DISPERSION ANALYSIS OF REFLECTANCE SPECTRA OF CRYSTALS Ag_2CdI_4 AND Ag_2HgI_4 IN THE FAR IR REGION

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We have investigated the reflectance spectra of superionic crystals Ag_2CdI_4 and Ag_2HgI_4 in the range 20—160 cm^{-1} and carried out their dispersion analysis in order to determine the main parameters of vibrational oscillators forming the reflectance bands in the far IR region. The force constants of the bonds between ions as well as the effective charges of ions in Ag_2CdI_4 and Ag_2HgI_4 are estimated.

Compounds Ag_2CdI_4 and Ag_2HgI_4 belong to the class of superionic materials of the A_2BI_4 group which exist in the system of iodides AI–BI_2 (A = Ag, Cu; B = Hg, Cd, Zn, Pb, etc.) [1]. The low-temperature β-phases of these compounds ($T \leq 325$ K for Ag_2HgI_4 [2] and $T < 320$ K for Ag_2CdI_4 [3]) belong to the tetragonal syngony (the space group S_4^2), where atoms are regularly arranged in the lattice: Ag^+ and B^{2+} ions are surrounded by I^- anions forming a tetrahedron. Moreover, the ion-covalent bond between the atoms in $[BI_4]$-complex is stronger than that in $[AgI_4]$. The parameters of the spatial lattice for Ag_2CdI_4 crystal are $a = b = 6.3421(5)$ Å, $c = 12.668(2)$ Å and $a = b = 6.3299(1)$ Å, $c = 12.6158(3)$ Å for Ag_2HgI_4 crystal. The volume of a primitive cell for both materials $V_{prim} = \frac{1}{2}a^2c$ is equal to $V_{prim}(Ag_2CdI_4) = 254.7756$ Å^3 and $V_{prim}(Ag_2HgI_4) = 252.7440$ Å^3. After the phase transition to the superionic state, the structure of both materials becomes cubic (α-phase), where Ag^+ ions statistically occupy crystallographic positions, whose number is larger than that of silver ions.

The essential influence of the lattice dynamics on structural transformations and electron and ionic transport in solid electrolytes stipulates the investigation

of their vibrational spectra, in particular, in the far IR region.

The reflectance spectra of Ag_2HgI_4 and Ag_2CdI_4 in the far IR region were investigated in a number of papers [2, 4, 7, 8, 11, 12]. The lattice dynamics of these crystals is related to the vibrations of Ag—I and $Hg(Cd)I_4^{2-}$. Moreover, the deformation vibrations take place in the low-frequency region ($\omega < 50$ cm^{-1}), while the valent vibrations belong to the high-frequency one ($\omega > 50$ cm^{-1}) [2, 7, 8, 11, 12].

In [2], the investigation of the reflectance spectrum of Ag_2HgI_4 at room temperature discovered seven vibrational modes characterized by the following frequencies of TO-vibrations: 24.8, 29.8, 35.1, 39.5, 95.0, 108.0, and 120.0 cm^{-1}. The bands with frequencies of 24.8 and 35.1 cm^{-1} are referred to the E symmetry, and those with frequencies of 29.8 and 39.5 cm^{-1} to the B symmetry. When determining the symmetry of the vibrations with frequencies of 95.0, 108.0, and 120.0 cm^{-1}, it was assumed that they belong to the B or E symmetry. The reflectance spectrum of Ag_2HgI_4 crystal obtained in [7] at room temperature includes five bands with TO (transverse oscillations) frequencies of 24.2, 28.9, 34.3, 39.0, and 89.8 cm^{-1}. Other investigations indicate the presence of the vibrational bands with TO-frequencies of 28.0, 36.0, 60.0, 96.0, 118.0, and 156.0 cm^{-1} [11]. The bands with TO-frequencies of 156.0 and 118.0 cm^{-1} are attributed to the symmetric valent vibrations of HgI_4^{2-} ion that belong to the A symmetry. The oscillations with TO-frequencies of 96.0, 60.0, and 36.0 cm^{-1} correspond to the vibrations of Me—I (Me = Ag, Hg) [11]. In this case, the bands at 96.0 and 60.0 cm^{-1}

were attributed to the symmetric vibrations of the A symmetry [11].

In the reflectance spectrum of Ag_2CdI_4, the following TO-bands were observed at room temperature [8]: 26.0 cm^{-1} which was attributed to the Ag—I deformation vibration; 36.0; 42.0 cm^{-1} (the Cd—I deformation vibration); 92.0 cm^{-1} (the Ag—I symmetric valent vibration); and 141.0 cm^{-1} (the CdI_4^2 symmetric valent vibration). The reflectance spectrum of Ag_2CdI_4 measured in [4] includes fifteen vibrational modes. They were attributed to the collections of multiplets appearing under the splitting of oscillations of free molecules CdI_4 in the crystal of Ag_2CdI_4 in the vicinity of frequencies 44 cm^{-1} and 145 cm^{-1} [6].

The cited literary data indicate the ambiguous and incomplete interpretation of experimental facts. There is practically no information concerning the parameters of the oscillators forming the bands in the far IR region of the spectrum of these compounds. That's why in the present work, we investigate the reflectance spectra of massive samples of Ag_2CdI_4 and Ag_2HgI_4 in the range 20—160 cm^{-1} in the β-phase and carry out their dispersion analysis with the purpose to determine the main parameters of the vibrational oscillators that form the bands in the far IR region and to estimate the force constants of the bonds between the ions and their effective charges.

Polycrystal samples of Ag_2CdI_4 and Ag_2HgI_4 were obtained using the solid-phase synthesis technique. For this purpose, fine-disperse powders of AgI and $Cd(Hg)I_2$ were taken in molar proportion 2:1, stirred, and pressed into tablets having 4 mm in thickness and ~ 8 mm in diameter at a pressure of 10^9 Pa. After that, the samples obtained in this way were annealed at the temperature $T \leq 350$ K during several days. The identification of phases was verified by X-ray phase analysis. The surfaces of the samples weren't preliminarily treated in order to investigate the reflectance spectra. In the range 20—160 cm^{-1}, the nonpolarized reflectance spectra of the samples obtained in this way were measured with the help of a LAFS-1000 Fourier spectrometer at a spectral resolution of 1.22 cm^{-1}. The spectrometer was automatized by using an IBM compatible computer, which allowed one to obtain an interferogram at various resolutions. A computer program was developed that enabled us to realize the fast Fourier transformation of interferograms and save the obtained spectra. When studying the reflectance spectra of Ag_2CdI_4 and Ag_2HgI_4 in the far IR region, working chambers were evacuated up to a pressure of not more than 10^{-2} Torr, which

prevented the appearance of vibrational bands of water vapors.

When carrying out dispersion analysis, the reflectance spectrum $R(\omega)$ was calculated on the basis of the spectrum of the complex dielectric permittivity $\varepsilon^*(\omega)$ using the formula:

$$R(\omega) = \left[|\sqrt{\varepsilon^*} - 1|/|\sqrt{\varepsilon^*} + 1| \right]^2. \tag{1}$$

In turn, the dielectric permittivity $\varepsilon^*(\omega)$ is specified by the model of independent damped oscillators [5]:

$$\varepsilon*(\omega) = \varepsilon_\infty \prod_{n=1}^{N_0} (\omega_{l,n}^2 - \omega^2 + i\omega\gamma_{l,n})/$$

$$/(\omega_{t,n}^2 - \omega^2 + i\omega\gamma_{t,n}), \tag{2}$$

where ε_∞ is the contribution of high-frequency oscillations to the dielectric permittivity, and $\omega_{l,n}$, $\omega_{t,n}$ and $\gamma_{l,n}$, $\gamma_{t,n}$ are, respectively, the frequencies and the damping constants of the n-th longitudinal (l) and transverse (t) oscillations, whose number is equal to N_0.

Oscillator strengths S were calculated on the basis of the approximate relation [5]

$$\omega_l - \omega_t \approx S\omega_t/2\varepsilon_\infty, \tag{3}$$

while the contribution of high-frequency oscillations to the dielectric permittivity ε_∞ was estimated by the formula

$$\varepsilon_\infty = \left[\frac{\sqrt{R_\infty} + 1}{\sqrt{R_\infty} - 1} \right]^2. \tag{4}$$

The values of R_∞ were obtained in the course of measuring the reflectance spectra of Ag_2CdI_4 and Ag_2HgI_4 in the range 710–970 cm^{-1}, and the values of ε_∞ calculated by formula (4) are equal to 4.45 and 5.21, respectively.

The essence of the dispersion analysis technique lies in selecting such parameters of relation (2), at which the spectrum calculated by (1) coincides with the experimental one in the best way. In order to speed up the fitting procedure, we used the methods of automatic optimization of the parameters: a Turbo Pascal routine was created which realized the successive fitting of the parameters in relation (2). The fitting accuracy was estimated by means of minimizing the average absolute value of the deviation of the curve calculated by formula (2) from the experimental one.

There exists a simple correlation of the reflectance spectrum with the frequencies of poles and zeros of $\varepsilon^*(\omega)$, that is, with transverse (TO) and longitudinal (LO)

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a   **b**
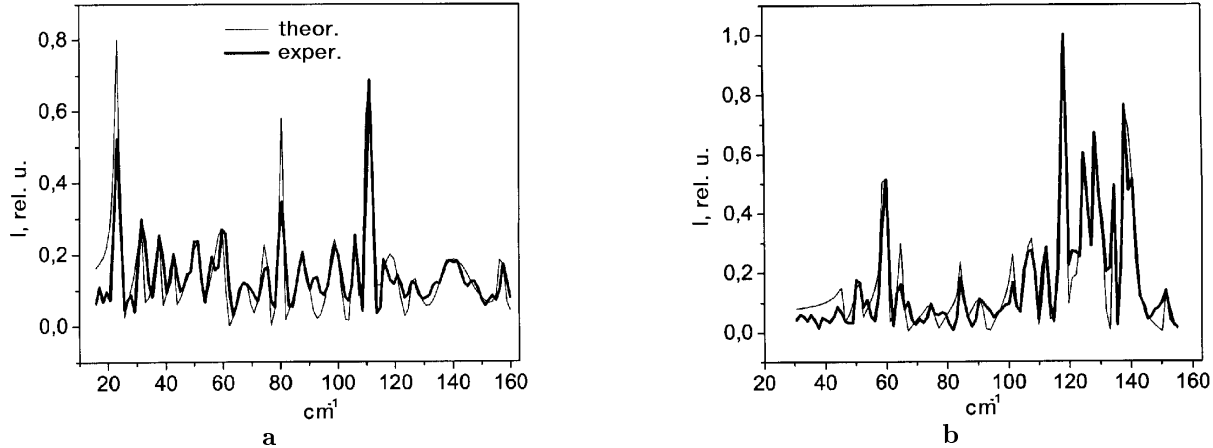
Experimental and theoretical (calculated by means of dispersion analysis) reflectance spectra of Ag_2HgI_4 (a) and Ag_2CdI_4 (b)

oscillations [5, 14]. The inflection point of the low-frequency slope of the n-th reflectance band is close to the frequency $\omega_{t,n}$, while that of the high-frequency one is close to $\omega_{l,n}$. The initial approximate parameters $\omega_{t,n}$, $\omega_{l,n}$, $\gamma_{t,n}$, and $\gamma_{l,n}$ were chosen on the basis of the experimental spectrum. For the purpose to accurately estimate the initial parameters, we used mathematical software package Microcal Origin.

In Figure,a, we represent the reflectance spectrum of a sample of Ag_2HgI_4 in the far IR region measured at room temperature.

In the range $20-160$ cm^{-1}, we observed fifteen vibrational bands of TO-frequencies given in Table 1. The bands of TO-frequencies 22.3, 31.3, 37.3, 42.4, 98.0, 105.6, 116.2, and 125.2 cm^{-1} correlate well with those listed in [2, 7, 11]. The appearance of additional bands as compared to the data in [2, 7, 11] of the TO-frequencies lying in the high-frequency range (51.0, 58.1, 67.4, 73.9, 79.3, 87.1, and 109.9 cm^{-1}) was associated with the

valent oscillations of Ag–I and HgI_4^{2-}. The intense band 116.2 cm^{-1} in Figure,a can be identified as the symmetric valent A-symmetry oscillation of the complex ion HgI_4^{2-}. As regards the oscillations of frequencies lower than 50 cm^{-1}, it is reasonable to associate them with the deformation oscillations of Ag—I and HgI_4^{2-}. The wide reflectance band in the vicinity of 140 cm^{-1} possibly corresponds to multiphoton processes.

In the reflectance spectrum of Ag_2CdI_4 (Figure,b) in the IR range $20-160$ cm^{-1}, we observed fifteen vibrational bands, whose numerical values are listed in Table 2.

The TO-bands with frequencies 45.8, 84.5, 101.3, and 136.8 cm^{-1} correlate well with those in [8]. The appearance of additional (as compared to [8]) bands in the high-frequency range ($\omega > 50$ cm^{-1}) of TO-frequencies 50.9, 58.7, 64.4, 105.7, 111.9, 117.2, 120.1, 123.7, 127.1, 133.7, and 151.2 cm^{-1} can be ascribed to the valent oscillations Ag—I and CdI_4^{2-}. The TO-band

T a b l e 1. The parameters of phonons in the Ag_2HgI_4 crystal obtained by means of dispersion analysis

ω_t, cm^{-1}	ω_l, cm^{-1}	γ_t, cm^{-1}	γ_l, cm^{-1}	S
22.3	24.5	0.5	0.3	0.8
31.3	32.4	1.3	1.5	0.3
37.3	38.3	1.2	1.2	0.2
42.4	43.2	1.5	1.4	0.1
51.0	52.6	3.4	2.1	0.3
58.1	61.0	5.5	0.8	0.4
67.4	69.8	4.7	3.1	0.3
73.9	76.1	2.5	1.1	0.2
79.3	80.7	1.3	0.02	0.1
87.1	91.4	3.8	4.5	0.4
98.0	102.0	2.6	3.5	0.3
105.6	106.3	0.2	2.5	0.1
109.9	112.2	0.2	2.3	0.2
116.2	122.2	6.5	4.5	0.4
125.2	127.3	2.4	6.7	0.1

T a b l e 2. The parameters of phonons of Ag_2CdI_4 crystal obtained by means of dispersion analysis

ω_t, cm^{-1}	ω_l, cm^{-1}	γ_t, cm^{-1}	γ_l, cm^{-1}	S
45.8	46.4	2.7	0.4	0.1
50.9	51.6	1.1	1.2	0.1
58.7	60.4	0.5	0.9	0.2
64.4	65.8	1.7	0.6	0.2
84.5	85.4	1.0	0.7	0.1
101.3	102.6	2.1	0.5	0.1
105.7	108.7	2.5	0.4	0.2
111.9	113.3	0.7	1.6	0.1
117.2	118.5	0.04	0.04	0.1
120.1	123.0	3.6	3.7	0.2
123.7	126.7	0.9	1.4	0.2
127.1	131.2	0.6	2.0	0.3
133.7	134.9	0.02	1.3	0.1
136.8	140.9	0.5	1.7	0.3
151.2	151.7	0.4	0.8	0.03

at 117.2 cm^{-1}, with regard for [8], can be identified as the valent mode of Ag—I of the A symmetry. It is known [13] that the spectral region 80—110 cm^{-1} mainly includes the oscillatory modes of Ag—I. That's why, it is reasonable to assume that most of the bands in Ag$_2$CdI$_4$ in this region correspond to oscillatory modes of Ag—I. The band 136.8 cm^{-1} in Figure,b correlates most probably with the internal valent oscillation of the tetrahedral complex CdI$_4^{2-}$, because, in the IR spectrum of a free molecule CdI$_4$, there exists the active oscillation of the F_2 symmetry with a frequency of 145 cm^{-1} [6]. In a crystal, this oscillation is splitted into a multiplet [4]. As one can see from Figure,b, the reflectance spectrum of Ag$_2$CdI$_4$ crystal includes a set of frequencies in the neighborhood of 44 cm^{-1}: 45.8, 50.9, 58.7, and 64.4 cm^{-1}. These modes can be identified as the deformation oscillations of Ag—I and CdI$_4^{2-}$, as it was done in [8].

The further analysis requires the identification of translation oscillations of Ag$_2$CdI$_4$ and Ag$_2$HgI$_4$ crystals. Using the table of the characters of irreducible representations of S_4 group, one can determine the symmetry of the translation oscillations of these compounds: $\Gamma_{\text{transl}} = B + E$. Under nonpolarized radiation, it is impossible to determine uniquely the symmetry of the translation oscillatory modes of Ag$_2$CdI$_4$ and Ag$_2$HgI$_4$ crystals. But some assumptions can be made on the basis of estimating the oscillator strengths of the observed vibrational bands. As the translation oscillations of the lattice are accompanied with a change of the mutual position of the centers of mass of silver ions and compound ionic tetrahedral complexes, they are considered as the external oscillations of the crystal and, therefore, are characterized by low values of frequencies. B-symmetry oscillations take place under the influence of the electric field directed along the Oz axis. At the same time. E-symmetry oscillations are excited by the electric field acting in the xOy plane. We can consider that, for polycrystal samples under nonpolarized radiation, one third of the electric field is distributed along an arbitrary Cartesian axis. This fact allows us to assume that only one third of the total number of oscillators is excited along the given axis of coordinates. On the basis of these considerations, we can state that the doubly degenerate modes of E symmetry should have [2] the twice larger oscillator strength as compared to the B-symmetry nondegenerate mode. In Ag$_2$HgI$_4$, four oscillations with the lowest frequencies of 22.3, 31.3, 37.3, and 42.4 cm^{-1} correlate well with this assumption.

Estimating the oscillator strengths of these oscillations (see Table 1), we can state that they correspond to the oscillations Ag—I and HgI$_4^{2-}$ of $B+E$ symmetry . That's why the modes with frequencies of 22.3 and 37.3 cm^{-1} are of E symmetry, while those with frequencies of 31.3 and 42.4 cm^{-1} are of B symmetry. The former two low-frequency oscillations can be attributed to the translation oscillations of HgI$_4^{2-}$ and Ag—I. The latter can correspond to the deformation oscillations of Ag—I and HgI$_4^{2-}$.

Estimating the oscillator strengths for Ag$_2$CdI$_4$ crystal (see Table 2), we can attribute the oscillations with frequencies of 45.8, 50.9, and 64.4 cm^{-1} to those of B symmetry, while the band at 58.7 cm^{-1} probably belongs to the E-symmetry oscillations. The B-symmetry oscillations with frequencies of 50.9 and 64.4 cm^{-1} should be ascribed to the deformation oscillations of Ag—I and CdI$_4^{2-}$, and that with a frequency of 58.7 cm^{-1} to the deformation oscillations of Ag—I and CdI$_4^{2-}$ of E symmetry. The low-frequency mode at 45.8 cm^{-1} with a low oscillator strength can be attributed to the translation oscillations of ions CdI$_4^{2-}$ and Ag–I of B symmetry.

Using the values of the frequencies of the translation oscillations for Ag$_2$CdI$_4$ and Ag$_2$HgI$_4$ crystals and assuming that the ions CdI$_4^{2-}$ and HgI$_4^{2-}$ oscillate bodily in these complexes, one can estimate the relative variation of the force constant k of the bond Ag-Cd(Hg)I$_4$. For this purpose, we use the simple relations between the frequencies of translation oscillations ω_{transl} and their reduced masses μ:

$$\omega_{\text{transl}}^2 = \frac{k}{\mu}, \tag{5}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \tag{6}$$

where m_1 is the mass of Cd(Hg)I$_4^{2-}$ ion, m_2 is the mass of Ag$^+$ ion. The force constant is approximately equal to 0.30 Hz^2·kg for Ag$_2$CdI$_4$ crystal and 0.14 Hz^2·kg for Ag$_2$HgI$_4$ crystal.

For T- and L-oscillations, one can calculate the values of the effective charges of ions (Szigeti charges). To this end, it is enough to use the frequencies of translation oscillations and internal oscillations of tetrahedrons. The transverse mode charge can be expressed in the following way [9]:

$$e_T^2 = \frac{\Delta \omega^2 \varepsilon_\infty V_{\text{prim}}}{4\pi Z^2}, \tag{7}$$

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where $\Delta\omega^2 = (2\pi c)^2(\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2)$, V_{prim} is the volume of the primitive cell, Z is the number of ion pairs in the primitive cell.

The ion charge e_T^* is related to the mode one by the simple formula [9]

$$(e_T^*)^2 = e_T^2\mu, \tag{8}$$

where μ is the reduced mass of a dipole oscillation. The mode Szigeti charge e_s and the transverse mode (ionic) charge e_T^* are connected by the following relation [9]:

$$e_T^* = \frac{\varepsilon_\infty + 2}{3}e_s. \tag{9}$$

Relation (8) is valid under the condition for the internal and external (translation) oscillations to be independent.

To calculate the effective charges of ions Cd^{2+} and I^-, we use the internal oscillations of the crystal Ag_2CdI_4 with a TO-frequency of 136.8 cm^{-1} and those of the crystal Ag_2HgI_4 with a TO-frequency of 116.2 cm^{-1}. For the purpose of determining the effective charges of ions Ag^+, let's use the external oscillations with frequencies of 45.8 and 31.3 cm^{-1} that belong to the crystals Ag_2CdI_4 and Ag_2HgI_4, respectively. The calculated values of the effective ionic charges expressed in units of electron charge are presented in Table 3.

The comparison of the charges demonstrates that the replacement of Cd by Hg gives rise to an increase of the bond ionicity. It is also accompanied by the rise of the coupling constant of Me—I. The interaction of the Ag—I type in Ag_2HgI_4 crystal also increases as compared to that in Ag_2CdI_4 crystal, which can be seen from the fact that the effective charges of ions Ag^+ and I^- in Ag_2HgI_4 crystal are larger in absolute magnitude. The latter indicates the mixing of the internal oscillations of the complex ions HgI_4^{2-} and the external (translation) oscillations of the cations Ag^+. But this mixing is small due to a large difference between the frequencies of the corresponding oscillations.

So, we have determined the parameters of the vibrational oscillators of the reflectance spectra for Ag_2CdI_4 and Ag_2HgI_4 crystals by means of the dispersion analysis technique. On the basis of the experimental results, the elastic constants of the bonds Ag—Cd(Hg)I$_4$ are calculated. Making use of the translation oscillations, we have established that the elastic constant k for Ag_2CdI_4 crystal is larger than the corresponding constant in Ag_2HgI_4 crystal. It is shown that, in compounds Ag_2MeI_4 (Me = Cd, Hg), internal and external oscillations can be classified only conditionally as the experimental data indicate the mixing of the internal oscillations of the complex ion MeI_4^{2-} and the external (translation) oscillations of the cations Ag^+.

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ДИСПЕРСІЙНИЙ АНАЛІЗ СПЕКТРІВ ВІДБИТТЯ КРИСТАЛІВ Ag_2CdI_4 I Ag_2HgI_4 В ДАЛЕКІЙ ІЧ-ОБЛАСТІ

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Р е з ю м е

Досліджено спектри відбиття суперіонних кристалів Ag_2CdI_4 та Ag_2HgI_4 в області 20–160 см$^{-1}$ та проведено їх дисперсійний аналіз з метою визначення основних параметрів коливальних осциляторів, які формують стуги відбиття в далекій ІЧ-області. Оцінено силові сталі зв'язків між іонами, а також ефективні заряди іонів в Ag_2CdI_4 та Ag_2HgI_4.

T a b l e 3. Effective charges of the ions in Ag_2CdI_4 and Ag_2HgI_4 (Szigeti charges)

Ag_2CdI_4			Ag_2HgI_4		
Ag^+	Cd^{2+}	I^-	Ag^+	Hg^{2+}	I^-
0.075	0.697	−0.174	0.090	0.971	−0.243