

LATTICE DYNAMICS AND PHASE TRANSITIONS

Lattice Dynamics of MF_3 Crystals ($M = \text{Al, Ga, and In}$)

V. I. Zinenko and N. G. Zamkova

Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

e-mail: zinenko@iph.krasnoyarsk.su

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Abstract—The phonon spectra, Born effective charges, and dielectric constants ϵ_∞ for the $\square\text{AlF}_3$, $\square\text{GaF}_3$, and $\square\text{InF}_3$ crystals (where \square is a vacancy) have been calculated in terms of the generalized Gordon–Kim method. The calculated spectra of lattice vibrations contain no imaginary vibrational frequencies. This suggests the stability of the cubic phase of these compounds but contradicts the observable structural transition from cubic to rhombohedral phase. It is assumed that such a transition in the $\square\text{AlF}_3$, $\square\text{GaF}_3$, and $\square\text{InF}_3$ crystals is brought about by structural defects. The calculated spectrum of lattice vibrations of the “completely defective” crystal $M\square\text{F}_3$ ($M = \text{Al, Ga, and In}$) indicates a strong instability of the cubic phase. Within the mean crystal approximation, the cubic phase of $M_xM_{1-x}\text{F}_3$ crystals appears to be unstable at small $x \leq 0.05$. © 2000 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Structural phase transitions and the nature of instability in compounds with a perovskite-type structure have been studied experimentally and theoretically over many years. The majority of the theoretical investigations were dedicated to oxide compounds with a perovskite-type structure. Calculations of the band structure, crystal lattice dynamics, and static mechanics of ferroelectric and antiferroelectric phase transitions in terms of the density functional method yielded the satisfactory results (see, for example, [1–6]). These calculations provided a deeper insight into the origin of crystal lattice instability and the nature of ferro- and antiferroelectricity in oxide compounds with a perovskite-type structure. At the same time, halide compounds with a perovskite structure, in which the structural phase transitions, as a rule, are associated with the crystal lattice instability toward antiferroelectric distortions, have received little attention in the *ab initio* calculations.

The crystals $\square\text{MF}_3$ ($M = \text{Al, Ga, and In}$; \square is a vacancy) are structurally isomorphic with the ReO_3 compound. The ReO_3 compound has the simplest perovskite-like structure. The metal ion is located at the center of an octahedron whose vertices are occupied by the anions (Fig. 1a). The centers of anionic cubooctahedra are empty. The MF_3 crystals undergo a phase transition from cubic to rhombohedral phase due to a “rotation” of the octahedron around the threefold symmetry axis of the cubic cell [7–9]. The phase transition and lattice dynamics of the AlF_3 , GaF_3 , and InF_3 crystals were the subjects for a few experimental and theoretical works, including the structural investigations by x-ray diffraction, calorimetric studies, measurements of the cutoff Raman-active frequencies of lattice vibrations in the distorted rhombohedral phase, and calculations of

the phonon spectrum of the cubic phase within the rigid ion model with adjustable parameters describing the short-range interactions [8, 9]. Information on the overall phonon spectrum of the crystal is of crucial importance for investigations into displacive phase transitions and the understanding of the nature of crystal lattice instability.

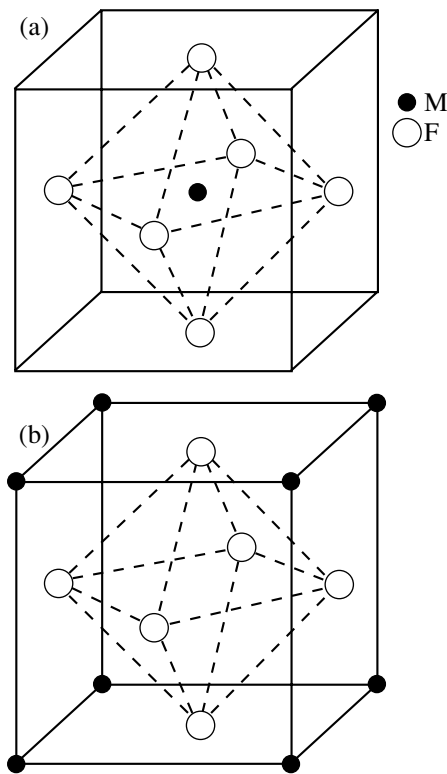


Fig. 1. Unit cells of (a) $\square\text{MF}_3$ crystals and (b) $M\square\text{F}_3$ hypothetical crystals.

The purpose of this work was to calculate the phonon spectra, Born dynamic charges, and rf permittivities of the AlF₃, GaF₃, and InF₃ crystals in terms of the microscopic ionic-crystal model, which takes into account the ion deformability and polarizability [10]. The calculation procedure is briefly described in Section 2. Section 3 presents the results of calculations. It is shown that, within the model employed, the calculated spectrum of lattice vibrations in the cubic phase of the crystals under consideration exhibits no vibrations with imaginary frequencies and, thus, indicates the stability of the cubic phase at zero temperature. However, the vibrational spectrum contains a branch (between the *R* and *M* points in the Brillouin zone) with anomalously low vibrational frequencies. We calculated the vibrational spectrum of an *M*□F₃ hypothetical crystal with the same cubic lattice in which the cations are located at the centers of cubooctahedra (Fig. 1b). The vibrational spectra of the hypothetical crystals show a large number of vibrations with imaginary frequencies. Within the mean crystal approximation, we also calculated the vibrational spectrum of the *M_xM_{1-x}F₃* crystals. It is found that the cubic phase of these crystals is unstable at small $x \leq 0.05$.

2. CALCULATION PROCEDURE

In the present work, the vibrational spectrum of the crystal lattice was calculated within the ionic crystal model proposed by Ivanov and Maksimov [10]. This model generalizes the Gordon–Kim approximation with due regard for the influence of crystalline environment on the ion deformability and polarizability. The total electron density of the crystal in this model is written as

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i).$$

Here, the summation is performed over all ions in the crystal. The total lattice energy within the pair interaction approximation has the form

$$E_{\text{cr}} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_i E_i^{\text{self}}(R_w^i) \quad (1)$$

$$+ \frac{1}{2} \sum_{i \neq j} \Phi_{ij}(R_w^i, R_w^j, |\mathbf{R}_i - \mathbf{R}_j|),$$

where Z is the charge of the i th ion,

$$\begin{aligned} & \Phi_{ij}(R_w^i, R_w^j, |\mathbf{R}_i - \mathbf{R}_j|) \\ &= E\{\rho_i(\mathbf{r} - \mathbf{R}_i) + \rho_j(\mathbf{r} - \mathbf{R}_j)\} \\ & - E\{\rho(\mathbf{r} - \mathbf{R}_i)\} - E\{\rho(\mathbf{r} - \mathbf{R}_j)\}, \end{aligned} \quad (2)$$

the $E\{\rho\}$ energy is calculated within the Thomas–Fermi approximation and in the local approximation for the kinetic and exchange–correlation energies [10],

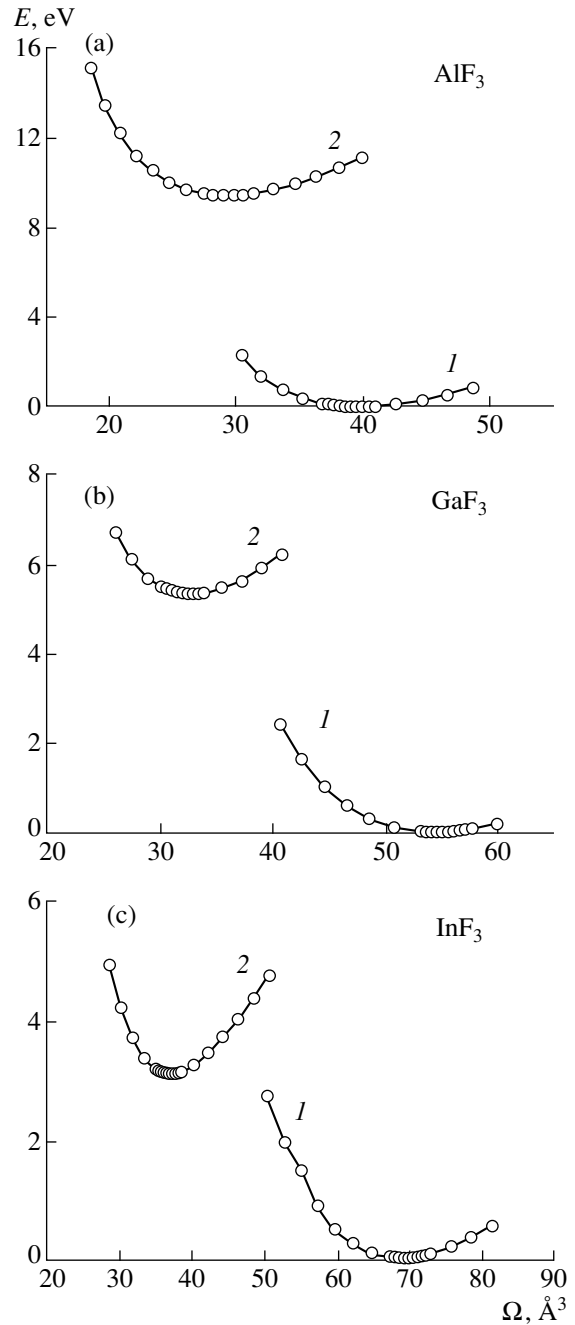


Fig. 2. Dependences of the total lattice energy on the volume. Curves 1 and 2 correspond to the $\square MF_3$ and $M\square F_3$ structures, respectively. The energies are reckoned from (a) -14965.6141 , (b) -61438.7235 , and (c) -168862.7272 eV.

and $E_i^{\text{self}}(R_w^i)$ is the self-energy of the ion. The electron density of an individual ion and its self-energy are calculated with allowance made for the crystal potential, which was approximated by the charged sphere (Watson's sphere)

$$v(r) = \begin{cases} Z_i^{\text{ion}}/R_w & r < R_w \\ Z_i^{\text{ion}}/r & r > R_w, \end{cases}$$

Table 1. Equilibrium values of the lattice parameters, Born effective charges (Z^*), rf permittivity ϵ_∞ , and ion polarizabilities α_M and α_F

Crystal	$a_0, \text{\AA}$ (calculation)	$a_0, \text{\AA}$ (experiment)	$Z^*(M)$	$Z_\perp^*(F)$	$Z_\parallel^*(F)$	ϵ_∞	$\alpha_M, \text{\AA}^3$	$\alpha_F, \text{\AA}^3$
$\square\text{AlF}_3$	3.42	3.56 ^a	3.08	-0.66	-1.76	1.86	0.03	0.65
$\square\text{GaF}_3$	3.80	3.69 ^b	2.87	-0.78	-1.32	1.64	0.12	0.69
$\square\text{InF}_3$	4.11	4.07 ^b	2.99	-0.79	-1.41	1.59	0.37	0.72

Note: ^a [8]. ^b [7].

Table 2. Calculated frequencies of modes at the $\Gamma(0, 0, 0)$ and $R(\pi/a, \pi/a, \pi/a)$ points of the Brillouin zone (PIB is the breathing ion model, and PPIB takes into account the ion deformability and polarizability)

Mode	$\square\text{AlF}_3$			$\square\text{GaF}_3$			$\square\text{InF}_3$		$M\square\text{F}_3$		
	PPIB	PIB	RI	PPIB	PIB	RI	PPIB	PIB	Al	Ga	In
$2\Gamma_{10}(3)$											
LO	651	735	765	521	564	553	449	495	465	407	357
TO	521	558	641	466	504	513	399	456	401	375	337
LO	307	503	481	245	374	392	200	304	350	306	294
TO	222	401	378	185	259	278	154	201	362i	27	44i
$\Gamma_9(3)$	194	240	219	152	172	194	126	137	225i	148i	143
$R_1(1)$	645	644	669	486	558	585	433	499	340	328	300
$R_{10}(3)$	445	446	487	265	267	265	193	195			
$R_4(3)$									449	376	311
$R_3(2)$	372	407	481	424	424	418	400	403	289	269	247
$R_4(3)$	246	415	383	210	305	338	189	195	272i	97	119
$R_5(3)$	58	79	50	68	73	50	63	65	490i	359i	253i

Note: The results of calculations within the rigid ion (RI) model [9] are presented for comparison. The parenthetic numerals indicate the mode degeneracy. Frequencies are given in cm^{-1} .

where R_w is the radius of the Watson sphere. The radius of the sphere R_w^i for each ion is determined from the condition of the minimum total energy of the crystal.

In order to calculate the crystal lattice dynamics, equation (2) should contain additional terms that describe the change in the energy upon displacements of the ions from their equilibrium positions. Moreover, the calculations of the vibrational spectrum allowed for the ion polarizability and deformability caused by the change in the crystal environment. The expression for the dynamic matrix was given in [11].

3. RESULTS AND DISCUSSION

The equilibrium unit cell parameters of the crystals under consideration were determined from the condition of the minimum total energy of the crystal as a function of the volume (Fig. 2). Table 1 presents the equilibrium lattice parameters, experimental data, and the calculated values of ion polarizability, rf permittiv-

ity ϵ_∞ , and the Born effective charges. For the metal ions, the effective charge tensor is isotropic and close in magnitude to the nominal charge of the ion (+3). The fluorine ion is characterized by two tensor components, namely, $Z_\parallel^*(F)$ and $Z_\perp^*(F)$, which correspond to the displacements of the F^- fluorine ion in the directions parallel and perpendicular to the $M-F$ bond, respectively. As is seen from Table 1, there is a substantial difference between $Z_\parallel^*(F)$ and $Z_\perp^*(F)$ components, as for oxide compounds with a perovskite structure, but the $Z_\parallel^*(F)$ values are considerably less than $Z_\parallel^*(O)$.

The calculated phonon spectra of the AlF_3 , GaF_3 , and InF_3 crystals are shown in Figs. 3–5. For comparison with the calculations within the rigid ion model [9], Table 2 lists the frequencies of vibrations at the $\Gamma(0, 0, 0)$ and $R(\pi/a, \pi/a, \pi/a)$ points of the Brillouin zone. Table 2 also presents the vibrational frequencies calculated in the present work in terms of the “breathing” ion model, i.e., without regard for the ion polarizability. It follows

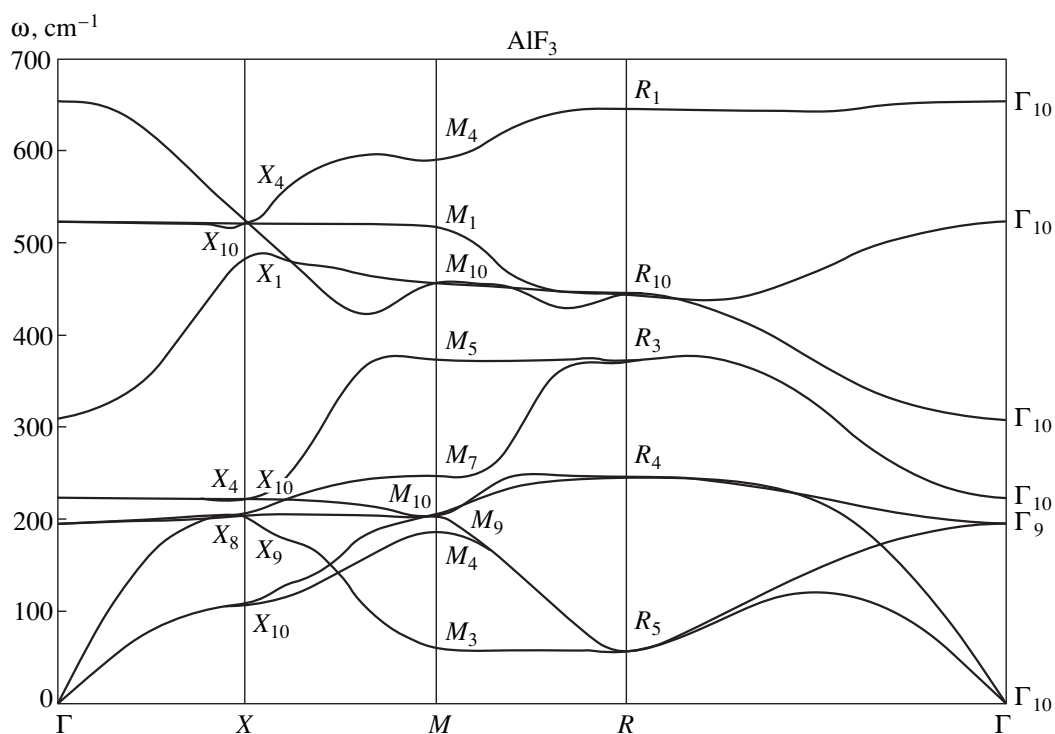


Fig. 3. Calculated phonon spectrum of the $\square AlF_3$ crystals.

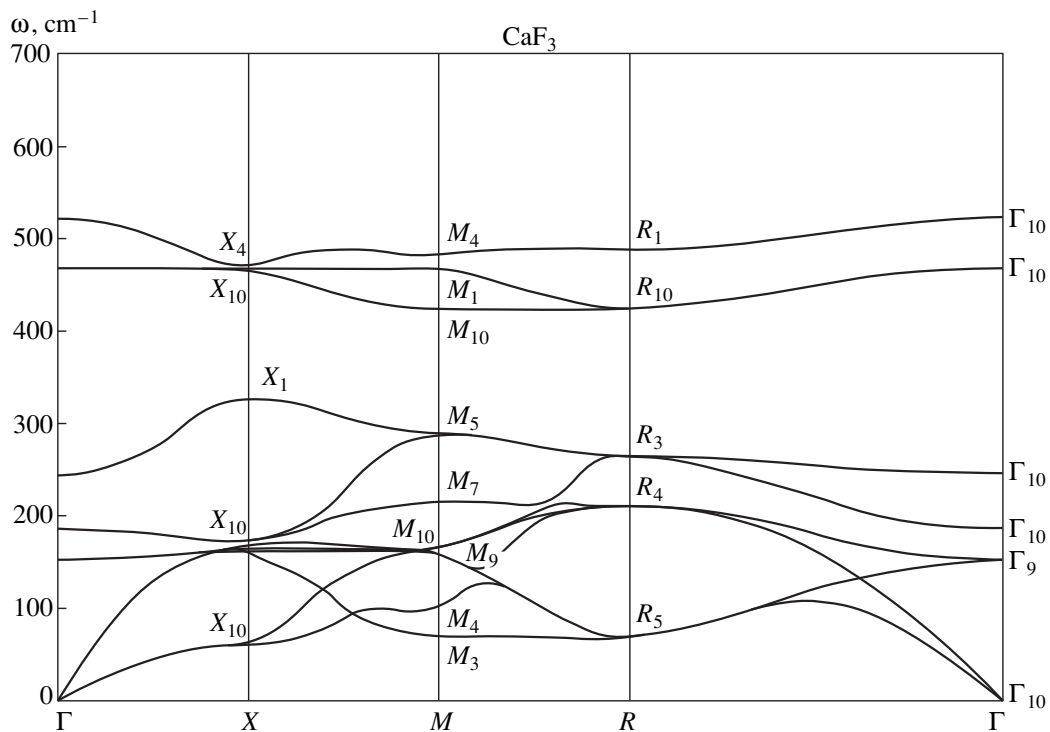


Fig. 4. Calculated phonon spectrum of the $\square GaF_3$ crystals.

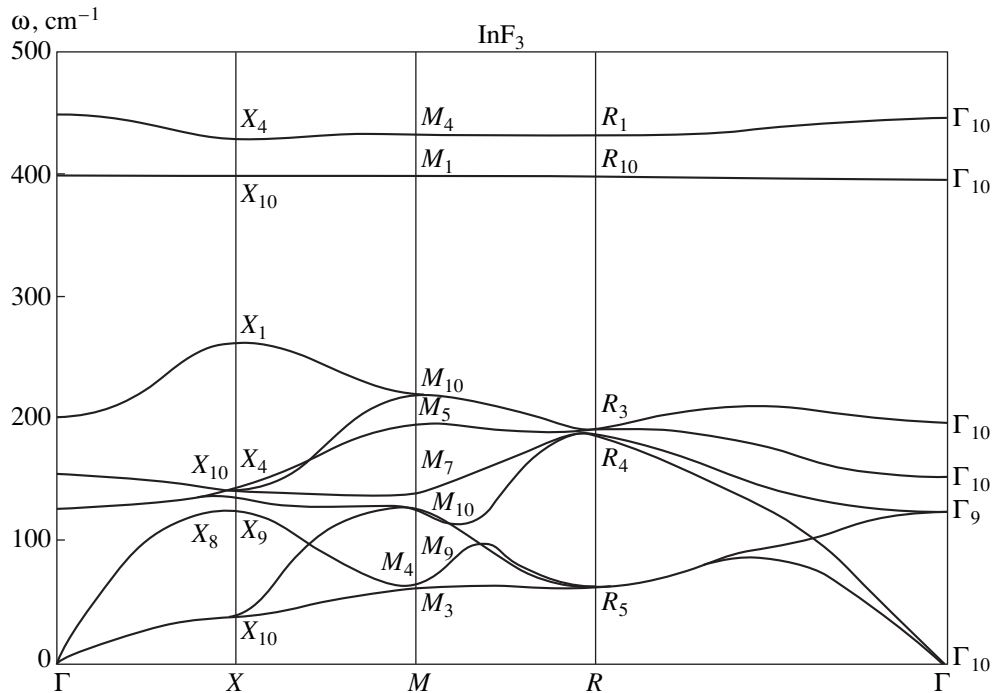


Fig. 5. Calculated phonon spectrum of the $\square\text{InF}_3$ crystals.

from Table 2 that the results of calculations within the rigid ion model with adjustable parameters describing the short-range interactions are in good agreement with those obtained in the breathing ion model, i.e., without adjustable parameters. At the same time, the inclusion of ion polarizability substantially affects the frequencies of lattice vibrations, in particular, significantly reduces the LO–TO splitting for frequencies of the IR-active modes.

As can be seen from Figs. 3–5 and Table 2, the vibrational spectra of all the studied crystals exhibit no imaginary frequencies but contain a weakly dispersive branch (between the M and R points in the Brillouin zone) with anomalously low frequencies ($\approx 60 \text{ cm}^{-1}$). The same result was obtained within the rigid ion model [8, 9]. Therefore, our calculations of the lattice dynamics within the method employed indicate that the cubic phase in the AlF_3 , GaF_3 , and InF_3 crystals remains stable to $T = 0$. However, this result is contradictory to the experiment, which revealed the structural phase transition in these compound at a finite tempera-

ture. The instability of the cubic phase in the crystals under study can be explained by the disturbance of the $\square\text{MF}_3$ perfect structure when a small number of metal ions occupy vacant sites at the center of a cubooctahedron. In order to verify this assumption, we calculated the phonon spectra of the “completely defective” hypothetical structure $M\square\text{F}_3$ ($M = \text{Al}, \text{Ga}, \text{and In}$). The total lattice energy in this structure considerably exceeds the energy in the $\square\text{MF}_3$ structure (Fig. 2). The calculated phonon spectra of the $\text{Al}\square\text{F}_3$, $\text{Ga}\square\text{F}_3$, and $\text{In}\square\text{F}_3$ hypothetical crystals essentially differ from the spectra of the $\square\text{AlF}_3$, $\square\text{GaF}_3$, and $\square\text{InF}_3$ crystals. For the defective structure, the phonon spectrum exhibits many imaginary frequencies of vibrations, and the unstable modes occupy the whole phase space in the first Brillouin zone. The calculated frequencies of lattice vibrations in the $M\square\text{F}_3$ crystals at the $\Gamma(0, 0, 0)$ and $R(\pi/a, \pi/a, \pi/a)$ points of the Brillouin zone are given in Table 2. As follows from this table, the “softest” mode is the threefold degenerate mode R_5 , which belongs to the boundary point of the Brillouin zone. The eigenvector of the R_5 mode corresponds to the “rotation” of the octahedron whose center, in this case, is free from metal ion. The phase transition experimentally observed in the AlF_3 , GaF_3 , and InF_3 compounds is associated with the condensation of just this R_5 mode, and, hence, this mode alone will be discussed below. The frequency of the R_5 mode in two structures ($\square\text{MF}_3$ and $M\square\text{F}_3$) is described by the same analytical expression

$$\omega^2(R_5) = \frac{4\pi e^2}{\Omega M_F}(S + C),$$

Table 3. Coulomb contribution of point charges C and contribution of short- and long-range dipole–dipole interactions S in $\omega^2(R_5)$ for MF_3 in two structures

Constant		$\square\text{MF}_3$	$M\square\text{F}_3$
C		0.68346	−0.82566
S	Al	−0.65178	−0.83688
	Ga	−0.62259	−0.17220
	In	−0.61643	0.25450

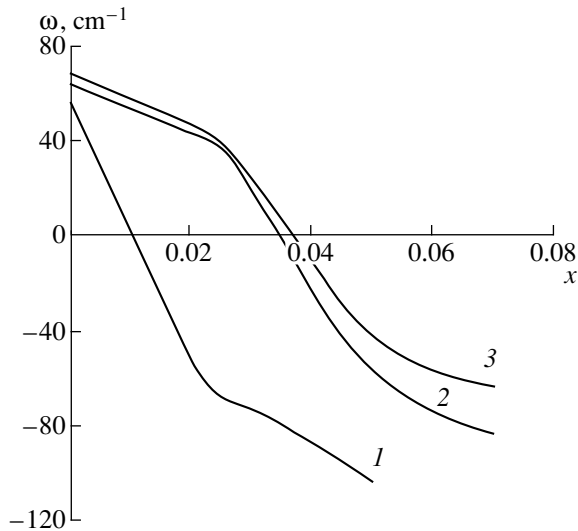


Fig. 6. Dependences of the frequency $\omega(R_5)$ on the concentration x for the $M_xM_{1-x}F_3$ crystals: (1) $M = \text{Al}$, (2) $M = \text{Ga}$, and (3) $M = \text{In}$. Negative value of ω signifies the imaginary quantity.

where Ω is the unit cell volume, and M_F is the mass of fluorine. The constant C describes the contribution of point charges to $\omega^2(R_5)$, and the constant S accounts for all short- and long-range dipole-dipole interactions. The constants C and S for the three crystals under consideration are listed in Table 3. It is seen from this table that, for the $\square MF_3$ structure, the sum of the C and S constants is positive but small in magnitude for all the crystals. On the other hand, the sum of the contributions for the $M\square F_3$ structure is negative but large in magnitude for all the crystals. It can be assumed that, in real crystals, a small number of metal ions occupy vacant sites at the center of the cubooctahedron formed by fluorine ions, and this imperfection results in the instability of the cubic phase. In order to make a rough estimate of the defect concentration at which the cubic phase becomes unstable, we calculated the vibrational spectrum of the "mean crystal" $M_xM_{1-x}F_3$ ($M = \text{Al}$, Ga , and In). The dependence of $\omega(R_5)$ on the concentration x for the mean crystals is displayed in Fig. 6. It is seen that the cubic phase at zero temperature appears to be unstable at a rather low concentration of defects.

Thus, we calculated the lattice dynamics of the $\square \text{AlF}_3$, $\square \text{GaF}_3$, and $\square \text{InF}_3$ crystals with a perovskite-type structure. The calculations were performed within the generalized Gordon-Kim model, which takes into account the ion polarizability and deformability. It was found that, for all the crystals at $T = 0$, the spectra of lattice vibrations contain no vibrations with imaginary

frequencies, which suggests the stability of the cubic phase in these crystals. In our opinion, the structural phase transition from cubic to rhombohedral phase, which is experimentally observed in these crystals, can be associated with structural defects when a number of metal ions are located at the centers of cubooctahedra that are vacant in the perfect structure. The origin of these defects remains unclear. Since the total lattice energy in the completely defective structure considerably exceeds the energy of the perfect structure, the formation of defects of this type at the expense of temperature is unlikely. However, these defects apparently can arise upon crystal growth. The above assumption on the origin of instability of the cubic phase in the MF_3 crystals requires the experimental verification.

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