

Lattice Vibration Spectra

LXXXVIII. Lattice Dynamics of Suzuki-Type $\text{Li}_6M^{\text{II}}\text{Cl}_8$ ($M^{\text{II}} = \text{Fe, Co, Ni}$)¹

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Lattice dynamical calculations of Suzuki-type Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 have been performed using various potential models (rigid-ion, central and angular force-constants). The potential energy is mainly controlled by Coulomb forces and short-range $M^{\text{II}}\text{-Cl}$ interactions ($K_1 = 0.79 - 0.82$, $\alpha_1 = 0.84 - 0.88 \text{ N cm}^{-1}$). There are significant differences between the corresponding TO and LO phonon modes (species F_{1u}), which are caused by the strong macroscopic field in these highly ionic compounds. The sequence of the Raman allowed modes taken from the literature has to be reversed as $A_{1g} > E_g > F_{2g}(1) > F_{2g}(2)$. The higher wavenumbers of the A_{1g} and E_g phonons are due to the involvement of the force-constant K_1 in the respective potential energies. FIR reflection spectra of the title compounds including oscillator-fit calculations are presented. © 1996 Academic Press, Inc.

INTRODUCTION

On substitution of the alkali metal ions of NaCl-type halides by bivalent ions M^{II} , vacancies in the cation sublattice are produced. These vacancies and also the bivalent metals are ordered if the concentration of M^{II} reaches about 10 mol% (1) and, hence, so-called Suzuki-type deficient NaCl superstructure $M_6^{\text{I}}M^{\text{II}}X_8$ (2, 3) are formed. On further increase of the M^{II} content to about 30 mol% another deficient NaCl superstructure, viz. that of the orthorhombic SnMn_2S_4 type (1, 4), exists. The Suzuki-type superstructures have been reported in the literature for ternary lithium fluorides, chlorides, and bromides, and sodium chlorides. The cubic crystal structure (space group $Fm\bar{3}m$, $Z = 4$) of Li_6MgBr_8 has been confirmed by X-ray single crystal studies (5), those of Li_6CoCl_8 and Li_6FeCl_8 by X-ray powder diffraction, and neutron powder and Mößbauer spectroscopic studies, respectively (6, 7).

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The most straight-forward technique examining the formation of Suzuki-type superstructures are Raman spectroscopic experiments (8–12). Suzuki-type halides display four relatively sharp Raman bands. Owing to the great ionicity producing large TO/LO splittings (see later) the infrared spectra of the title compounds only reveal broad bands with some inflections (11). The assignment of the observed bands to species A_{1g} , E_g , and F_{2g} allowed with the Raman experiments (9, 13) was performed by single-crystal Raman studies (8). In connection with the interpretation of the Raman spectra of the related SnMn_2S_4 -type halides (14), we doubted this assignment in the meantime.

Therefore, we performed lattice dynamical calculations on the title compounds by using both a rigid-ion model (RIM) (15) and a central and angular force-constant model (CF-AF) (16). The calculation procedures are described elsewhere (17, 18). The input parameters are the fractional coordinates u (6, 7), the lattice constants a (6, 7, 11), the masses of the atoms involved, the symmetry coordinates q_n (11, 13), and the phonon energies. The force constants and the effective dynamical charges are treated as variable parameters to give the best fit of the experimental frequencies.

In order to obtain at least crude data of the transversal (TO) and the longitudinal optic (LO) phonons of the IR allowed species F_{1u} we recorded the infrared reflection spectra of Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 computing the phonon energies by using the four-parameter oscillator-fit model (19, 20). The Raman spectroscopic data are taken from the literature (11).

EXPERIMENTAL

Suzuki-type ternary halides Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 were prepared by fusing the binary compounds in evacuated borosilicate glass ampoules as described elsewhere (11). Pellets with mirror-like surfaces were obtained by pressing polycrystalline samples at 750 MPA using

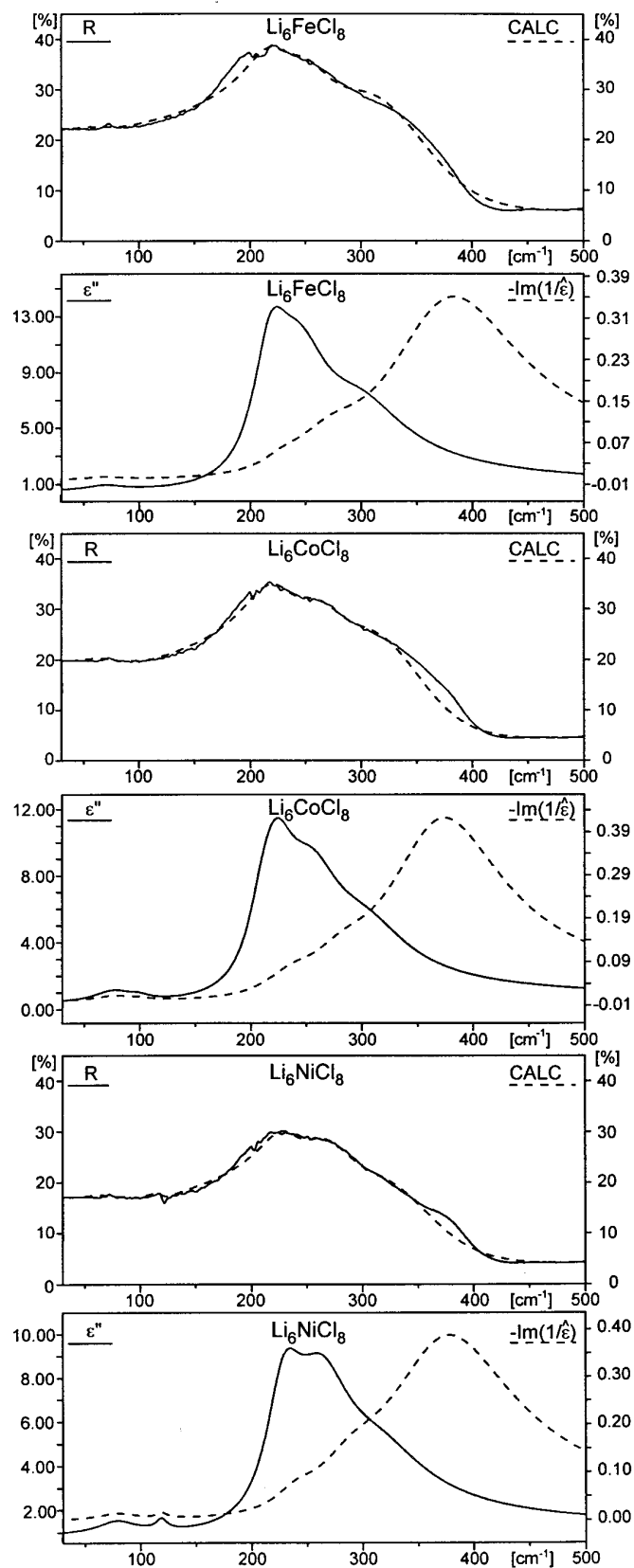


FIG. 1. IR reflection spectra (R, pressed pellets, Bruker IFS 113v; fitted, dashed line) and dispersion functions of the dielectric constant ϵ'' (full line) and $-\text{Im}(1/\hat{\epsilon})$ (dashed line) of Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 .

TABLE 1

Oscillator Parameters (Damping Constant γ (cm^{-1}) and Dielectric Constant ϵ_∞) and TO and LO Phonon Energies (cm^{-1}) of the Zone-Center Modes (Species F_{1u} , Unit-Cell Group O_h) of Suzuki-Type Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 Obtained from IR Reflection Spectra of Pressed Pellets Using the Four-Parameter Oscillator-Fit Method

Oscillator no.	Li_6FeCl_8				Li_6CoCl_8				Li_6NiCl_8			
	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}
1	300.8	93.1	378.6	147.4	306.1	86.5	370.0	126.3	314.8	97.8	374.9	138.8
2	245.0	61.1	272.0	75.2	255.0	62.5	282.5	77.0	262.7	63.1	289.4	76.6
3	219.1	41.1	228.2	44.6	222.9	42.8	234.9	47.6	229.7	41.4	239.0	44.8
4	195.5	55.2	195.5	55.2	211.2	33.2	212.8	33.7	198.1	16.3	198.1	16.3
5	120.8	323.3	120.8	323.3	100.2	22.5	100.5	22.5	119.2	12.5	119.6	12.5
6	72.0	39.7	72.7	39.7	78.8	44.0	80.6	44.0	81.8	44.8	83.5	44.8
ϵ_∞	3.5340				3.1212				2.9140			

highly polished pistons. The spectra were recorded at near normal incidence using a Bruker 113v Fourier transform interferometer (reference: Au mirror, resolution $<2 \text{ cm}^{-1}$). The spectra were converted into the dielectric dispersion functions by the four-parameter oscillator-fit method (factorized form). Details are given in Ref. (20).

RESULTS

The infrared reflection spectra of Li_6FeCl_8 , Li_6CoCl_8 , and Li_6NiCl_8 as well as various dispersion relations are shown in Fig. 1. The oscillator parameters and the wavenumbers of the TO and LO phonon modes are given in Table 1.

The symmetry coordinates of the lattice modes ($|\mathbf{q}| = 0$) of Suzuki-type compounds (11, 13) are given in Table 2. They differ from those of most other compounds in such a manner that the coordinates of one lattice site of both the M^I and X ions are splitted into two coordinates.

The short-range force constants (K_i and F_i , RIM; α_i and α'_i , CF-AF) chosen for the lattice dynamical calculations are shown in Fig. 2. The number of the force constants which can be used for the calculation is limited because of the small number of observable modes. The wavenumbers of the IR allowed modes are not precisely known as discussed above.

Phonon energies observed (FRQ) and calculated (FRC), short-range force constants (see above), eigenvectors of the phonon modes, and potential energy distributions (PED) determined are compiled in Tables 3–6. The vibrational modes of the zone-center phonons are shown in Fig. 3.

The main results obtained are the following: (i) the results of the rigid-ion model (RIM) and the central and angular force-constant model (CF-AF) calculations match nicely. (ii) The assignment of the Raman modes reported by Bates *et al.* (8) has to be interchanged, i.e., the wavenumbers of the E_g modes are larger than those of the two F_{2g}

bands (see Table 3). (iii) The Raman allowed modes of species A_{1g} and especially E_g are governed by the $M^{\text{II}}\text{-Cl}$ bonds, and those of F_{2g} by the Li-Cl bonds. (iv) Coulomb forces are involved in the A_{1g} and both F_{2g} modes (see Table 5). (v) Mixing of the internal and external modes of species F_{2g} cannot be neglected. (vi) The six IR allowed modes of species F_{1u} are partly unmixed, i.e., characteristic modes of the $M^{\text{II}}\text{Cl}_6$ and the LiCl_6 octahedra (thus, for example, the $F_{1u}(2)$ TO and the $F_{1u}(5)$ TO phonon modes correspond to ν_3 and ν_4 of the $M^{\text{II}}\text{Cl}_6$ octahedra), and partly strongly mixed typical lattice modes as, for instance, $F_{1u}(6)$ TO (see Fig. 3). (vii) The short-range force constants due to the $M^{\text{II}}\text{-Cl}$ bonds are about 0.8 N cm^{-1} slightly increasing on going from the iron to the nickel compound,

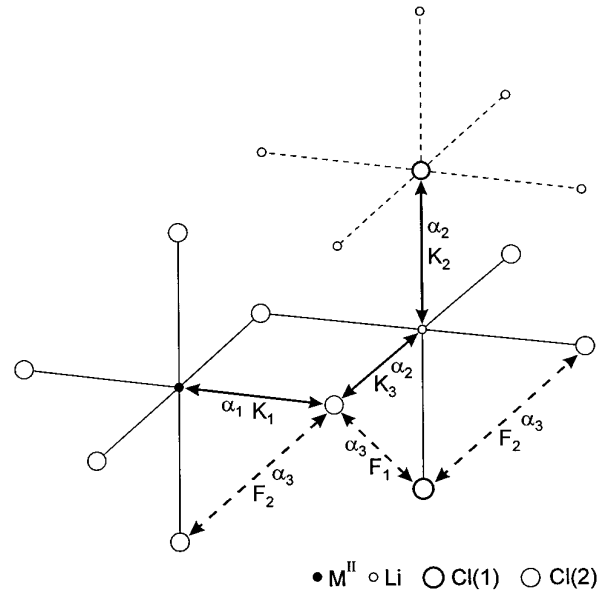


FIG. 2. Sketch of the Suzuki structure $\text{Li}_6M^{\text{II}}\text{Cl}_8$ with the short-range force constants K_i , F_i , and α_i .

TABLE 2
Symmetry Coordinates of the Zone-Center Phonon Modes of Suzuki-Type $M_6^I M^{II} X_8$ with Cartesian Basis
Coordinates $x, y, z(13)^a$

Species	No.	Atom	x	y	z	Atom	x	y	z	Atom	x	y	z	Atom	x	y	z	Atom	x	y	z				
A_{1g}	q_1	$X(2)_1$	1	0	0	$X(2)_2$	-1	0	0	$X(2)_3$	0	1	0	$X(2)_4$	0	-1	0	$X(2)_5$	0	0	1	$X(2)_6$	0	0	-1
A_{2u}	q_2	M_1^I	1	0	0	M_2^I	-1	0	0	M_3^I	0	1	0	M_4^I	0	-1	0	M_5^I	0	0	1	M_6^I	0	0	-1
E_g	q_3	$X(2)_1$	1	0	0	$X(2)_2$	-1	0	0	$X(2)_3$	0	-1	0	$X(2)_4$	0	1	0								
E_u	q_4	M_1^I	1	0	0	M_2^I	-1	0	0	M_3^I	0	-1	0	M_4^I	0	1	0								
F_{1g}	q_5	$X(2)_1$	0	1	0	$X(2)_2$	0	-1	0	$X(2)_3$	-1	0	0	$X(2)_4$	1	0	0								
F_{1u}	q_6	M_1^I	1	0	0	M_2^I	1	0	0																
	q_7	M_1^I	0	0	1	M_2^I	0	0	1	M_3^I	0	0	1	M_4^I	0	0	1								
	q_8	M_1^I	0	1	0	M_2^I	0	-1	0	M_3^I	1	0	0	M_4^I	-1	0	0								
	q_9	M^{II}	1	0	0																				
	q_{10}	$X(1)_1$	1	0	0	$X(1)_2$	1	0	0																
	q_{11}	$X(2)_1$	1	0	0	$X(2)_2$	1	0	0																
	q_{12}	$X(2)_1$	0	0	1	$X(2)_2$	0	0	1	$X(2)_3$	0	0	1	$X(2)_4$	0	0	1								
F_{2g}	q_{13}	$X(1)_1$	1	0	0	$X(1)_2$	-1	0	0																
	q_{14}	$X(2)_1$	0	1	0	$X(2)_2$	0	-1	0	$X(2)_3$	1	0	0	$X(2)_4$	-1	0	0								
F_{2u}	q_{15}	M_1^I	0	1	0	M_2^I	0	-1	0	M_3^I	-1	0	0	M_4^I	1	0	0								
	q_{16}	M_1^I	0	0	1	M_2^I	0	0	1	M_3^I	0	0	-1	M_4^I	0	0	-1								
	q_{17}	$X(2)_1$	0	0	1	$X(2)_2$	0	0	1	$X(2)_3$	0	0	-1	$X(2)_4$	0	0	-1								

^a In the case of double and triple degenerated species only one of the two or three coordinates are given.

TABLE 3
Observed (FRQ) and Calculated (FRC) Phonon Energies (cm^{-1}) of Suzuki-Type Halides

Species	Li_6FeCl_8			Li_6CoCl_8			Li_6NiCl_8		
	FRQ	FRC		FRQ	FRC		FRQ	FRC	
		CF-AF	RIM		CF-AF	RIM		CF-AF	RIM
A_{1g}	238	232	235	237	232	238	240	244	242
E_g	203	209	202	209	208	203	213	216	207
$F_{2g}(1)$	144	147	143	139	148	149	155	159	155
$F_{2g}(2)$	106	107	109	111	108	112	116	112	113
$F_{1u}(1)$ TO	301	306	328	306	311	346	315	312	346
$F_{1u}(1)$ LO	379		351	370		368	375		368
$F_{1u}(2)$ TO	245	227	293	255	229	289	263	230	296
$F_{1u}(2)$ LO	272		298	283		295	289		301
$F_{1u}(3)$ TO	219	225	210	223	227	210	230	227	212
$F_{1u}(3)$ LO	228		235	235		235	239		238
$F_{1u}(4)$ TO	196	206	186	211	207	186	198	207	189
$F_{1u}(4)$ LO	196		210	213		210	198		212
$F_{1u}(5)$ TO	121	105	113	100	106	114	119	117	119
$F_{1u}(5)$ LO	121		123	101		124	120		130
$F_{1u}(6)$ TO	72	69	76	79	70	77	82	76	82
$F_{1u}(6)$ LO	73		79	81		79	84		83
$\Delta\omega$			12.3			15.9			12.9

Note. RIM and CF-AF, rigid-ion and central and angular force-constant models, respectively; figure of merit $\Delta\omega = \sqrt{1/N \sum_{i=1}^N (\text{FRQ}(i) - \text{FRC}(i))^2}$.

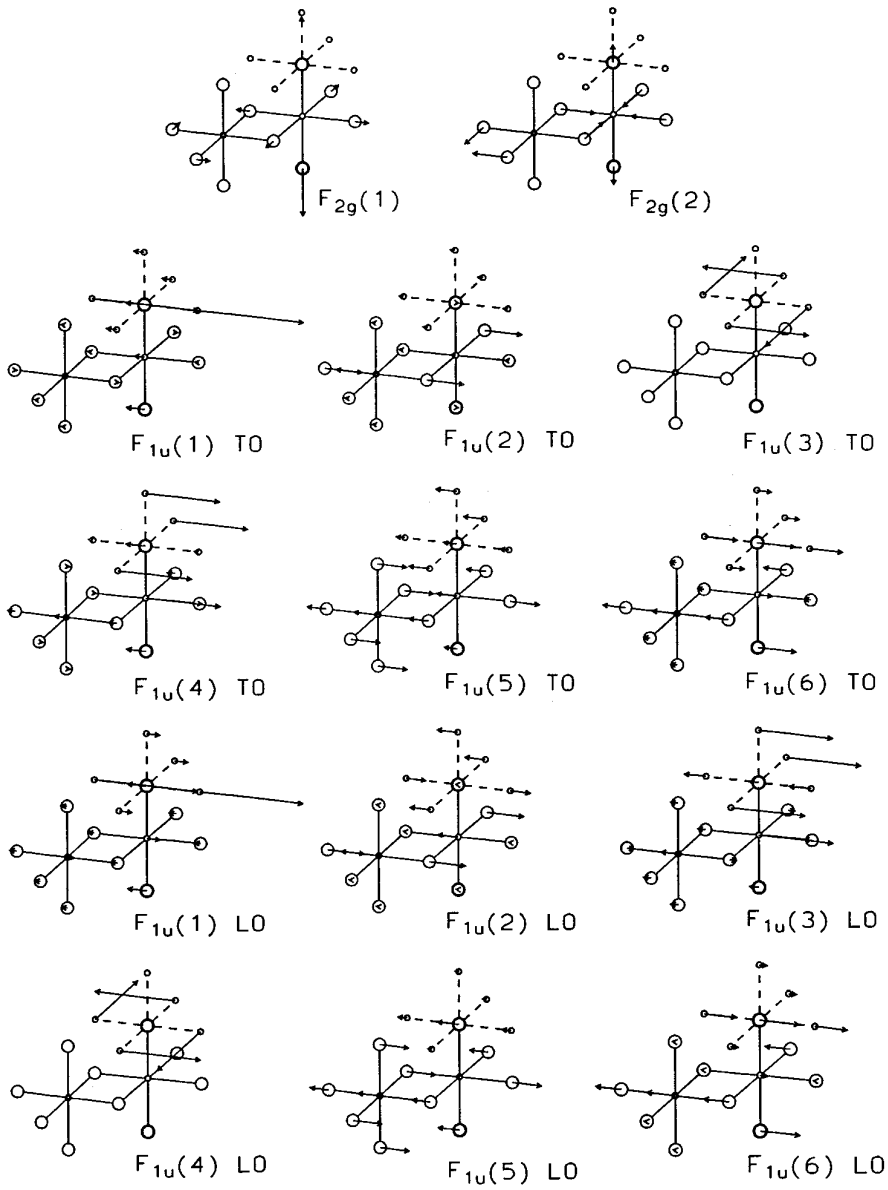


FIG. 3. Vibrational modes of the zone-center phonons of Li_6CoCl_8 obtained by rigid-ion model calculation; for the symmetry restricted vibrational modes of the phonons of species A_{1g} and E_g see (11).

TABLE 4
Interatomic Distances (pm) and Force Constants (Central and Angular, Rigid-Ion Force Constant Models) (N cm^{-1}) of Suzuki-Type Halides $\text{Li}_6M^{\text{II}}\text{Cl}_8$

Internal coordinate	Force constant	Li_6FeCl_8			Li_6CoCl_8			Li_6NiCl_8		
		Distance ^a	CF-AF	RIM	Distance ^b	CF-AF	RIM	Distance ^c	CF-AF	RIM
$M\text{-Cl}(2)$	α_1, K_1	248.1	0.838	0.79	249.8	0.832	0.79	255.9	0.883	0.82
$\text{Li-Cl}(1)$	α_2, K_2	257.3	0.083	0.20	256.9	0.084	0.22	255.9	0.084	0.22
$\text{Li-Cl}(2)$	α_2, K_3	257.5	0.083	0.07	257.0	0.084	0.07	255.9	0.084	0.07
Li-Cl	α'_2		0.002	—		0.002	—		0.002	—
$\text{Cl}(1)\text{-Cl}(2)$	α_3, F_1	364.0	0.035	0.00	363.4	0.036	0.00	361.9	0.045	0.01
$\text{Cl}(2)\text{-Cl}(2)$	α_3, F_2	350.8	0.035	0.03	353.3	0.036	0.03	361.9	0.045	0.04
		377.0			373.3					

^a $a = 1031.11(1)$ pm, $u = 0.2410(2)$ (7).

^b $a = 1025.84(3)$ pm, $u = 0.243(1)$ (6).

^c $a = 1023.5(1)$ pm, $u = 0.250$ (11).

TABLE 5
Potential Energy Distributions (RIM, PED%) of the Raman Allowed Zone-Center Phonons of Suzuki-Type $\text{Li}_6\text{M}^{\text{II}}\text{Cl}_8$

Species	Force constant	Li ₆ M ^{II} Cl ₈		
		Li ₆ FeCl ₈	Li ₆ CoCl ₈	Li ₆ NiCl ₈
A_{1g}	K_1	68	67	67
	K_2	0	0	0
	K_3	0	0	0
	F_1	0	0	0
	F_2	21	23	23
	LRFC	10	10	10
E_g	K_1	92	92	91
	K_2	0	0	0
	K_3	0	0	0
	F_1	0	0	0
	F_2	7	8	8
	LRFC	0	0	1
$F_{2g}(1)$	K_1	0	0	0
	K_2	81	86	75
	K_3	4	3	4
	F_1	0	0	8
	F_2	4	3	4
	LRFC	10	8	9
$F_{2g}(2)$	K_1	0	0	0
	K_2	22	18	23
	K_3	45	44	42
	F_1	0	0	1
	F_2	43	46	45
	LRFC	-10	-8	-11

Note. LRFC, long-range Coulomb forces; for definition of the short-range force constants and further explanations see Table 4.

those due to the Li-Cl bonds and the repulsive Cl-Cl interactions being <0.25 and <0.05 N cm⁻¹, respectively. (viii) The dynamical effective charges are $z_{\text{Li}} = 0.47$ e, $z_{\text{M}}^{\text{II}} = 0.45$ e, $z_{\text{Cl}(1)} = -0.44$ e, and $z_{\text{Cl}(2)} = -0.40$ e for all chlorides under study.

DISCUSSION AND CONCLUSION

The lattice vibrations of Suzuki-type halides resemble those of other highly ionic compounds. This is shown by the large contributions of Coulomb forces to the potential energy and the large TO/LO splittings of the respective phonons. Of the short-range force constants only those due to the partly covalent $M^{\text{II}}\text{-Cl}$ bonds is of some importance. The large long-range Coulomb forces also cause the respective TO and LO phonons to differ with respect to eigenvectors (see Fig. 3) more strongly than in the case of less ionic compounds. Thus, the LO mode that belongs to $F_{1u}(4)$ TO is $F_{1u}(3)$ LO, not $F_{1u}(4)$ LO. The higher wavenumber of the E_g mode compared to the F_{2g} modes

TABLE 6
Potential Energy Distributions (RIM, PED%) of the IR Allowed Zone-Center Phonons of Suzuki-Type $\text{Li}_6\text{M}^{\text{II}}\text{Cl}_8$

Species	Force constant	Li ₆ FeCl ₈		Li ₆ CoCl ₈		Li ₆ NiCl ₈	
		TO	LO	TO	LO	TO	LO
$F_{1u}(1)$	K_1	0	2	0	1	0	1
	K_2	106	87	106	91	106	90
	K_3	0	1	0	1	0	1
	F_1	0	0	0	0	0	0
	F_2	0	0	0	0	0	0
	LRFC	-6	9	-6	7	-6	7
$F_{1u}(2)$	K_1	99	88	98	87	98	87
	K_2	0	6	0	4	0	4
	K_3	0	1	0	2	0	2
	F_1	0	0	0	0	0	0
	F_2	4	3	4	4	4	4
	LRFC	-3	2	-3	4	-2	4
$F_{1u}(3)$	K_1	0	9	0	10	0	9
	K_2	0	3	0	2	0	3
	K_3	72	56	72	56	72	56
	F_1	0	0	0	0	0	0
	F_2	0	0	0	0	0	0
	LRFC	28	32	28	31	28	31
$F_{1u}(4)$	K_1	0	0	1	0	1	0
	K_2	7	0	6	0	6	0
	K_3	75	72	74	72	72	72
	F_1	0	0	0	0	1	0
	F_2	0	0	0	0	0	0
	LRFC	18	28	20	28	21	28
$F_{1u}(5)$	K_1	2	1	2	1	2	1
	K_2	2	10	1	9	1	9
	K_3	83	28	83	27	87	26
	F_1	0	0	0	0	7	8
	F_2	39	31	41	33	34	27
	LRFC	-25	30	-27	31	-32	29
$F_{1u}(6)$	K_1	1	2	1	2	1	2
	K_2	5	8	4	7	3	4
	K_3	22	2	24	2	10	1
	F_1	0	0	0	0	10	8
	F_2	13	19	12	20	20	26
	LRFC	60	69	58	69	56	59

Note. LRFC, long-range Coulomb forces; for definition of the short-range force constants and further explanations see Table 4.

is caused by participation of the relatively large force constant K_1 ($M^{\text{II}}\text{-Cl}$ interaction) in the former mode as it has also been analytically established.

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REFERENCES

1. M. Schneider, P. Kuske, and H. D. Lutz, *Thermochim Acta* **215**, 219 (1993).
2. J. S. Kasper and J. S. Penner, *Acta Crystallogr.* **7**, 246 (1954).
3. K. Suzuki, *J. Phys. Soc. Jpn.* **16**, 67 (1961).
4. M. Wintenberger and J. C. Jumas, *Acta Crystallogr. Sect. B* **36**, 1993 (1980).
5. M. Schneider, P. Kuske, and H. D. Lutz, *Z. Naturforsch. Sect. B* **48**, 1 (1993).
6. R. Kanno, Y. Takeda, A. Takahashi, O. Yamamoto, R. Suyama, and M. Koizumi, *J. Solid State Chem.* **71**, 189 (1987).
7. E. Riedel, D. Prick, A. Pfitzner, and H. D. Lutz, *Z. Anorg. Allg. Chem.* **619**, 901 (1993).
8. J. B. Bates, R. F. Wood, G. E. Shankle, and M. Mostoller, *Phys. Rev. Sect. B* **15**, 3267 (1977).
9. J. M. Calleja, A. Ruiz, F. Flores, V. R. Velasco, and E. Lilley, *J. Phys. Chem. Solids* **41**, 1367 (1980).
10. A. De Andres, J. M. Calleja, I. Pollini, and G. Benedek, *J. Chem. Phys.* **83**, 4967 (1985).
11. H. D. Lutz, P. Kuske, and K. Wussow, *Z. Anorg. Allg. Chem.* **553**, 172 (1987).
12. K. Wussow, H. Haeuseler, P. Kuske, W. Schmidt, and H. D. Lutz, *J. Solid State Chem.* **78**, 117 (1989).
13. K. Wussow, Doctoral Thesis, University of Siegen (1987).
14. H. D. Lutz, M. Schneider, P. Kuske, and H.-J. Steiner, *Z. Anorg. Allg. Chem.* **592**, 106 (1991).
15. A. Yamamoto, T. Utida, H. Murata, and Y. Shiro, *J. Phys. Chem. Solids* **37**, 693 (1976).
16. J. De Launey, *Solid State Phys.* **2**, 219 (1956).
17. H. D. Lutz, J. Himmrich, and H. Haeuseler, *Z. Naturforsch. Sect. A* **45**, 893 (1990).
18. H. C. Gupta, A. Parashar, V. B. Gupta, and B. B. Tripathi, *Phys. Status Solidi Sect. B* **160**, K19 (1990); *Physica (Amsterdam) Sect. B* **167**, 175 (1990).
19. A. S. Chaves and S. P. S. Porto, *Solid State Commun.* **13**, 865 (1973).
20. J. Himmrich, G. Schneider, J. Zwinscher and H. D. Lutz, *Z. Naturforsch. Sect. A* **46**, 1095 (1991).