

Lattice dynamics of crystals having R_2MX_6 structure

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The theory of lattice dynamics in the harmonic approximation using a rigid-ion model due to Born and Huang [*Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954)], is applied to ionic crystals of the R_2MX_6 type with antifluorite structure namely, K_2SnCl_6 , K_2PtBr_6 , Cs_2SnBr_6 , and Rb_2SnBr_6 in the cubic phase. The model expresses the potential energy as the sum of long-range Coulomb interactions and repulsive short-range interactions between ions in the primitive cell. A function of axially symmetric type is used to approximate the short-range part, and the number of force constant parameters were reduced utilizing stability conditions in the manner described by Katiyar [J. Phys. C **3**, 1087 (1970)]. The remaining constants were determined by a nonlinear least-squares analysis of some experimental frequencies at the critical point Γ . The long-range contributions were calculated using the Ewald transformation as described by Cowley [Acta Crystallogr. **15**, 687 (1962)]. Phonon frequencies and the normal modes of vibrations at the zone center were obtained; of particular interest is the resulting lowest librational frequency for each crystal. We obtained excellent agreement between the calculated and the observed frequencies. The resulting effective charge parameters indicated that these crystals are partially ionic. In general, the results offered a better vision of the structural phase transition mechanism involving the rotational mode T_{1g} . [S0163-1829(97)09737-3]

I. Introduction. R_2MX_6 -type crystals are ionic in the octahedral form, where R^+ is a cation and MX_6^{2-} is the anion. Most of these hexahalometallic crystals tend to adopt an antifluorite cubic structure at high temperature. The most interesting feature is in the observed crystallographic structural phase transitions, with decreasing temperature to lower symmetric arrangements. Experimental studies were carried out¹⁻¹³ to measure phase transition temperatures and structural parameters using nuclear quadrupole resonance, Raman, Mössbauer, and neutron-diffraction studies. K_2SnCl_6 and K_2PtBr_6 may be considered two of the most studied crystals of this family. At room temperature these are cubic and belong to space group O_h^5 . If the temperature is lowered the crystals undergo structural transitions at 261 K (D_{4h}^6) and 160 K (C_{4h}^5), respectively. A second transition occurs at 254 K (C_{2h}^5) and at 141 K (C_{2h}^6), respectively. Finally, K_2PtBr_6 undergoes another transition at 120 K (D_{4h}^6). In a recent work, Rössler and Winter⁸ found that the transition temperatures are shifted to lower values with increasing size of cations and decreasing size of the halogen ligands.

Some of the structural phase transitions that these crystals undergo are rotational type. O'Leary and Wheeler¹⁴ established that these materials exhibit phase transitions that are driven by a soft mode: the longitudinal rotational mode which involves librational motion of the MX_6^{2-} octahedron as a solid body.

Experimental studies of phonons in these crystals were carried out¹⁵⁻¹⁸ using Raman, infrared, and neutron-scattering techniques. We perform a theoretical study of phonons in the cubic phase, using rigid-ion model¹⁹ with

long-range Coulomb forces and short-range axially symmetric forces with some approximations.²⁰

II. Crystal structure and normal mode symmetries. Crystals of R_2MX_6 chemical composition having the cubic antifluorite structure belong to the space group $F_{m3m}(O_h^5)$ in the high temperature cubic phase. In this phase the M^{4+} ions, which form a fcc lattice, are surrounded by an X_6 octahedral with the $M-X$ bonds along the cubic axes. The R^- ions are surrounded by MX_6^{2-} octahedra in a tetrahedral coordination. The primitive cell contains nine atoms in the following positions:¹⁰

k	Atom	Position	k	Atom	Position
1	M	$(0,0,0)a_0$	6	X	$(0,u,0)a_0$
2	R	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a_0$	7	X	$-(0,u,0)a_0$
3	R	$-(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a_0$	8	X	$(0,0,u)a_0$
4	X	$(u,0,0)a_0$	9	X	$-(0,0,u)a_0$
5	X	$-(u,0,0)a_0$			

For lattice dynamical calculations we introduced an identification index K for each ion in the primitive cell. The room temperature lattice parameters for each crystal are listed in Table I.

We have classified the normal modes of vibrations for the critical point Γ as follows:

$$A_{1g}(X) + E_g(X) + 2T_{2g}(R;X) + T_{1g}(X) + T_{2u}(X) + 4T_{1u}(M;R;X), \quad (1)$$

TABLE I. Structural parameters for the R_2MX_6 crystal family.

Crystal	a_0 (Å)	u (Å)	Ref.
K_2SnCl_6	9.9877	0.2412	7
Rb_2SnCl_6	10.118	0.240	10
K_2PtBr_6	10.293	0.2393	1
Rb_2SnBr_6	10.64	0.245	10
Cs_2SnBr_6	10.81	0.245	10

where the ions involved in a particular normal mode of vibration are in parentheses. Three modes of T_{1u} symmetry are IR-active, ($T_{1g} + T_{2u}$) are inactive, and the remaining modes are Raman active. The basis vectors can be obtained using the projection-operator technique²¹ and they are listed in Table II. The normal modes of vibrations are the linear combinations of the basis vectors, belonging to the same species, with the linear constants involving the force constants parameters.

III. Dynamic formulation and the rigid-ion model. In lattice dynamical theory^{19,22,23} the dynamical matrix is constructed in terms of force constants- $\Phi_{\alpha\beta}(l'l'k'k)$ that are second derivatives of the crystal potential energy with respect to the displacement $u_{\alpha}(l'k')$ of the ion (l, k) in “ α ” direction. Following the rigid-ion model approximation the potential energy may be written as the sum of the long-range Coulombic energy and the short-range repulsive energy:

$$\Phi = \phi^c + \phi^r. \quad (2)$$

The Coulombic energy, known as Madelung energy,¹⁹ is expressed as follows:

$$\phi^c = \alpha' (Ze)^2 / r_0. \quad (3)$$

We introduce the axially symmetric model to represent the repulsive energy ϕ^r that involves two force constants, namely $A_{kk'}$ (radial force) and $B_{kk'}$ (tangential force) for each ion pair:

$$\left. \frac{\partial^2 \phi^r}{\partial r_{kk'}^2} \right|_0 = \frac{e^2}{2V} A_{kk'}, \quad \left. \frac{1}{r_{kk'}} \frac{\partial \phi^r}{\partial r_{kk'}} \right|_0 = \frac{e^2}{2V} B_{kk'}. \quad (4)$$

The elements of the dynamical matrix can be separated into the Coulomb sums and the repulsive part. Eigenvalues of this matrix are the frequencies of the normal modes, and the eigenvectors represent the normal modes of vibrations.

A. Potential energy and force constants. The potential energy of the primitive cell is written as follows:

$$\Phi = -(Ze)^2 (\alpha' / r_0) + 6\phi_{14}^r + 24\phi_{24}^r + 12\phi_{46}^r. \quad (5)$$

We only take into account the contributions of the nearest ions; the numbers in front of the short-range potential constants represent identical interactions. In order to reduce the force constant parameters we have neglected the short-range interactions for distances larger than 4 Å. The model has six short-range potential constants: A_{14} , A_{24} , A_{46} , B_{14} , B_{24} , B_{46} ; and three additional constants from the Coulomb potential: the effective ionic charges Z_R , Z_M , Z_X . The number of force constants can be reduced using the stability conditions of the unit cell and the charge neutrality condition. The potential energy of the primitive cell is then minimized²⁴ with respect to each structural parameter in order to insure structural stability. For each crystal we have two structural parameters, namely, “ a_0 ” and “ u ,” and therefore, the two stability conditions may be expressed as follows:

$$3a_0u^2B_{14} + 12a_0u^2B_{46} + 12a_0\left[\left(\frac{1}{4} - u\right)^2 + \frac{1}{8}\right]B_{24} = \frac{VZ^2}{r_0} \left. \frac{\partial \alpha'}{\partial a_0} \right|_0, \quad (6a)$$

$$3ua_0^2B_{14} + 12ua_0^2B_{46} + 12a_0^2\left(u - \frac{1}{4}\right)B_{24} = \frac{VZ^2}{r_0} \left. \frac{\partial \alpha'}{\partial u} \right|_0. \quad (6b)$$

From these equations we determine two constants, namely B_{14} and B_{24} . Using the charge neutrality condition of the primitive cell we determine another constant, Z_m , thus reducing the number of constants from nine to six. These remaining constants were determined by nonlinear least-squares analysis of some experimental frequencies at the critical point Γ . The best fitted values are listed in Table III.

The charge parameters are smaller than the free ionic charges suggesting that these crystals are partially ionic. An interesting feature is the linear dependence of the cationic effective charge with the size of the unit cell, shown in Fig. 1. The cation effective charge (Z_R) increases with increasing

TABLE II. Basis vectors for the normal modes of the R_2MX_6 structure.

Critical point	Mode	a	b	c	
Γ	A_{1g}	$x_4 - x_5 + y_6 - y_7 + z_8 - z_9$			
	E_g	$x_4 - x_5 + y_6 - y_7 - 2z_8 + 2z_9$	$x_4 - x_5 - y_6 + y_7$		
	T_{2g}	$x_2 - x_3$		$y_2 - y_3$	$z_2 - z_3$
		$y_8 - y_9 + z_6 - z_7$		$x_8 - x_9 + z_4 - z_5$	$y_4 - y_5 + x_6 - x_7$
	T_{1g}	$y_8 - y_9 + z_7 - z_6$		$x_9 - x_8 + z_4 - z_5$	$y_5 - y_4 + x_6 - x_7$
	T_{2u}	$-x_6 - x_7 + x_8 + x_9$		$y_4 + y_5 - y_8 - y_9$	$-z_4 - z_5 + z_6 + z_7$
	T_{1u}	x_1		y_1	z_1
		$x_2 + x_3$		$y_2 + y_3$	$z_2 + z_3$
		$x_6 + x_7 + x_8 + x_9$		$y_4 + y_5 + y_8 + y_9$	$z_4 + z_5 + z_6 + z_7$
		$x_4 + x_5$		$y_6 + y_7$	$z_8 + z_9$

TABLE III. Short-range potential constants and the effective charges. The effective charges are multiples of e .

Parameter	K_2SnCl_6	K_2PtBr_6	Cs_2SnBr_6	Rb_2SnBr_6
Z_R	0.123	0.298	0.950	0.934
Z_X	-0.360	-0.143	-0.542	-0.402
Z_M	1.914	0.259	1.354	0.545
A_{14}	301.3	344.5	273.1	237.9
A_{24}	6.827	9.109	19.12	14.37
A_{46}	47.22	44.29	37.72	45.92
B_{14}	15.53	41.06	25.22	29.12
B_{24}	0.200	-0.065	-0.257	-0.663
B_{46}	-8.510	-10.48	-10.87	-8.560

the unit cell volume. As expected, the radial force constants parameters between M and X (A_{14}) are large compared to the other constants (these are the nearest ions). The A_{24} constants are smaller, since repulsive forces decay rapidly with increasing the distance. The trends in the $B_{kk'}$ parameters seem to be similar in all the crystals, though their effect on the frequencies is much smaller in comparison to the contribution from the A_{kk} coefficients. Therefore, small variations in these coefficients should not affect the final results.

B. Normal modes of vibrations. The proposed rigid ion model for R_2MX_6 type of compounds enabled us to determine the short-range coefficients. The long-range contributions were calculated using the Ewald transformation²⁵ and the method described by Cowley.²⁶ The eigenvalues of the dynamical matrix at the zone center were obtained. Values for the observed and computed phonon frequencies are listed in Table IV. We obtained excellent agreement between the calculated and the observed frequencies, with a maximum disagreement of $\sim 3.5\%$ for ν_2 in K_2PtBr_6 crystal. These differences may be explained due to the fact that we neglected the electronic polarizability and the short-range inter-

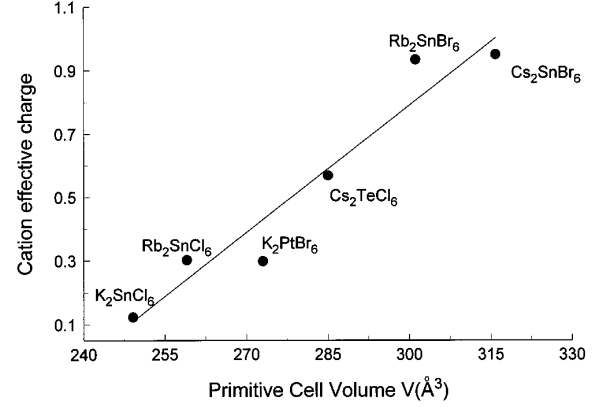


FIG. 1. Z_R as a function of primitive cell volume V . (Data for Cs_2TeCl_6 and Rb_2SnCl_6 crystals taken from Torres.²⁷)

actions larger than 4 \AA . These calculations enable us to compute the phonon frequencies belonging to T_{1g} and T_{2u} modes which cannot be observed with infrared or Raman techniques.

We determined the normal modes of vibrations from the computed eigenvectors for $\mathbf{q}=0$ (Z direction). Of particular interest is the rotational mode, T_{1g} , which involves the librational movement of the MX_6^{2-} octahedral as a rigid body. Following O'Leary and Wheeler¹⁴ the temperature dependence of this longitudinal mode may describe the structural phase transitions in these crystals with antifluorite structure. In Figs. 2(a) and 2(b) we have plotted some of the normal modes of vibrations of the crystals studied. The mode with the lowest frequency and the structure transition occurs when this mode freezes out.

IV. Conclusions. The theory of lattice dynamics in the harmonic approximation and the rigid-ion model was applied to ionic crystals of R_2MX_6 type with antifluorite structure. The effective charges and the short-range force constants were determined by nonlinear least-squares analysis. All of

TABLE IV. Observed and calculated frequencies (cm^{-1}) at the critical point Γ .

Mode	K_2SnCl_6		K_2PtBr_6		Cs_2SnBr_6		Rb_2SnBr_6	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$A_{1g}(\nu_1)$	324	321	213	217	184	184	190	189
$E_g(\nu_2)$	244	247	191	178	136	136	142	142
$T_{2g}(\nu_3)$	72	73	73	73	62	58	62	62
$T_{2g}(\nu_4)$	172	174	110	113	108	105	107	106
$T_{1u}(\nu_6)$	84	82(TO) 82(LO)	80	80(TO) 84(LO)	60	62(TO) 78(LO)	60	60(TO) 85(LO)
$T_{1u}(\nu_7)$	175	175(TO) 89(LO)	128	120(TO)	118	119(TO)	119	19(TO)
$T_{1u}(\nu_8)$	324 323(TO)		122(LO)		125(LO)		123(LO)	
			244		221			
$T_{1g}(\nu_9)$	331(LO)		249(TO)		220(TO)		226(LO)	
$T_{2u}(\nu_{10})$	43	42	249(LO)		229(LO)		--	29
	--	106	--	38	--	30	--	64
			--	67	--	59		

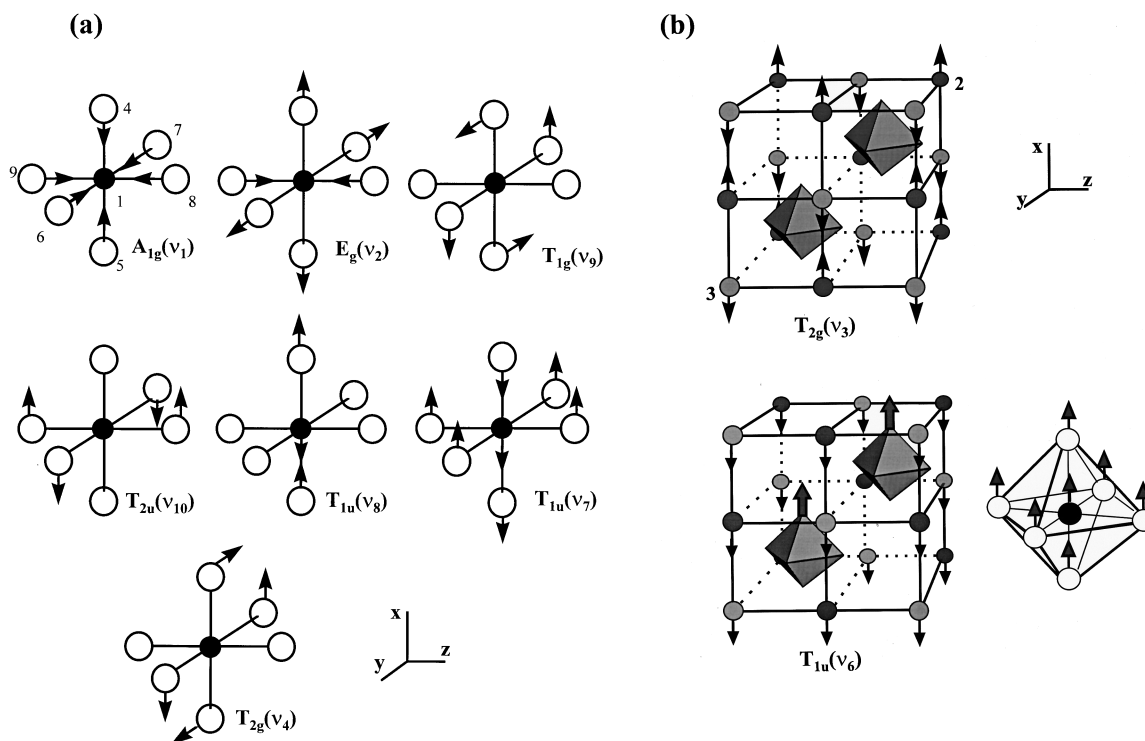


FIG. 2. (a) Some of the normal modes of vibrations for R_2MX_6 crystals in which only MX_6 octahedra vibrate. (b) $T_{2g}(\nu_3)$ and $T_{1u}(\nu_6)$ vibrations for R_2MX_6 in which alkali ions also participate.

the computed parameters appear to be physically acceptable. The effective charge parameters suggest that these crystals are partially ionic. These results and the computed frequencies and the normal modes of vibration for the rotational mode T_{1g} may be useful for future experimental and theoretical investigations in determining elastic, dielectric, or piezoelectric behavior as a function of structural phase transitions.

The normal modes of vibrations have been determined and these have been shown pictorially for the zone center phonons.

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