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Far-infrared Reflection Spectra, Raman Spectra and Lattice Vibrations of $CsMgCl_3$ and $CsCaCl_3$

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Far-infrared reflection spectra of single crystals of $CsMgCl_3$ and $CsCaCl_3$ have been measured, and the frequencies of transverse and longitudinal modes of infrared active vibrations have been determined using Kramers-Kronig relation. For $CsMgCl_3$ a measurement of polarized Raman spectra has been made. A normal coordinate analysis of the optically active lattice vibrations has been performed, in which the rigid ion model for long range Coulomb interactions and the central force field including the 1st differential coefficients of the pair-wise potential functions have been used. The obtained short range force constants K(Mg–Cl) and K(Ca–Cl) are 0.715 and 0.63 mdyn/Å, respectively, which indicate that some amount of covalent character exists in the Mg–Cl and Ca–Cl bonds.

During the course of our studies on the lattice vibrations and interionic interations in the metal halide crystals of the type MX_2 and AMX_3 (M: divalent metal, A: alkali metal, and X: halogen), the rigid ion model for the Coulomb interaction and the central force field for the short range interaction have been used successfully for the normal coordinate analysis of the optically active vibration of crystals.[1,2] In order to establish the interionic potential in the metal halide crystals, further investigations for various types of crystals are needed.

In this paper we present the far-infrared reflection spectra and Raman spectra of $CsMgCl_3$ and $CsCaCl_3$ crystals and the results of the calculation for the interionic potential constants and effective ionic charges. There have been no data of the crystal spectra for these salts, although McPherson and Chang reported the infrared transmission spectra of the powder sample of $CsMgCl_3$.[3]

The crystal structure of $CsMgCl_3$ belongs to the space group D_{6h}^4-$P6_3/mmc$, and a primitive unit cell consists of 2 formula units (Fig. 1).[4] The crystal structure of $CsCaCl_3$ is the cubic perovskite structure with the space group O_h^1-Pm3m and a primitive unit cell consists of 1 formula unit (Fig. 2).[5] The numbers of optically active lattice vibrations in different species are determined by factor group analysis. The results are shown in Table 1.

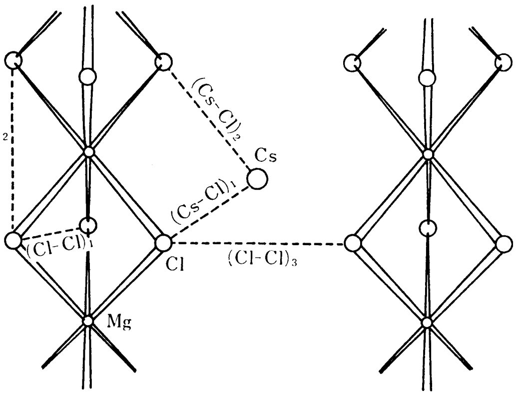

Fig. 1. Crystal structure of $CsMgCl_3$.

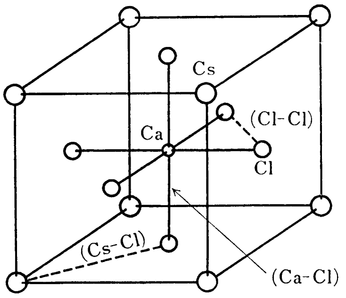

Fig. 2. Crystal structure of $CsCaCl_3$.

TABLE 1. RESULTS OF FACTOR GROUP ANALYSIS FOR OPTICALLY ACTIVE LATTICE VIBRATIONS OF $CsMgCl_3$ AND $CsCaCl_3$

Compound	Space group	Number of modes in each species
$CsMgCl_3$	D_{6h}^4-$P6_3/mmc$	$1a_{1g}+1a_{2g}+2b_{1g}+1e_{1g}+3e_{2g}+2a_{2u}+1b_{1u}+2b_{2u}+3e_{1u}+2e_{2u}$ (IR active: a_{2u}, e_{1u}; Raman active; a_{1g}, e_{1g}, e_{2g} $^{a)}$)
$CsCaCl_3$	O_h^1-Pm3m	$3f_{1u}+f_{2u}$ (IR active: f_{1u})

a) Raman tensor; $\alpha_{xx}=\alpha_{yy}$, α_{zz}: a_{1g}, $\alpha_{xz}=\alpha_{yz}$: e_{1g}, α_{xy}, $\alpha_{xx}=-\alpha_{yy}$: e_{2g}.

Experimental

$CsMgCl_3$ was prepared from CsCl and $MgCl_2$. Equimolar amounts of CsCl and $MgCl_2$ were heated in the atmosphere of dry HCl gas for several hours, and then fused in vacuum. Polycrystalline samples of $CsMgCl_3$ were sealed into quartz ampoules, and single crystals were grown from the melt by Bridgman method. Obtained crystals cleave readily along the (110) plane. This cleavage plane includes the c axis of the hexagonal lattice, and was used for polarized infrared reflection measurements. Size of the reflecting plane was about 7×10 mm.

For polarized Raman measurements, a specimen of approximately 2×2×5 mm, which was sealed into a glass tube to protect from hydration, was used.

$CsCaCl_3$ was prepared from CsCl and $CaCl_2$. A method of preparation and a single crystal growth were the same as in the case of $CsMgCl_3$. Obtained crystals cleave along the (100) plane of the cubic lattice. This cleavage plane was used for infrared reflection measurements.

Spectrometers used for infrared reflection measurements were a Hitachi 285 infrared spectrometer for the range 4000—250 cm^{-1} and a Hitachi 070 far-infrared interferometer for the range 400—10 cm^{-1}, with wire-grid polarizers. A chromium mirror was used for the reference.

Polarized Raman spectra were recorded using a Narumi model 750Z-1200 double monochromator with a 514.5 nm line of an Ar^+ ion laser as a source.

Observed Spectra and Vibrational Frequencies

Observed reflection spectra of $CsMgCl_3$ by two types of linearly polarized light are shown in Figs. 3(a) and 3(b). When the polarization of the incident light is parallel to the c axis, the spectrum is related to the a_{2u} modes of lattice vibrations (Fig. 3(a)). When the polarization is perpendicular to the c axis, the spectrum is related to the e_{1u} modes (Fig. 3(b)).

The TO and LO frequencies were obtained by the procedure described in the previous paper,[2] among which one of the LO frequencies for the e_{1u} mode was determined from the maximum of $-\mathrm{Im}(1/\hat{\varepsilon}(\nu))$ as shown in Fig. 3(b).[6]

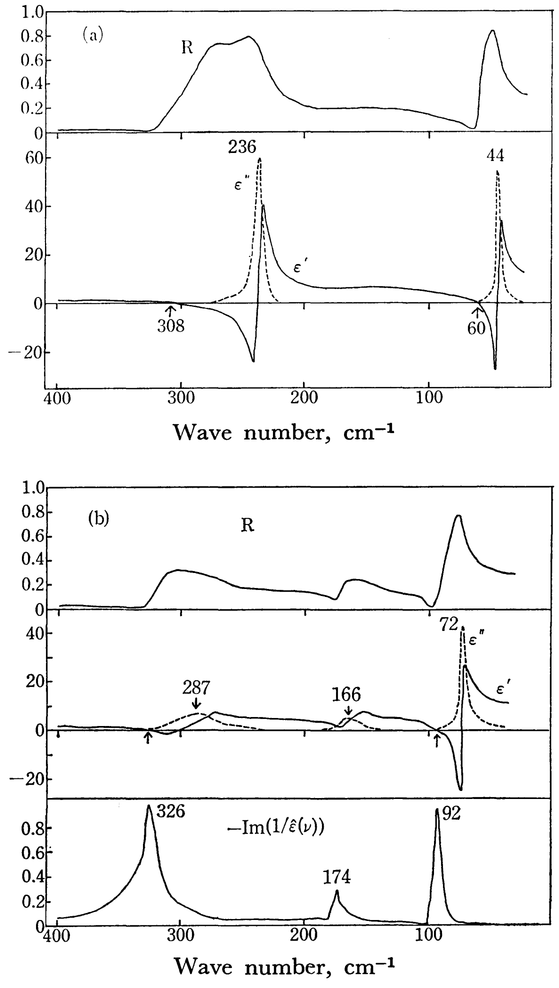

Fig. 3. Reflectivity and dielectric constants of $CsMgCl_3$. (a) The polarization of the light is parallel to the c axis, and (b) the polarization of the light is perpendicular to the c axis.

Figure 4 shows Raman spectra of $CsMgCl_3$, where the notations by Damen, Porto, and Tell are given.[7] A z-axis was taken to be parallel to the c axis of the crystal, and x,y-axes were taken to be perpendicular to the c axis.

The observed reflection spectrum and dielectric constants of $CsCaCl_3$ are shown in Fig. 5.

The observed frequencies of $CsMgCl_3$ and $CsCaCl_3$ are listed in Tables 3 and 5, respectively.

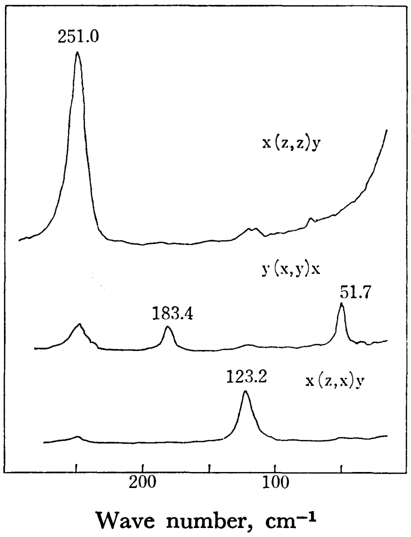

Fig. 4. Polarized Raman spectra of $CsMgCl_3$.

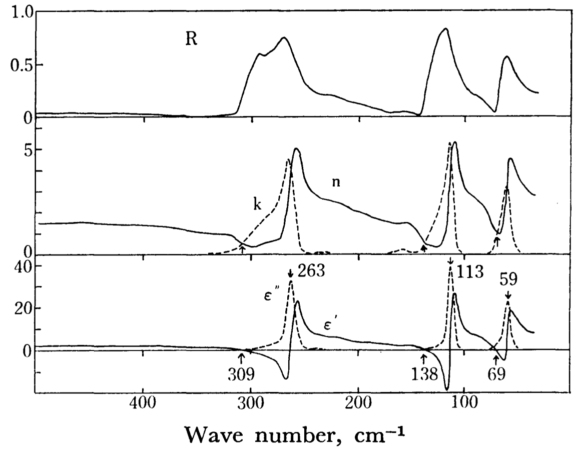

Fig. 5. Reflectivity, optical constants and dielectric constants of $CsCaCl_3$.

Normal Coordiante Analysis for the Optically Active Lattice Vibrations

The procedure of the normal coordinate analysis has been described in the previous paper.[2]

The relation between the effective ionic charges and the TO-LO splittings is expressed as:[8]

$$\frac{4\pi}{v_a}\left(2\frac{Z_{Cs}^2e^2}{m_{Cs}}+2\frac{Z_{Mg}^2e^2}{m_{Mg}}+6\frac{Z_{Cl}^2e^2}{m_{Cl}}\right)=\sum_i(\lambda_i(LO)-\lambda_i(TO)) \qquad (1)$$

for $CsMgCl_3$,** and

$$\frac{4\pi}{v_a}\left(\frac{Z_{Cs}{}^2e^2}{m_{Cs}}+\frac{Z_{Ca}{}^2e^2}{m_{Ca}}+3\frac{Z_{Cl}{}^2e^2}{m_{Cl}}\right)=\sum_i(\lambda_i(\mathrm{LO})-\lambda_i(\mathrm{TO})), \tag{2}$$

for $CsCaCl_3$,** where v_a is the volume of the unit cell, Z_A and m_A are the effective ionic charge and mass of the A ion, and λ_i is the frequency parameter $4\pi^2\nu_i{}^2$ of the i-th mode of vibration. On considering a further condition on the electrical neutrality of a crystal as a whole ($\Sigma Z_i=0$), only one Z_i becomes independent in each crystal.

The short range interactions for the ion pairs within a distance of 4.0 Å were taken into account, which are shown in Figs. 1 and 2. The force constants are listed in the first column of Table 2 ($CsMgCl_3$) and Table 4 ($CsCaCl_3$). K(A–B) denotes $[\varphi''_{\mathrm{A-B}}(r)]_{r=r_0(\mathrm{A-B})}$, and k(A–B) denote $[(1/r)\varphi'_{\mathrm{A-B}}(r)]_{r=r_0(\mathrm{A-B})}$, where $\varphi_{\mathrm{A-B}}(r)$ is the centrosymmetric potential function between A and B.

The equilibrium condition for the 1st differential coefficients of the pair-wise potential functions

$$\sum_{k,l'k'}\left[\frac{\mathrm{d}r}{\mathrm{d}\rho}\varphi'_{kk'}(r)\right]_{r=r_0(lk;\,l'k')}+\left[\alpha_{\mathrm{M}}\frac{e^2}{\rho^2}\right]_{\rho=\rho_0}=0 \tag{3}$$

was taken into consideration, where α_M is the Madelung constant referred to ρ, and $r_0(lk;l'k')$ is an interionic distance between the k-th ion in the l-th unit cell and the k'-th ion in the l'-th unit cell. The Madelung constant of $CsMgCl_3$ referred to a_0, 34.03, was used. This value was calculated by Ewald's method. As for $CsCaCl_3$, the Madelung constant referred to a_0, 12.377, was used, which was calculated by Sherman for the cubic perovskite structure.[9)]

Table 2. Short-range repulsive force constants and effective ionic charges of $CsMgCl_3$[a)]

Short-rang repulsive force constants (mdyn/Å)		Corresponding interionic distances (Å)
K(Mg-Cl)	0.715 (0.029)	2.50
k(Mg-Cl)	−0.376 (0.037)	
$K(\text{Cs-Cl})_1$	0.225 (0.028)	3.64
$k(\text{Cs-Cl})_1$	0.109 (0.044)	
$K(\text{Cs-Cl})_2$	−0.007 (0.016)	3.82
$k(\text{Cs-Cl})_2$	0.001 (0.040)	
$K(\text{Cl-Cl})_1$	0.0472[b)]	3.39
$k(\text{Cl-Cl})_1$	−0.0017[b)]	
$K(\text{Cl-Cl})_2$	0.0105[b)]	3.66
$k(\text{Cl-Cl})_2$	0.0002[b)]	
$K(\text{Cl-Cl})_3$	0.0019[b)]	3.88
$k(\text{Cl-Cl})_3$	0.0005[b)]	
Effective ionic charges		
Z_{Cs}	0.604	
Z_{Mg}	1.376	
Z_{Cl}	−0.660	

a) Throughout this paper 1Å=0.1 nm, 1 mdyn/Å=10^2 N/m. The values in parenthesis denote standard deviations. b) Estimated from the nonbonded Cl···Cl interaction potential of Lennard-Jones 6-12 type.

Table 3. Observed and calculated frequencies of $CsMgCl_3$ in cm^{-1}

	Obsd	Calcd
a_{1g}	251.0	219.6
e_{1g}	123.2	120.2
e_{2g}	183.4	177.9
e_{2g}	—	162.9
e_{2g}	51.7	50.9
a_{2u}(TO)	236	250.5
a_{2u}(TO)	44	50.3
a_{2u}(LO)	308	320.3
a_{2u}(LO)	60	59.8
e_{1u}(TO)	287	273.4
e_{1u}(TO)	166	161.3
e_{1u}(TO)	72	69.8
e_{1u}(LO)	326	327.6
e_{1u}(LO)	174	180.9
e_{1u}(LO)	92	80.0

The short range repulsive force constants between chlorine ions, $K(\text{Cl–Cl})_i$ and $k(\text{Cl–Cl})_i$, were estimated from the nonbonded chlorine-chlorine interaction potential of Lennard-Jones 6-12 type.[10)] Other short range force constants were determined by the least squares method for several sets of effective ionic charges which satisfy Eqs. 1 and 2 and the condition of electrical neutrality for each crystal.

In the case of $CsMgCl_3$, the set of effective ionic charges corresponding to $Z_{Cl}=-0.66$ gives a most satisfactory result. (The sum of the squared deviations of the calculated frequencies from the observed ones becomes minimum for this set of Z_i's when Z_{Cl} is varied from −0.58 to −0.82). Obtained force constants and calculated frequencies are given in Tables 2 and 3.

In the case of $CsCaCl_3$, the sum of the squared deviations is more or less alike for the sets of Z_i's when Z_{Cl} is varied in the range $-0.78\lesssim Z_{Cl}\lesssim-0.58$. The converged sets of the short-range force constants and the calculated frequencies for three sets of effective ionic charges in the above range of Z_{Cl} are listed in Tables 4 and 5. Among these three sets of short range force constants and effective ionic charges, the set III may be most appropriate, on comparing the values of Z_{Cs} and Z_{Ca} in $CsCaCl_3$ with those of Z_{Cs} and Z_{Mg} in $CsMgCl_3$.

Discussion

The assumptions used in the calculation are the following:

(1) Ions are rigid and not deformable.

(2) Ions interact with neighbouring ions through central forces. Unlike valence force potential, angle bending forces are not taken into consideration.

(3) The interaction potential between the chlorine ions is the 6-12 Lennard-Jones type potential which

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** The relations of Eqs. 1 and 2 hold for each IR active species; *i.e.* for both a_{2u} and e_{1u} species of $CsMgCl_3$ and for f_{1u} species of $CsCaCl_3$. In $CsMgCl_3$, the relation for a_{2u} species was used to get Z_i's.

Table 4. Short-range repulsive force constants and effective ionic charges of $CsCaCl_3$

	Short-range repulsive force constants (mdyn/Å)			r_0[a] (Å)
	Set I	Set II	Set III	
K(Ca-Cl)	0.630(0.007)	0.635(0.012)	0.636(0.011)	2.70
k(Ca-Cl)	−0.186(0.012)	−0.183(0.016)	−0.199(0.012)	
K(Cs-Cl)	0.046(0.004)	0.036(0.005)	0.032(0.004)	3.82
k(Cs-Cl)	0.016(0.003)	0.015(0.004)	0.019(0.003)	
K(Cl-Cl)	0.0035[b]	0.0035[b]	0.0035[b]	3.82
k(Cl-Cl)	0.0005[b]	0.0005[b]	0.0005[b]	
Effective ionic charges				
	Set I	Set II	Set III	
Z_{Cs}	0.009	0.268	0.554	
Z_{Ca}	1.791	1.712	1.606	
Z_{Cl}	−0.600	−0.660	−0.720	

a) r_0: Corresponding interionic distances. b) See footnote b) of Table 2.

Table 5. Observed and calculated frequencies of $CsCaCl_3$ in cm^{-1}

	Obsd	Calcd		
		Set I	Set II	Set III
f_{1u}(TO)	263	263.5	263.4	264.3
f_{1u}(TO)	113	109.8	109.3	108.9
f_{1u}(TO)	59	61.5	63.4	59.7
f_{1u}(LO)	309	307.9	307.8	306.8
f_{1u}(LO)	138	143.1	145.7	146.4
f_{1u}(LO)	69	68.0	63.5	65.9

is applicable in the case of molecular force field. This model is simple but it explains quantitatively the TO-LO splittings, which are characteristic to ionic crystals.

The agreement between the observed and calculated frequencies is satisfactory as a whole . The metal-chlorine repulsive force constant K(Mg–Cl) 0.715 mdyn/Å in $CsMgCl_3$ is comparable with K(Ni–Cl) 0.764 mdyn/Å in $CsNiCl_3$.[2)] This is quite reasonable, on comparing the interionic distance r_0(Mg–Cl)= 2.50 Å with r_0(Ni–Cl)=2.44 Å. K(Ca–Cl)=0.63 mdyn/Å in $CsCaCl_3$ is smaller than K(Mg–Cl), reflecting that r_0(Ca–Cl)=2.70 Å is longer than r_0(Mg–Cl)=2.50 Å. It is to be noted that K(Ca–Cl) is larger than K(Cd–Cl)=0.540 mdyn/Å in $CdCl_2$, although r_0(Ca–Cl) is almost equal to r_0(Cd–Cl)= 2.69 Å in $CdCl_2$.[1)] This is explained by the fact that the ionic radius of Cd^{2+} 0.95 Å is smaller than that of Ca^{2+} 1.00 Å and accordingly the contact of the metal ion with the chlorine ion is more tight in $CsCaCl_3$ than in $CdCl_2$.[11)]

Since the metal-chlorine force constants K(Mg–Cl) and K(Ca–Cl) in $CsMgCl_3$ and $CsCaCl_3$ are rather larger than K(Na–Cl) or K(K–Cl) ≈0.2 mdyn/Å in NaCl or KCl crystals which are considered to be purely ionic crystals,[12)] there may exist some amount of covalency in Mg–Cl and Ca–Cl bonds.

As for the potential constants corresponding to the $Cs^+\cdots Cl^-$ interaction, reasonable values of K(Cs–Cl) and k(Cs–Cl) were obtained with small standard deviations for $CsCaCl_3$. However, for $CsMgCl_3$ which has two kinds of $Cs^+\cdots Cl^-$ (3.64 and 3.82 Å), the converged force constants have rather large standard deviations as seen in Table 2. The values of $K(\text{Cs–Cl})_1$ and $k(\text{Cs–Cl})_1$ are too large while those of $K(\text{Cs–Cl})_2$ and $k(\text{Cs–Cl})_2$ are too small, on considering the corresponding interionic distances.***

Finally, the displacement of each ion for each vibration will be discussed for the AMX_3 crystal of cubic perovskite structure. This may be described on the basis of the eigenvectors $\boldsymbol{L}_x$ for $\boldsymbol{M}^{-1}(\boldsymbol{F}_x{}^{R}+\boldsymbol{F}_x{}^{C})$, $\boldsymbol{X}=\boldsymbol{L}_x\boldsymbol{Q}$, where $\boldsymbol{F}_x{}^{R}$ and $\boldsymbol{F}_x{}^{C}$ are $\boldsymbol{F}$ matrices, in terms of Cartesian displacement coordinates, corre-

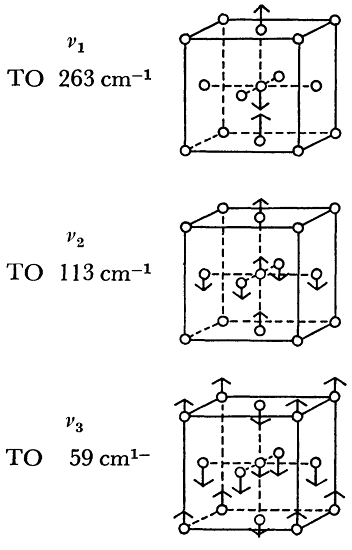

Fig. 6. Displacement of ions for three infrared active vibrations of $CsCaCl_3$.

*** The interionic distance $(\text{Cs}\cdots\text{Cl})_2$ in $CsMgCl_3$ equals to that for (Cs···Cl) in $CsCaCl_3$. If we assume the values of $K(\text{Cs–Cl})_2$ and $k(\text{Cs–Cl})_2$ take the same values as those for $CsCaCl_3$ and perform the least squares calculation, the values of $K(\text{Cs–Cl})_1$ and $k(\text{Cs–Cl})_1$ would be converged to smaller values with less standard deviations.

sponding to the short-range repulsive and long-range Coulomb potentials. The result for $CsCaCl_3$ is given schematically in Fig. 6, which shows that the highest vibration ν_1 is a Ca–Cl stretching mode, ν_2 is a Ca–Cl bending mode and the lowest one ν_3 is a Cs- *vs.* -$CaCl_3$ type lattice mode. This result is in correspondence with that for BMO_3 studied by Last,$^{13)}$ but in contrast with that for AMF_3 where the ν_1 mode is a M–F bending mode and the ν_2 mode is a M–F stretching mode.$^{14)}$

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