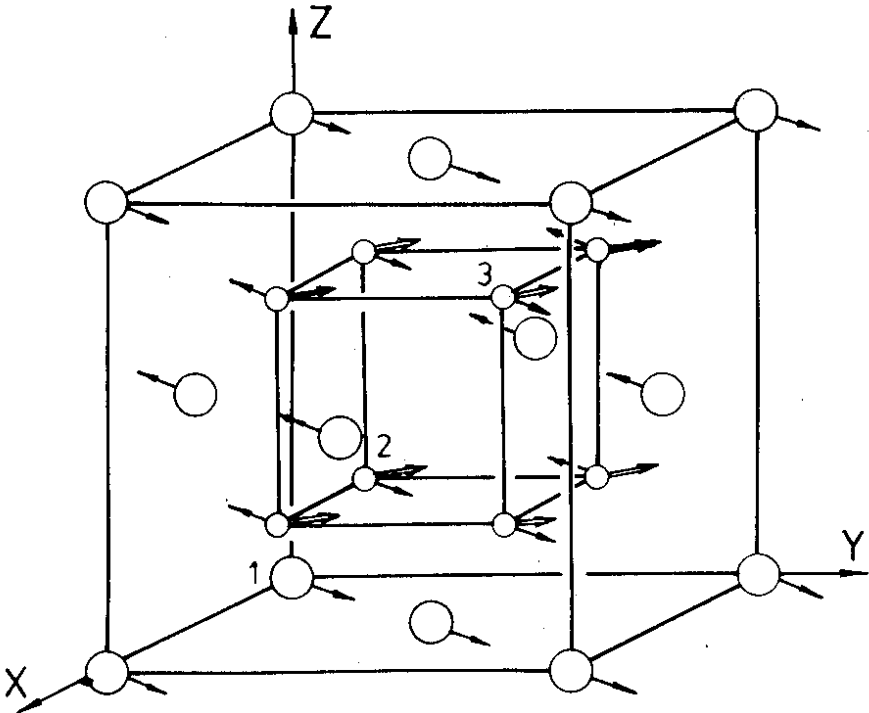


Fig. 2. The displacement vectors of the normal mode at the point \bar{X} associated with the irreducible representation τ^{10} . Arrows and double arrows denote translational displacements and axial vectors of rotational displacements, respectively. The ions 1, 2, 3 belong to the fcc primitive unit cell.

in neighbouring unit cells were found from the phase difference of the plane wave defined by k_{10} and propagating along [001] direction. Notice, that the hexamine octahedrals do not rotate in mode τ_{10} .

Interchanging the role of the translational and rotational vectors we can treat fig. 2 as an illustration of $e_1^{(9)}$ eigenvector. Then, the rotation of all ions might occur but translational motion of the hexamine octahedron is forbidden. The eigenvectors $e_3^{(j)}$, $e_4^{(j)}$ and $e_5^{(j)}$, $e_6^{(j)}$ correspond to the doubly degenerate modes propagating along [010] and [100] directions, respectively, and can be found without difficulties.

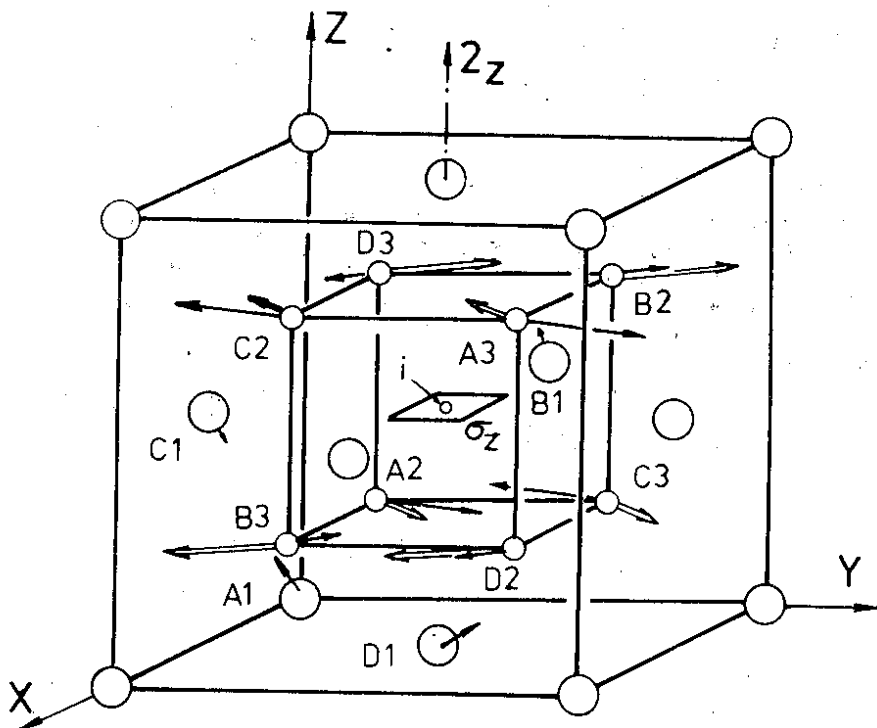


Fig. 3. The displacement vectors associated with the phase transition $Fm\bar{3}m \rightarrow (k_{10}^j, \tau_{10}, c_3=c_4=0, c_5=c_6) \rightarrow P2_1/b$. Arrows and double arrows denote translational displacements and axial vectors of rotational displacements, respectively. The location of the inversion (i), symmetry plane (σ_z) and two-fold symmetry axis (2_z) of $P2_1/b$ space group are indicated.

4. PHASE TRANSITION FROM PHASE I TO PHASE II

As argued in section 2, the lowering of the symmetry from the cubic phase I to the monoclinic phase II of NHP, MHP and NHT is entirely specified by the following diagram

$$Fm\bar{3}m \rightarrow (\{k_{10}\}, \tau^{10}, c_3=c_4=0, c_5=-c_6) \rightarrow P2_1/b,$$

where c_1 and c_2 are arbitrary. Knowing the eigenvectors $e_1^{(10)}$, $e_2^{(10)}$ of τ^{10} , it is easy to write down the eigenvectors $e_5^{(10)}$ and $e_6^{(10)}$. Combining them in agreement with the phase shift defined by the wave vectors $k_{10}^{(z)}$ and $k_{10}^{(x)}$ and the restrictions obeyed by c_i it is possible to find the general positions of molecular groups in the monoclinic unit cell (Table 3). The free parameters of the structure, a, b, d, c_1, c_2, c_5 have to be fixed by an experiment. So, the phase transition from phase I to phase II which provokes the hindrance of stochastic motion of anions, may involve the shift of anions in the plane parallel to the unique symmetry plane and fix relative orientations of anions in agreement with the axial vectors listed in Table 3. The displacement vectors for a particular choice of parameters ($a=b=c=1, c_1=c_5=3, c_2=1$) are shown in fig. 3.

In order to describe the structure of phase II one should know not only the displacement vectors of all the groups of atoms in phase I, but also their equilibrium positions and orientations from which these displacements are measured. In the hexamine complexes these data are known except for the anion groups which are expected to perform a kind of stochastic rotational motion^{6,8/} and therefore their orientational equilibrium positions are not specified. However, the site symmetry at $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$ and the point symmetry of the anion groups are the same, therefore, the form of the orientational potential admits only two positions of extrema to be present, the first in which the oxygen or fluorine atoms are directed towards the nearest nickel or magnesium atoms, the second outwards. One of these extrema is a maximum, one is a minimum. On these grounds it is possible to consider the axial vectors of displacements listed in Table 3 as rotational distortions of the mentioned orientational equilibrium position.

5. DISCUSSION

In the light of the experimental data and symmetry rules the properties of the hexamine complexes can be character-

Table 3

General positions of ions in the hexammine complexes deduced from the normal modes for the phase transition

$$Fm\bar{3}m - (1/2, 1/2, 1/2, c_3 = c_4 = 0, c_5 = c_6) - P2_1/b$$

Position	Ion	Phase I Fm $\bar{3}m$	Phase II P2 $_1$ /b	
			Ions positions	Axial vectors
A1	M(NH $_3$) $_6^{++}$	0,0,0	A, B, C	0,0,0
B1		0, 1/2, 1/2	-A, 1/2-B, 1/2+C	0,0,0
C1		1/2, 0, 1/2	1/2-A, -B, 1/2-C	0,0,0
D1		1/2, 1/2, 0	1/2+A, 1/2+B, -C	0,0,0
A2	(XY $_4$) $^-$	1/4, 1/4, 1/4	1/4+D, 1/4+E, 1/4	G, I, 0
B2		1/4, 3/4, 3/4	1/4-D, 3/4+E, 3/4	-G, H, 0
C2		3/4, 1/4, 3/4	3/4-D, 1/4-E, 3/4	-G, -I, 0
D2		3/4, 3/4, 1/4	3/4+D, 3/4-F, 1/4	G, -H, 0
A3		3/4, 3/4, 3/4	3/4+D, 3/4+E, 3/4	-G, -I, 0
B3		3/4, 1/4, 1/4	3/4-D, 1/4+F, 1/4	G, -H, 0
C3		1/4, 3/4, 1/4	1/4-D, 3/4-E, 1/4	G, I, 0
D3		1/4, 1/4, 3/4	1/4+D, 1/4-F, 3/4	-G, H, 0

$$A = a(c_1 + c_2), \quad B = a(c_1 - c_2), \quad C = 2ac_5,$$

$$D = b(c_1 - c_2), \quad E = b(2c_5 + c_1 + c_2), \quad F = b(2c_5 - c_1 - c_2),$$

$$G = d(c_1 - c_2), \quad H = d(2c_5 + c_1 + c_2), \quad I = d(2c_5 - c_1 - c_2).$$

a, b, d, c $_1$, c $_2$, c $_5$ are adjustable parameters.

rized as follows. In the cubic phase I the perchlorate ions perform stochastic jumps probably of rotational type. This conclusion follows from the broadening of E (463 cm $^{-1}$) and T $_2$ (625 cm $^{-1}$) internal modes of ClO $_4^-$ ions observed in phase I in the Raman spectra^{6,8/}. It follows also from the temperature dependence of the Raman active lattice mode T $_{2g}$ at ca. 60 cm $^{-1}$. The T $_{2g}$ mode which involves translational antiphase longitudinal displacements only of perchloride ions shows an anomalous increase in intensity when the temperature rises. If the ions would perform harmonic oscillations and librations, the system would have well defined short-lived phonons, and the Raman first-order spectrum would consist of sharp zone-center phonons. If the perchloride ions perform stochastic jumps of any kind, as is expected, the selection rule for the first-order Raman spectra is broken. Then, with increasing temperature, modes with still larger wave vectors contribute to the experimentally observed spectrum. In effect, the intensity of such a band increases faster than predicted by the Bose-Einstein population factor, in accordance with observations^{6/}.

While lowering the temperature of the hexamine complexes being in the phase I, one mode at the point X of the fcc Brillouin zone becomes active. One might expect that the active mode would exhibit either as a wide central peak or as a soft mode. In the first case the presence of stochastic motion of perchloride ions may destroy the phonon mode to such a degree that instead of well defined peaks of the active mode at a finite frequency the central elastic wide peak, as indicated in ^{16/}, would appear at the point X of the reciprocal lattice. In the second case, when the active mode remains a well defined phonon mode, the softening of it would be expected on the zone-boundary.

In phase II the active mode becomes a zone-center mode and it should be in principle detected by the Raman experiment. In the case of the central peak the active phonon peak should appear below the phase transition point, at a finite, more or less constant frequency. In the case of the soft mode the frequency of the active phonon peak should increase as the temperature decreases. No such effects have been reported so far, probably because the data were taken on polycrystalline samples which provide an additional background which may obscure not intense peaks.

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